

STUDY THE EFFECT OF PARAMETERS INFLUENCING SILANISATION AND ITS OPTIMIZATION IN RUBBER COMPOUNDING

Submitted in partial fulfillment of the requirements for the award of
Bachelor of Technology degree in Chemical Engineering

By

DHINAKARAN. Y (40690005)



**DEPARTMENT OF CHEMICAL ENGINEERING SCHOOL OF BIO
AND CHEMICAL ENGINEERING**

SATHYABAMA

**INSTITUTE OF SCIENCE AND TECHNOLOGY (DEEMED TO BE UNIVERSITY)
Accredited with Grade "A++" by NAAC**

JEPPIAAR NAGAR, RAJIV GANDHI SALAI, CHENNAI - 600 119

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Jeppiaar Nagar, Rajiv Gandhi Salai, Chennai – 600 119
www.sathyabama.ac.in



DEPARTMENT OF CHEMICAL ENGINEERING

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the bonafide work of **DHINAKARAN Y (40690005)** who carried out this Project entitled "**Study the effect of parameters influencing silanization and its optimization in Rubber compounding**" under my supervision from June 2023 to October 2023.


Internal Guide 4/11/23
Dr.D. PRABU, M.S. (Research). Ph.D.,
Associate professor


External Guide
Ms. SIJO JOSE
Group Manager-TBR


Head of the Department
Dr. S. SATHISH, M.E., Ph.D.
Associate Professor

HEAD OF THE DEPARTMENT
DEPARTMENT OF CHEMICAL ENGINEERING
SATHYABAMA
INSTITUTE OF SCIENCE AND TECHNOLOGY
(DEEMED TO BE UNIVERSITY)
Jeppiaar Nagar, Rajiv Gandhi Salai
Chennai – 600 119

Submitted for Viva-voce Examination held on 4.11.23 October 2023.


Internal Examiner


External Examiner

DECLARATION

I, **DHINAKARAN Y (40690005)**, hereby declare that this Project report entitled
“**Study the effect of parameters influencing silanization and its optimization
in Rubber compounding**” done by me under the guidance of **Dr D. PRABU,
M.S (by Research), PhD, Associate professor**, Sathyabama Institute of
Science and Technology and **Ms. SIJO JOSE, Group Manager-TBR Technology**,
Apollo Tyres is submitted in partial fulfilment of the requirements for the award of
Bachelor of Technology degree in Chemical Engineering.

DATE:

04/11/23

PLACE:

Chennai



SIGNATURE OF THE CANDIDATE

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DHINAKARAN Y

ABSTRACT

Increasingly stringent demand for a fuel-saving tire with low rolling resistance, the application of silica filler is governing the tire industry day by day. Unlike carbon black-filled rubber compounds, silica compound is rather complicated as it demands reactive mixing where mixing parameters of the internal mixer play a vital role in the degree of silanization reaction.

In this paper, a design of experiments (DOE) is carried out to screen the factors that significantly affect the silanization reaction during mixing. Taguchi method with orthogonal array is employed to determine the significance of mixing parameters on the degree of silanization reaction.

To quantify the significance of each mixing parameter on silanization, such as mixing temperature, mixing time, fill factor and temperature control unit of Banbury mixer is explored.

Key properties like $\tan \delta$ at 60°C and Payne effect ($\Delta G'$) are considered responses for the DOE. It was observed that the silanization temperature and time were the most influencing factors in silanization using the contribution plot.

In contrast, ram pressure and feed door condition have the least significance/influence on the degree of silanization. Mixing temperature, time, Batch weight is more influencing the Silanisation process, if silanisation not good all the properties are good. It is the main key role of the mixing process for the rubber compounding.

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LIST OF ABBREVIATIONS

- (i) Rubber process analyzer – RPA
- (ii) Dynamic Mechanical Analysis - DMA
- (iii) Styrene-butadiene – SBR
- (iv) Technically Specified Rubber - TSR
- iv) bis(3-triethoxysilylpropyl) tetra sulfide -TESPT
- v) bis (3-triethoxysilylpropyl) disulphide -TESPD
- vi) Natural Rubber – NR
- vii) Truck Bus Radial- TBR

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CHAPTER 1

1.1 INTRODUCTION

1.1.1 TRUCK BUS RADIAL TIRE

Truck Bus Radial (TBR) tires contain body ply cords which are present radially from bead-to-bead area, it will be at a 90-degree angle to the centerline of the tread portion. More than two belts are present diagonally in the tread region to improve strength and stability.

Radial plies are that run perpendicular towards the travel direction. For this, we are getting very little heat generation and very smooth riding.

Radial tire's advantages,

- (i) Sidewalls give good flexibility.
- (ii) Fuel consumption will get less because of less rolling resistance.
- (iii) Softer while riding and vibration is also less.
- (iv) Due to less heat generation tire life can be extended.

The disadvantages of radial tires when compared to a bias ply tire include:

- (i) Difficult for transport handling.
- (ii) Sidewall bulge which could cause tire puncture and damage in the sidewall region,
- (iii) Overloading and improper air inflating may cause tire damage.
- (iv) Sometimes Belt edge filler damage may cause Belt separation on tire failure.



Figure 1 Radial Body ply & Belt

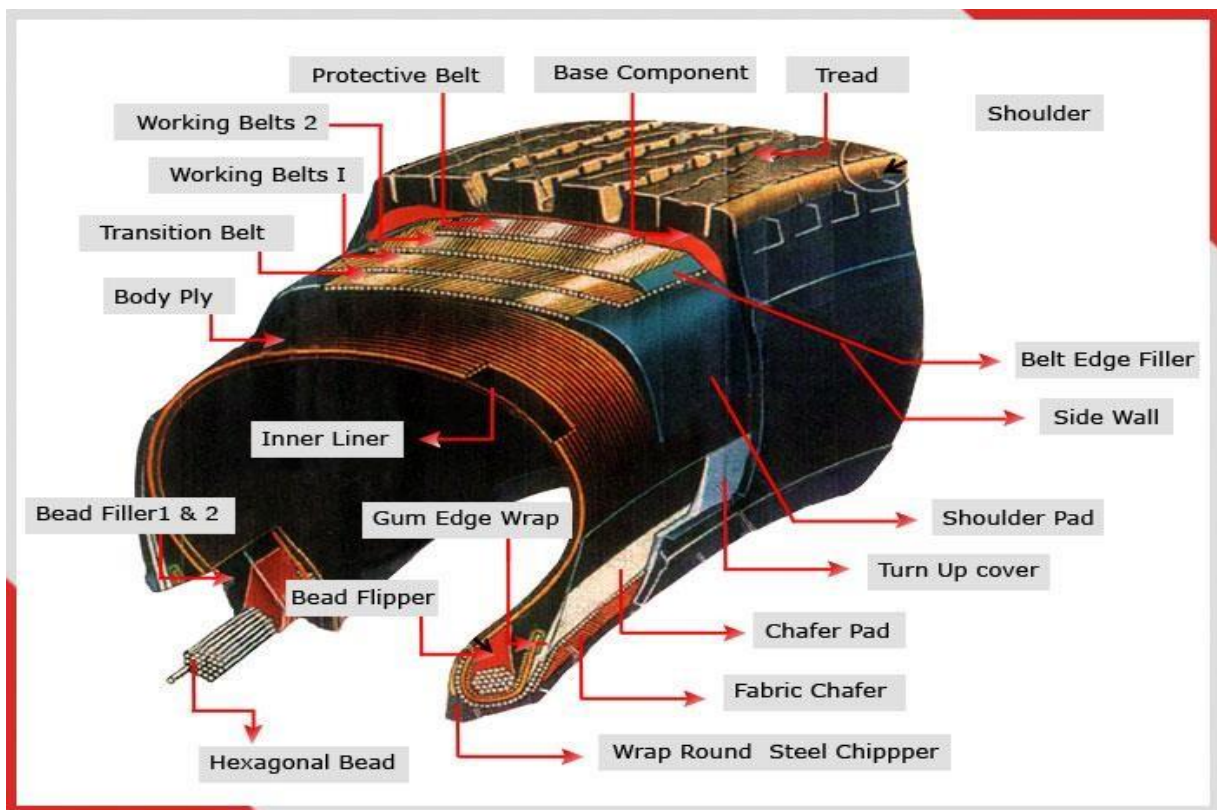


Figure 2 Truck bus radial Components

1.1.2 COMPONENTS OF RADIAL TIRE

(1) Inner liner (IL)	(11) Belt edge filler (BEF)
(2) Squeeze	(12) Belt edge gum (BEG)
(3) Transition belt 1	(13) Body ply (BP)
(4) Protection belt 1	(14) Sidewall (SW)
(5) Working belt 1(WB1)	(15) Bead seat profile
(6) Tread cushion (TC)	(16) Soft apex (SA)
(7) Tread Base (TB)	(17) Hard apex (HA)
(8) Tread Cap	(18) Steel chafer
(9) Shoulder cushion/pad	(19) Nylon chafer
(10) Flipper	(20) Bead

Tires are part of the vehicle; they help to carry the weight and move forward on the road. Our vehicles mostly pass through very harsh environments such as high and low temperatures or wet regions. That is the reason rubber is used in tires with additives and fillers to strengthen the tire; It will maintain the grip and good stable on the rough surface places.

A Radial tire is a composite material which has rotational symmetry. It contains several rubber components bound together and textile or other steel reinforcement materials give more strength to the tire.

1.1.3 TYRE TREAD ASSEMBLY

The tread is the part of the tire that contacts the road's surface and protects the inner casing from road hazards. Apart from tread pattern, tire performance depends strongly on tread properties.

Tyres were made with synthetic and natural rubber. The tread portion contains three parts si base, cap, and shoulder.

1.1.4 FUNCTION OF TYRE COMPONENTS

- (i) The Radial tire tread part must provide good wear and tear resistance and good wet grip in all the road conditions. The tread base reduces the rolling resistance and temperature.
- (ii) For driving stability multi-ply steel belt Steel cords embedded in the rubber compound Enhance and minimise the rolling resistance, which will give a long service life.
- (iii) For driving comfort steel casing Steel cord is used, which gives the tire structural strength.
- (iv) To prevent the diffusion of air and moisture in tubeless tires mostly Inner liner Rubber compounds were used.
- (v). SW compounds protect against and effects of weather-related defects.

1.4 COMPOUNDS IN THE TYRE TREAD:

The tread compound formulation comprises five materials: rubber, reinforcement materials or fillers, antioxidants and other compound protectants, processing aids, and the vulcanization system.

The selection of the elastomers will depend on the mission profile and design parameters for the tire but will, in all cases, be selected to provide wear resistance, traction under both wet and dry conditions, low rolling resistance, and contribute toward good vehicle fuel economy, and resistance to damage caused by cutting or tearing of the tread.

Tread compound development is a complex field in materials science, polymer chemistry and technology, and chemical blending to optimize the required mechanical properties.

Rolling resistance, damage resistance, and contribution to tire-vehicle handling qualities further impact formulation composition.

Silica is used as filler in the tire tread compound mixing and it results in fuel savings of 5% to 13% compared to tire tread type of compounds (contains carbon black used as filler). silica in the tire tread compounds reduce rolling resistance by up to 25%, and less greenhouse gas emission also.

Tyre tread processing conditions can impact tire performance such as RRC (Rolling resistance), WC (wet traction), and WR (wear resistance). tyres (low rolling resistance tyres), several coupling agents and high surface area silica filler were researched widely and used in rubber vulcanizate.

Highly dispersible silica enhances the degree of dispersion in the rubber compound than conventional types of silica filler. While mixing, the silane will react with silica filler leading to hydrophobization of the silica to the filler surface, thereby breaking down the agglomeration of silica fillers, **which is called a silanization reaction.**

This hydrophobization can reduce the silica-to-silica bonding and makes the polar silica more than compatible with non-polar rubber materials, leading to ease of processing and reducing the flocculation and good dispersion.

During cross-linking, Sulphur available in the coupling agents creates a covalent bond between the rubber chain and forms a chemical bond linkage.

RPA- Rubber Process Analyzer machine is used to measure fluctuation rate and filler-to-filler dispersion level, it indicates the **degree of silanization.**

Some of the mixing parameters can significantly influence the silanisation reaction, and it affects the energy consumption during mixing and the final performance properties of the radial tire. Much of the research had been carried out to optimize the silanisation temp and time in both silica-filled Styrene-Butadiene Rubber (SBR) compound and Natural Rubber (NR) compound.

This project study is to statistically determine the significance of proper mixing parameters on the degree of silanization and energy consumption in an actual Tandem /Banbury mixer using the DOE (design of experiments).

*Tread strip (Rubber compound) – The tread strip must provide high wear resistance and good grip in all road conditions.

*Multi-ply steel belt (Steel cords embedded in the rubber compound) - Enhances driving stability, reduces rolling resistance, and gives the tire its long service life.

*Steel casing (Steel cord) - it gives the tire structural strength & deflection characteristics that substantially enhance driving comfort.

*Inner liner (Rubber compound)- Prevents the diffusion of air & moisture in tubeless tires.

*Sidewall (Rubber compound) – Protects from lateral scrubbing and the effects of weather.

*Bead reinforcement (Nylon, steel cord) – secures the end of the steel cord ply to the bead core and reinforces the bead against high shear forces.

*Bead core (Steel wire embedded in the rubber compound) – Ensures firm fit of the tire to the rim.

1.5 NATURAL RUBBER & SYNTHETIC RUBBER

Synthetic and natural rubbers are used in tire manufacturing.

The consumption of natural rubber in the tire industry is almost 75% of its production. The conversion from bias to radial tires increased the genuine rubber requirement in tires. It improves the green strength, tears strength, rolling resistance, etc.

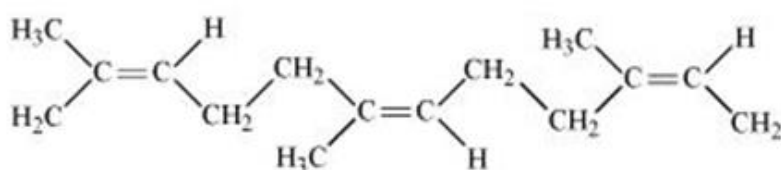
In winter tires, mostly synthetic rubbers are used, but if the requirement of load-carrying capacity is high, the tire size increases to almost 100% natural rubber.

Synthetic rubbers like SBR, Polybutadiene, and butyl rubbers were used in tire manufacturing. The introduction of SBR in tire compounds to passenger car tires leads to the improvement in the wet skid and traction properties of the tire. Adding butadiene in tread and sidewalls gives good abrasion resistance and enhances tread impression performance and resistance to cut propagation.

Table-1 Properties of natural rubber and synthetic rubber

NR (Natural Rubber)	SBR (Styrene-Butadiene rubber)
(i) Good tensile strength, Good resilience	(i) non-polar, (ii) Type of non-crystalline copolymer
(iii) Lower hysteresis	(iii) Less tensile strength
(iv) Good tear strength	(iv) Good glass transition temperature High
(v) Less heat generation	(v) Good tire traction
(vi) Better fatigue resistance	(vi) Well handling performance
(vii) Good cutting resistance	

Natural Rubber-



Natural rubber

- (i) Natural rubber occurs in almost 2000 plant species, out of which only a few are commercially important.
- (ii) The most important species is *Hevea Brasiliense* (tree).
- (iii) It is a tree which can grow up to 30m high with a main trunk of about 50cm diameter.
- (iv) It grows in tropical regions with high rainfall.
- (v) Applications in tyre- Tread, Body ply and Belts.



Figure 3 Different type of NR

1.6 FILLERS

The other important additive during compounding is fillers. Natural or synthetic rubber cannot be used in its purest form because they don't have the strength, hardness, and wear resistance. The addition of fillers will improve properties. A wide variety of fillers are used in rubber compounding. The array includes expensive reinforcing fillers to low-cost non-reinforcing fillers.

The selection of fillers depends on the requirement of the compound. Fillers improve rubber's mechanical, thermal, and electrical properties. The reinforcing fillers can increase the modulus and the elongation at break in an elastomeric compound. Mainly Silica and Carbon black were used in the tire industry. Carbon black and silica were in the category of reinforcing fillers.

1.7 CARBON BLACK

Carbon black contains elemental carbon in the form of spherical particles of colloidal size coalesced into particles of aggregates and agglomerates. Carbon black increases the strength, wear resistance, and fatigue properties of the tire. Carbon black can be produced from hydrocarbon combustion methods in different ways.

The classification includes furnace black, channel black, and thermal black; where the channel and thermal blacks are used in early times, it is not that popular. Its aggregate size and structure is directly influencing the compound properties. For a rubber compound increase in carbon black aggregate size increases the cut and growth strength.

A reduction in particle size results in high abrasion resistance and tear strength. In the tire industry, the carbon black amount influences the properties.

(i) Minimizing carbon black loading lowers tire rolling resistance. In constant black loading, an increase in oil level will increase rolling resistance but also improve traction (at less oil levels, an increase in oil level may decrease compound hysteresis by improving carbon black dispersion).

(ii) Fineness carbon black raises both RR (rolling resistance) and traction performance.

(iii) Increased aggregate size distribution to reduce the tire RRc with constant area and DBP test may help for this analysis.

(iv) Tread-grade carbon blacks can be selected to meet defined performance parameters of rolling resistance, traction, wear, etc.

Tread compound based on a blend of Solution SBR and Butadiene rubber filled with highly dispersible (HD) precipitated silica with an optimized amount of sulfur-functional organosilane resulting in lower rolling resistance and better wet traction than the traditional tread compounds.

(v) Carbon black characterization- Particle size, Surface area, structure.

(vii) Carbon black is made by either incomplete combustion of hydrocarbon or by thermal decomposition of the hydrocarbons.

1.8 CARBON BLACK VS SILICA

Compared to carbon black, silica contains fewer permanently fused particles. But their tendency to form agglomerates is higher—more traction properties and rolling resistance. Silica does not produce greenhouse gases, which is why it is environmentally friendly, and silica tires are known as green tires.

Three significant properties of CB, these three properties can be attributed to distinguishing the features of CB as well as silica, but with modifications.

The surface area measurement determines the particle size of silica. Silica gives abrasion property are lower than carbon black. The highly dispersed silica is an excellent alternative to conventional silica, with better RRc (Rolling resistance), Better traction properties, and good abrasion resistance.

The major problem concerning carbon black is the wet reduction and increasing rolling resistance; it affects the safety of tires and increases vehicle fuel consumption. The addition of silica can overcome these disadvantages. Silica can increase the wet grip and decrease the rolling resistance. Precipitated silica contains a silanol group on the surface, interacting weaker than carbon black. It leads to more hysteresis. In higher elongation, silica compounds have less modulus due to the slippage of rubber molecules.

First letter indicates the cure rate:

S=Slow

N=Normal

The second digit indicates particle size.

Lower=Smaller

- **N100 – N199: SAF (Super abrasion furnace)**
- **N200 – N299: ISAF (Intermediate super abrasion furnace)**
- **N300 – N399: HAF (High abrasion furnace)**
- **N400 – N499: FF (Fine furnace)**
- **N500 – N599: FEF (Fast extrusion furnace)**
- **N600 – N699: GPF (General purpose furnace)**
- **N700 – N799: SRF (Semi reinforcement furnace)**
- **N880: FT (Fine thermal)**

Figure 4 Carbon black grades

The use of silica in place of carbon black leads to a comparable tan delta at lower temperatures, providing an ice and wet grip on tires. The hysteresis of silica-filled rubber increases with the temperature due to a stable covalent bond between the silica and polymer network. The influence of silica on the properties of rubber compounds has been demonstrated in literature. However, there is still scope to understand the behavior of rubber–silica compounds, especially the tear and wear properties.

1.9 SILICA

- (i) It contains natural minerals, and it is used as the second major filler after carbon black.
- (ii) Silica – as a sustainable filler.
- (iii) Highly dispersible type of silica material can significantly enhance the degree of dispersion % and so lead to good filler–rubber interaction.
- (iv) Silica is an inorganic filler.
- (v) The particle size of silica ranges from 1-30 nanometers

Uses- Excellent winter properties, Low rolling resistance, Excellent wet grip, Extension of the magic triangle,

Types- Precipitated silica, Ground silica, Fumed silica.

If considering cristobalite which has an open network and instead of silica Al, Na, and Ca be in the system but, still 95%, SiO_2 can still be produced from it.

Tire-containing silica fillers have been popular because of reducing rolling resistance and improve the frictional force on wet and snow-covered roads. However, silica's polar nature makes it challenging to blend with non-polar rubber.

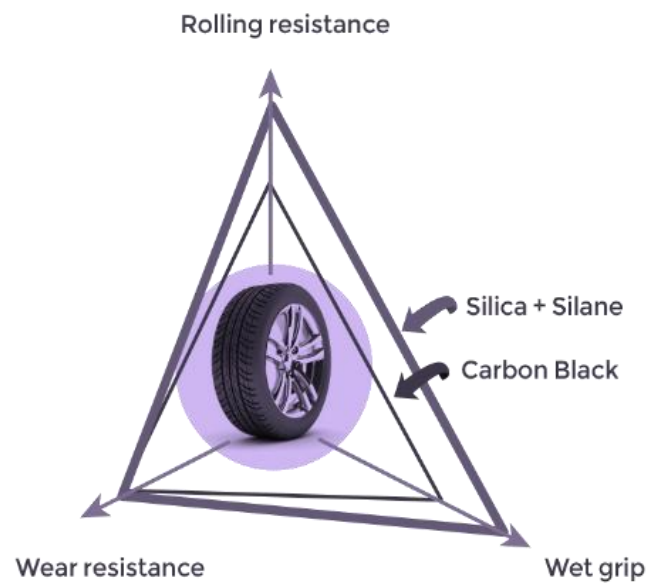


Figure 5 Tire Magic Triangle

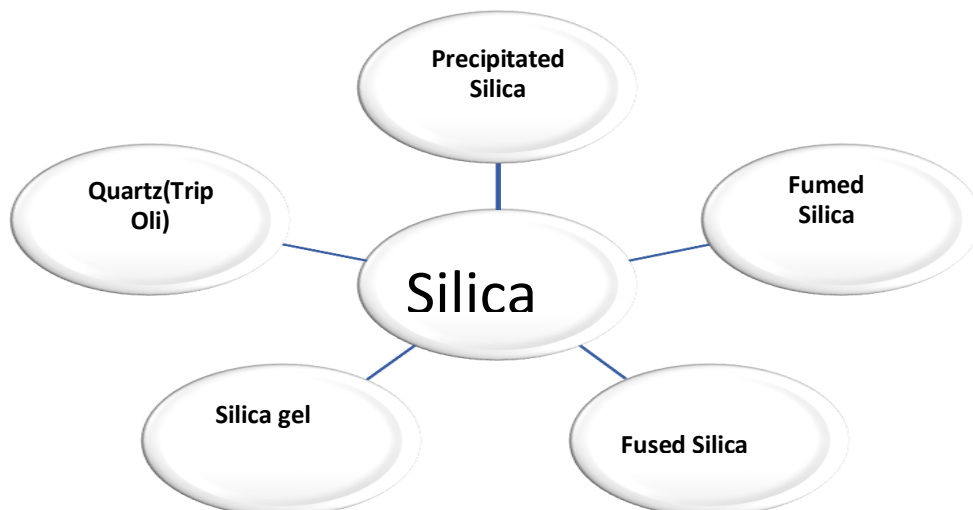


Figure 6 Classification of silica

1.9.1 PRECIPITATED SILICA

Precipitated silica is a form of synthetic amorphous silicon dioxide derived from quartz. The synthesis of precipitated silica is from the reaction of water glass and mineral acids. Precipitated silica is produced by four steps, precipitation, filtration, drying, and granulation. The precipitated silica's surface contains hydroxyl groups with active hydrogen atoms for reaction.

The surface area of silica is very high; it possesses a filler-filler solid network. This will directly influence the adhesion and tear resistance properties. However, the processability of the material is affected inversely. This will directly influence the curing efficiency. As a result, longer cure time and fewer sulfur crosslinks can be seen in the vulcanized rubber compound. Glycol or an active amine ingredient can be added to silica-filled compounds to tie up the active silica surface and reduce its affinity for curative chemicals.

Silica is hygroscopic; moisture remains after mixing and can interfere with non-sulfur cure systems, including peroxides. The reinforcement mechanism of silica- the silane system in the rubber compound. Three significant properties that directly influence silica mixing are Surface area, Structure, and surface chemistry.

1.9.2 COUPLING AGENT

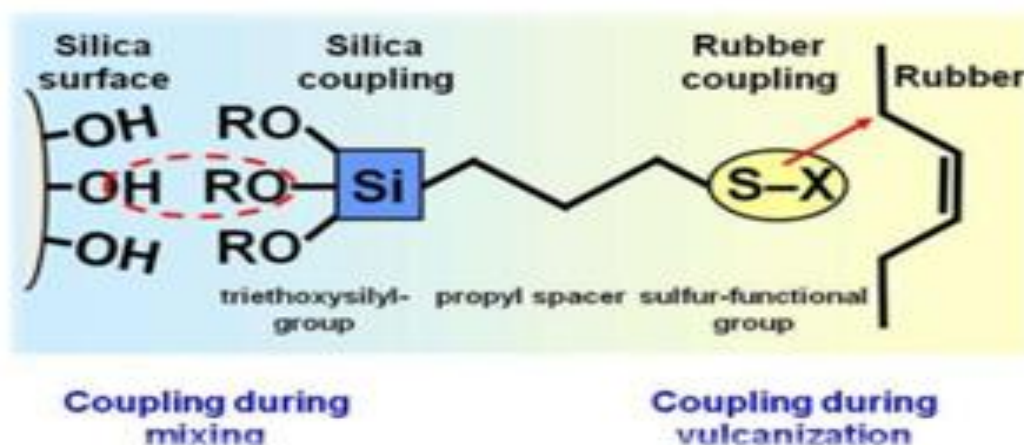


Figure 7 Silane coupling agent.

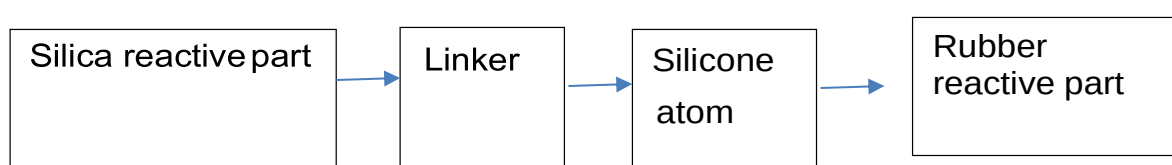
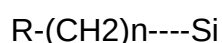
"Silane coupling agent: It will act as a bridge between the rubber and silica which results in the desired reinforcement of silica-filled rubber."

(i)Silica-polar

(ii)Rubber -Nonpolar

Examples: TESPT, TESP, Mercapto propyl trimethoxy silane.

The use of silanes allows a modification of the polar silica surface area and increases the compatibility of the silica with the rubber matrix. The monofunctional alkyl alkoxysilanes, which couple only to the silica, make the silica surface more hydrophobic. This leads to a substantial reduction of the silica-silica network. Lower viscosity and improved processability are the benefits.



1.1.5 PROCESS OIL

These materials can improve processability and reduce cost without affecting physical properties. Different types of rubber are used based on the product applications; Different types of rubber process oils are selected. For this compound paraffin oils were chosen as the process oils.

(a) Butyl rubber	-	Paraffinic type oil
(b) NR	-	Aromatic type oil
(c) BR	-	Aromatic type oil
(c) SBR	-	Highly Aromatic type oil

1.1.5 ACTIVATORS-STEARIC ACID

Stearic Acid is also called Fatty acids, it contains long molecules of Hydrocarbon Chains. It is used mainly in the activator system of the Rubber mixing compounding and is specific for the Curing process based on the vulcanization agent (Sulfur) in the accelerator-activator network bond. because of this Dual nature of hydrophilic and hydrophobic nature of the Stearic Acid, It is very helpful in the activator system of the rubber compounding as this will help Zinc Oxide to convert into a soluble form - rubber in effective dispersions of Zinc Oxide into the rubber matrix.

1.1.6 RESIN & MBTS

It is also called a tackifying agent. It increases adhesive and tack properties. Resins modify the optical and mechanical properties of polymer blends. Aromatic 500 resins offer better compatibility with Natural Rubber (NR), (BR) butyl rubber, and polybutene rubber.

MBTS (2'-Dibenzothiazole Disulfide) is used as a retarder. It is easily dispersed in mixed rubber compounds. MBTS are given below 3.2 phr dosage level to avoid blooming. MBTS is non-discoloring and non-staining but can turn yellow on exposure to light. It will not bloom at normal dosage.

1.1.7 SULPHUR & ZNO

Zinc Oxide (ZnO) and sulfur together are utilized as the curing method or agent. The oldest vulcanization agent still in use today for unsaturated rubbers is sulfur. It requires accelerators and activators to generate cross-links with rubber macromolecules, which is an efficient and quick process. Unsaturated rubbers are first vulcanized with sulfur in three phases.

Zinc oxide (ZnO) operates as a cross-linking agent for rubbers that contain carboxyl or halogen groups, in addition to triggering sulfur cures. Rubbers such as carboxylate nitrile (XNBR), bromo butyl elastomer (BIIR), and chloroprene rubber.

1.1.8 SILANISATION BENEFITS

- * Improved fuel economy and performance by the proper silanization.
- * Amorphous precipitated silica is utilized as a filler in the tyre tread and gives fuel savings of 3% to 15% compared to carbon black as a filler.

- * Incorporating silica into tyre tread compounds can reduce rolling resistance, and wear resistance, reducing heat buildup by up to 30%, resulting in decreased greenhouse gas emissions.

- * The chemical formulation of tyre tread compounds and their processing conditions can significantly impact tyre performance like rolling resistance, wet traction, and wear resistance.

- * Highly dispersible silica enhances the degree of dispersion in the rubber compound than conventional silica filler.

- * During mixing, the silane reacts with silica leading to hydrophobization of the silica surface, thereby breaking down the agglomeration of silica fillers, which is called as "Silanization reaction".

CHAPTER-2

2.1 LITERATURE REVIEW

Silica has polar nature rubber has a non-polar nature; during processing, it is difficult to interact with the whole amount of silica with the rubber matrix. Non-uniform dispersion causes negative results on fuel efficiency. Compared to weak filler-filler interaction, the strong filler-polymer interaction results in difficulties in silica mixing. Processing aids known as dispersing agents are introduced during compounding to overcome these difficulties.

The dispersant is a processing aid that lowers the viscosity to improve the surface roughness. As filler dispersion in the polymer, mixing consumes significant power and is time-consuming. Poor distribution can result in inferior physical and dynamic properties, mainly increased heat buildup and hysteresis.

To improve silica dispersion, it is conventional to use coupling an agent with the silica to couple or polymer-polymer collection. Such coupling agents are conventionally silica silane-based compounds with a silane-based which is reactive with hydroxyl groups such as silanols, found on the surface of silica and having another moiety, such as a polysulfide bridge, which may interact with a conjugated diene-based elastomer.

Examples:

bis(3-triethoxysilylpropyl)disulphide (TESPD)

Mercapto-type silane coupling agents,

3-mercaptopropyl tri methoxy silane,

3-mercaptopropyltriethoxysilane,

2-mercaptoethanol tri methoxy silane,

and mercaptoethanol triethoxysilane etc.

2.2 LITERATURE SURVEY

LITERATURE-1

S. H. Song, "Study on silica-based rubber composites with epoxidized natural rubber and solution styrene butadiene rubber," Polym. Compos., vol. 29, no. 9, pp. 1422–1429, Nov. 2021, doi: 10.1177/0967391120971391

(i)The purpose of the investigation was to study the effects of fillers, especially various types of carbon black.

(ii)Independent of the type of carbon black, the permeability is reduced by only about 30 per cent by the addition of 50 parts by weight of carbon black per 100 parts of rubber. The permeability of a rubber mixture to a gas is increased considerably.

(iii)This fact can be explained by assuming that gas is adsorbed by carbon black in rubber and thereby rendered inactive.

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LITERATURE-2

S. Maghami, "Silica-filled tire tread compounds: an investigation into the viscoelastic properties of the rubber compounds and their relation to tire performance," University of Twente, Enschede, The Netherlands, 2016. doi: 10.3990/1.9789036541282 (i)Carbon black with large particle size and very low structure can be used to reduce air permeability mainly because of its high loading capability.

LITERATURE-3

"Compounding with carbon black and oil" By S. Laube, S. Monthey, M-J. WangPg No-308 [2]

Decreasing the surface area (increase in particle size) usually increases the permeability resistance.

LITERATURE-4

A new Cabot carbon black for improved performance in peroxide cured injection moulded compounds [2] Presented by S.Bussolori, S.Laube at ACS rubber division meeting,2000 Paper no 98

- Use of low-structure semi-reinforcing carbon blacks to achieve higher carbonblack loading which improves air impermeability.

2.3 CONCLUSION OF LITERATURE SERVEY

From all the above literature we can conclude that the use of semi-reinforcing, low structure and high particle size carbon black as filler can reduce the air permeability of the compound. The reason for this can be due to

- (i) High filler loading in the rubber compound.
- (ii) High dispersion of the filler
- (iii) The gases get absorbed onto a carbon-black surface.

Some of the advantages of using such carbon black are,

- (i) High load ability in halo butyl inner liner compounds compared to using only GPF grades.
- (ii) Reduction of permeability in inner liners at high carbon black loading.
- (iii) Reduction of compound cost due to high black loading.
- (iv) Possibility for reduction of inner gauge providing cost savings.

Some of the advantages of using such Silica are,

* Silica and silica coupling agents are typically used in passenger car tire treads. The silica/silane coupling agent system improves tire tread wear and enhances abrasion resistance).

It can improve the dynamic property of rubber vulcanizate; in particular, it reduces hysteresis, which can be translated into better rolling resistance and leads to fuel-saving without affecting the wet grip.

* However, whether the product is compounded with a known coupling agent, the optimum dispersion can still not be attained. Furthermore, as a result of using a silane coupling agent, the reaction between the silane and hydroxyl group on the surface of synthetic amorphous silica results in the release of alcohol (ethanol). Which escapes from rubber compositions represents an environmental issue.

* In addition, reducing the amount of silica coupling agent is desired. Since use in a conventional amount significantly adds to the cost of the rubber. The release of alcohol can be avoided by adding other silanes than those of TESPD or TESPT.

* Most of them have been appropriately selected depending on the composition and use of rubber, contributing to productivity improvement such as improving the dispersion of fillers, shortening the mixing time, and increasing the extrusion speed.

* These dispersants are effective in carbon black rubber compositions that use carbon black as fillers. But it doesn't act as a dispersant in silica. If the dispersing agent is added, the silica as filler is utilized to improve dispersion, shorter mixing time, and extrusion. The speed will increase, but the dispersant can lower the viscosity, reducing physical properties.

*. The silica content of tire rubber is increased; silica contains many hydrophilic, and rubber includes a small hydrophobic group that re-agglomerates after dispersing. So, a lot of energy wastage happens in silica dispersion.

* The dispersant is added to the rubber matrix with the silica for better silica dispersion. Silica dispersant reduces the viscosity of the rubber during compounding. It reduces the time and energy required to disperse the rubber by bonding with the hydrophilic group on the silica surface not connected to the silane coupling agent.

* Most rubber compositions contain a reinforcing filler such as carbon black and silica or a combination of both. Silica is an amorphous white filler, Silica also known as silicate. Raw rubber composition comprises a relatively large amount of silica in the tire tread, generally known as green tire. These rubber compositions typically do not contain carbon black or a lesser amount of carbon black (ranges from 5 to 20 phr).

CHAPTER-3

3.1 AIM & SCOPE

(I) To study the effect of parameters, influencing silanization and its optimization in Rubber compounding.

(II) Screening of mixing parameters based on their significance on the extent of silanization and filler to filler to interaction, Filler to rubber incorporation.

(III) In this paper, a design of experiments (DOE) is carried out to screen the factors that significantly affect the silanization reaction during mixing.

3.2 PROBLEM STATEMENT

“The rising demand for fuel-saving tires with low rolling resistance, minimal heat build-up, and enhanced wear resistance highlights the need for optimizing the mixing of silica filler in tire compound mixing to meet these increasingly stringent requirements”.

(i) Silanization temperature and time were identified as the most influencing factors in the Silanization process using the contribution plot.

(ii) Tan delta and Payne effect properties are used as the monitoring parameters to find effective silanization.

3.3 OBJECTIVES

*Silica dispersibility in a silica-rubber compound is essential in determining an automobile tire tread's braking performance, wear resistance, and rolling resistance, low heat resistance.

*To study the effect of mixing variables on silanization during the mixing process to reduce the Payne effect and tan delta variation for achieving better performance.

CHAPTER 4

4. EXPERIMENTAL (Materials & Methods)

4.1 MATERIALS

- (i) Sulfur & Accelerator
- (ii) Synthetic Rubber
- (iv) Carbon black & Silica
- (v) Activators & Antioxidants
- (vii) Processing oil
- (viii) Coupling agent
- (ix) Sulphur & Silane
- (xii) Ozone-protecting wax.
- (xiii) Terpene phenolic resin

4.2 FORMULATION

INGREDIENTS	PHR
SSBR	80
PBD- HIGH CIS BR Nd	20
SILICA	86
N339 CARBON BLACK	5
RAE PROCESS OIL	10
TESPD -SILANE	7.5
TERPENE PHENOLIC RESIN	25
ZINC OXIDE	3
STEARIC ACID	2
TMQ ANTIOXIDANT	1
6PPD	6
WAX	2
SULPHUR	2
DPG ACCELERATOR	2.25
CBS ACCELERATOR	1.80
TBZD ACCELARATOR	0.45
Total	254

4.3 MIXING & COMPOUNDING

4.3.1 Mixing

- * Mixing refers to the process of combining different ingredients or raw materials to create a homogeneous mixture.
- * In the rubber industry, mixing involves blending various rubber polymers, fillers, plasticizers, curatives, and other additives to produce a uniform rubber compound.
- * The mixing process aims to distribute the ingredients evenly throughout the compound to ensure consistent properties and performance.

4.3.2 Compounding

- * Compounding, on the other hand, refers to the overall process of formulating a rubber compound by selecting and proportioning the appropriate ingredients.
- * It involves determining the specific recipe or formulation for a particular rubber product, considering factors such as the desired properties, processing requirements, end-use application, and cost considerations.

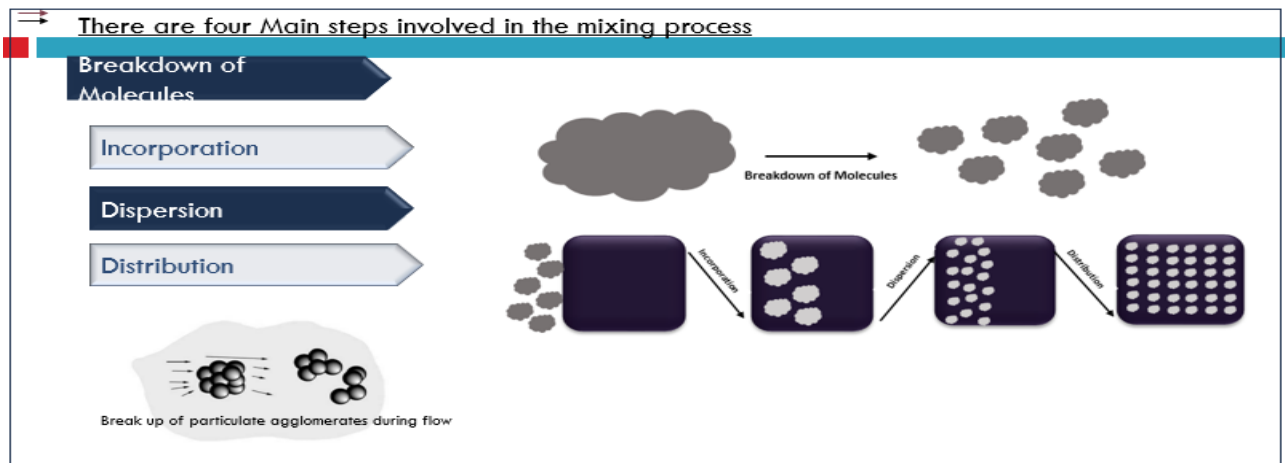


Figure 8 Mixing mechanism.

4.3.3 Principle of Mixing

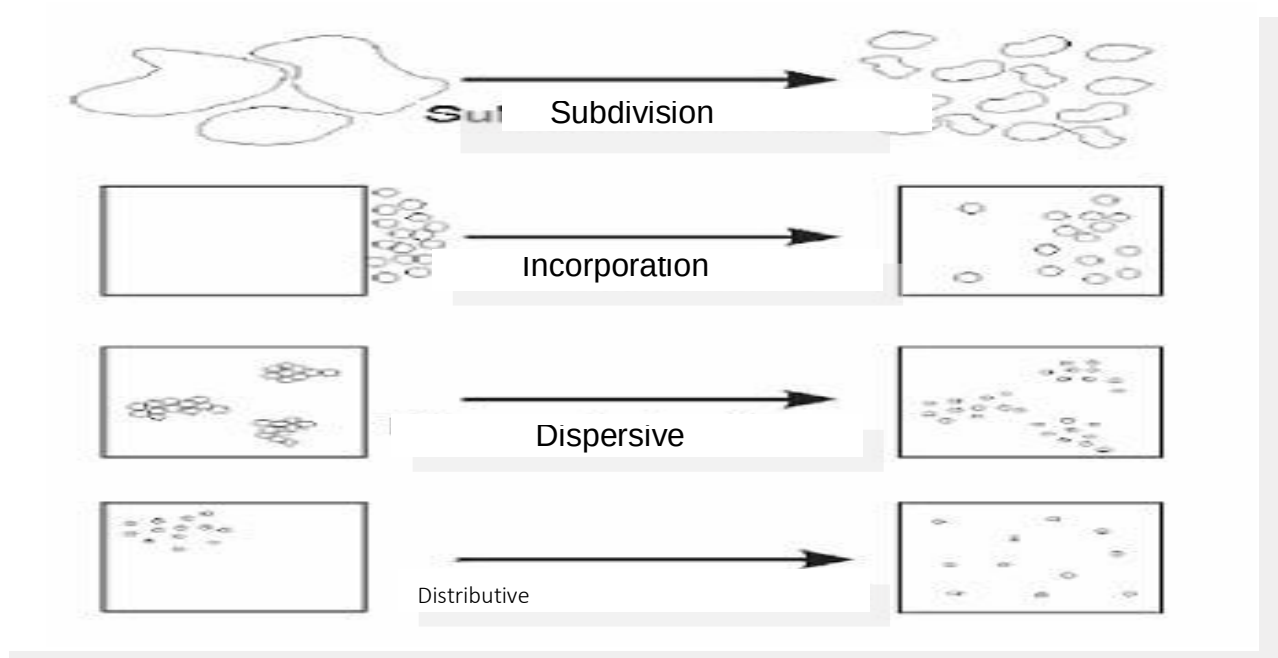


Figure 9 Principle of mixing

4.3.4 Four basic steps are involved in the mixing operation.

- (i)Incorporation: is the first stage of mixing during which the previously separate ingredients form a coherent mass.
- (ii)Dispersion: is the process during which the carbon black agglomerates are reduced to their ultimate size.
- (iii)Distribution: is simple homogenization, during which the various ingredients are randomly distributed throughout the mass of the mix.
- (iv)Plasticization: during this operation, the mix reaches its final viscosity as plasticizers effectively lubricate the mix.

4.3.5 Banbury (tangential 4 wing rotor mixer)

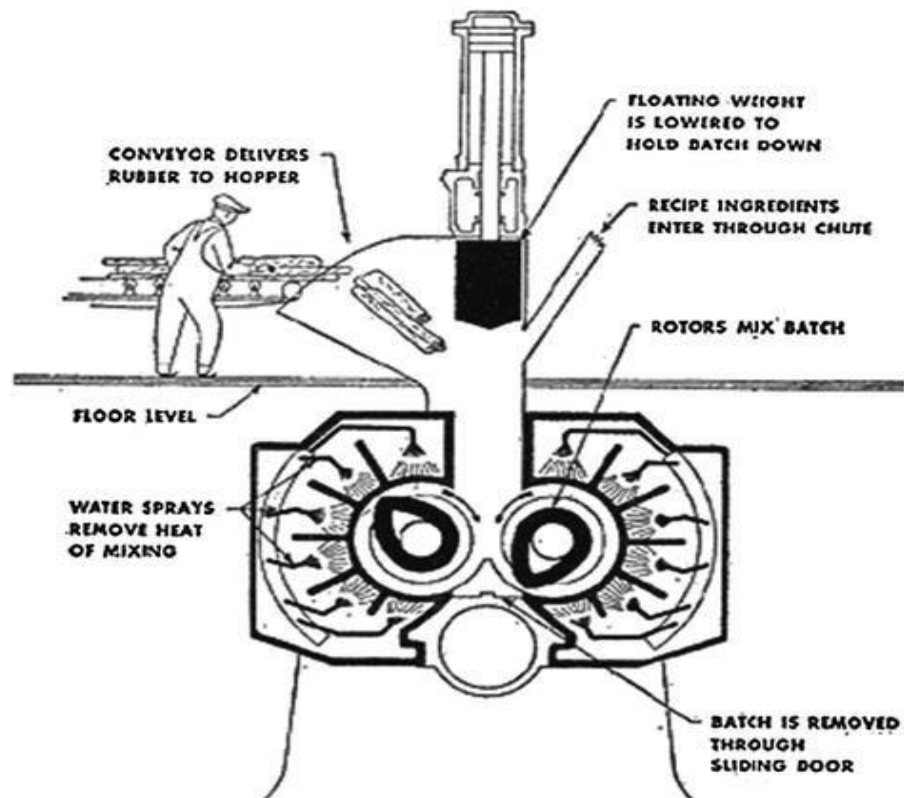
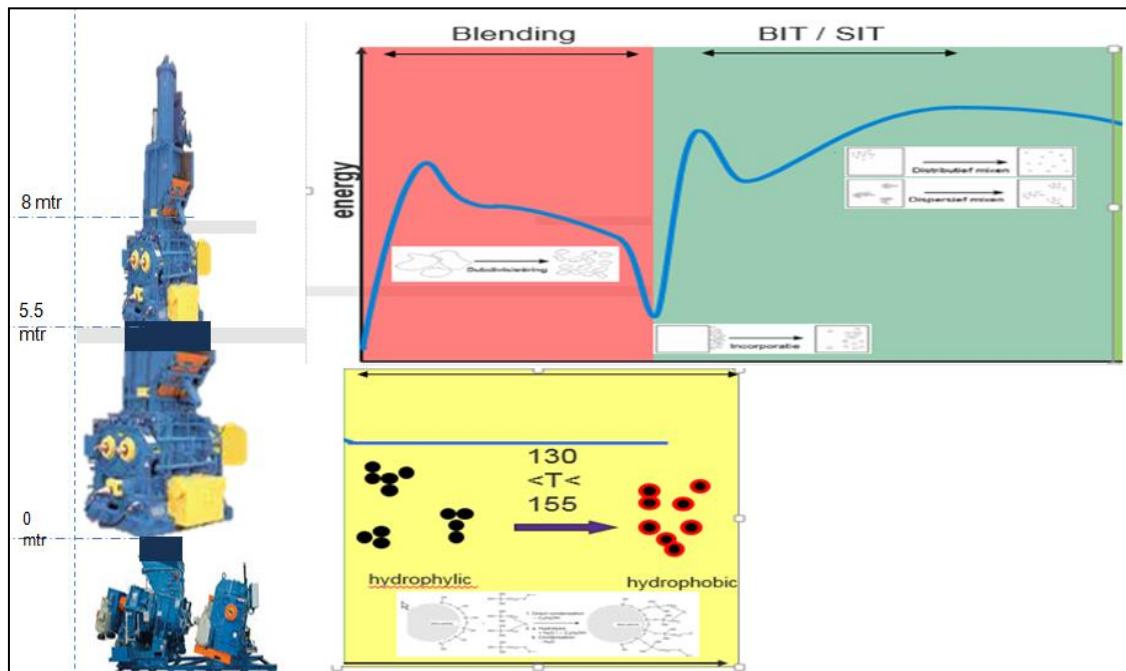


Figure 10 Banbury normal Mixer



Figure 11 Mixer blade

4.3.6 Tandem mixer Process



Tandem technology separates the two main tasks called *dispersion and distribution*.

Dispersion means the breaking down of solid materials such as fillers.

Distribution involves achieving homogeneity within a rubber mix compound with its different chemicals added.

- (i) In Tandem technology two mixers are interconnected in series where a type mixer does dispersion well while the other tandem mixer does the task of distribution.
- (ii) Between the two mixers is a discharge flap and chute which would be always closed except when the lower tandem mixer receives the master batch dump from above.
- (iii) The Rubber, chemicals, Fillers, oil, and silane are added in the first mixer, and it gets mixed for a fixed time after that it is dumped into the bottom mixer where the chemical reaction takes place.
- (iv) In the meantime, the next batch will start in the first mixer and then it is dumped into the second mixer before that the second mixer completes its mixing and dumps the batch into TSS.

Advantages & Disadvantages

- (i) Effective Shear is high.
- (ii) Poor material intake behaviour
- (iii) Cooling efficiency is High.
- (iv) Spiral Cooling
- (v) Less productivity
- (vi) Less fill volume
- (vii) Both Dispersive and Distributive

4.3.7 Normal Mixing

Normal mixing is the process in which the raw materials are blended and mixed using Physical Reaction.

- (i) Mechanism:
- (ii) Breakdown of molecules
- (iii) Incorporation
- (iv) Dispersion

4.3.8 Silica Mixing

In Silica mixing the raw materials will undergo the physical blending process as well as which also includes the chemical reaction between the raw materials silica and silane called *Silanization*. This type of mixing is also called Reactive Mixing.

The reaction will start at a temperature around 120°C and the temperature should be maintained constantly. This reaction is Temperature sensitive.



Figure 12 Tandem Mixer blade

Mixing is a process by which two or more components are converted to a homogenous dispersion. Rubber has to be mixed with compounding ingredients like carbon black, sulphur, accelerators etc

First, we have to calculate the weight of every ingredient.

$$\text{Weight of an ingredient} = \frac{\text{weight of the ingredient in formulation} \times \text{BW}}{\text{Total weight of ingredients in formulation}}$$

Batch weight (BW)= chamber volume*s.g*fill factor

Then we have to design the mixing cycle. Mixing is mainly done in two stages. First, we will prepare a masterbatch, then the final mix. The master batch will have every ingredient except curing agents, accelerators, and retarders.

Masterbatch is mainly prepared at higher mixing speeds(40-60rpms). Dumping is based on temperature and energy.

The variables fixed for the master batch are.

- (i) Rotor rpm
- (ii) Ram pressure
- (iii) Oil addition temperature and energy
- (iv) Ram up temperature
- (v) Dumping temperature and energy.

For final batch compounds, we set 2 energy limits and a temperature for ram up and down. Two energy limits and a temperature for dumping

Three parameters are considered for dumping.

Temperature, Energy and Time.

4.4 CHARACTERISATION

(i) Rubber processing analyzer - Payne effect & Tan delta

(ii) Dynamic Mechanical Analysis (DMA)

(i) Payne Effect (Standard: ASTM D 6204)

Condition: Temperature- 100°C, Time – 10 minutes, Frequency- 0.01Hz

It is a low-amplitude dynamic test, performed on filled rubber compounds. This test is a strainsweep with the stress measured in the elastic modulus.

Payne effect test data describe the stress-strain behaviour of a filled rubber compound, precisely the filler network's strength. In the test a drop in storage modulus characterizes the test as the sinusoidal oscillation amplitude increases, reflecting the filler network's weakening. Filled rubber is a candidate for a vital part of mechanical energy during deformation.

This behavior is the character behavior drop of elastic modulus G' when shear strain amplitude increases while the loss modulus G'' passes through a maximum. The loss tangent increases quickly, revealing a significant amount of emancipation process.

The strength of the filler network comes from the Vander Waals force in the case of carbon black and hydrogen bonding in the case of silica filler. Depending on the compound, filler networks are held together by either or both.

The amount of softening in a compound from increased strain can be attributed to mixing conditions.

Dynamic mechanical analysis (DMA),

Standard: ASTM D 7028

The viscoelastic behaviour of a material can be identified by analyzing the dynamic property.

Dynamic Modulus: The ratio of stress to strain under vibratory conditions. It is usually expressed in pascals or pounds per square inch for unit strain.

A set of consistent testing procedures has also been formulated. Measured values of dynamic properties of rubber may be influenced by the apparatus and method used, so it is not sufficient to specify a specific dynamic modulus, for example unless the details of its measurement are also limited.

The tests can generally be classified as impact rebound, forced vibration in both resonance and non-resonance conditions, and free vibration.

The dynamic mechanical analysis (DMA) of the SBR compound was studied using XPANDER DMA in tension mode from -80 to 80 °C at a testing frequency of 10 Hz. The heating rate of 3 °C/min was applied to the samples with a dimension of $15 \times 6 \times 2$ mm³. A DMA analysis is conducted to investigate the microstructure, viscoelastic properties, and rubber-filler interaction of the SBR compound.

The results of the DMA analysis are summarized. The variation of storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) with temperature. The E' is the energy stored in the material. D2<Control<D1<D3.

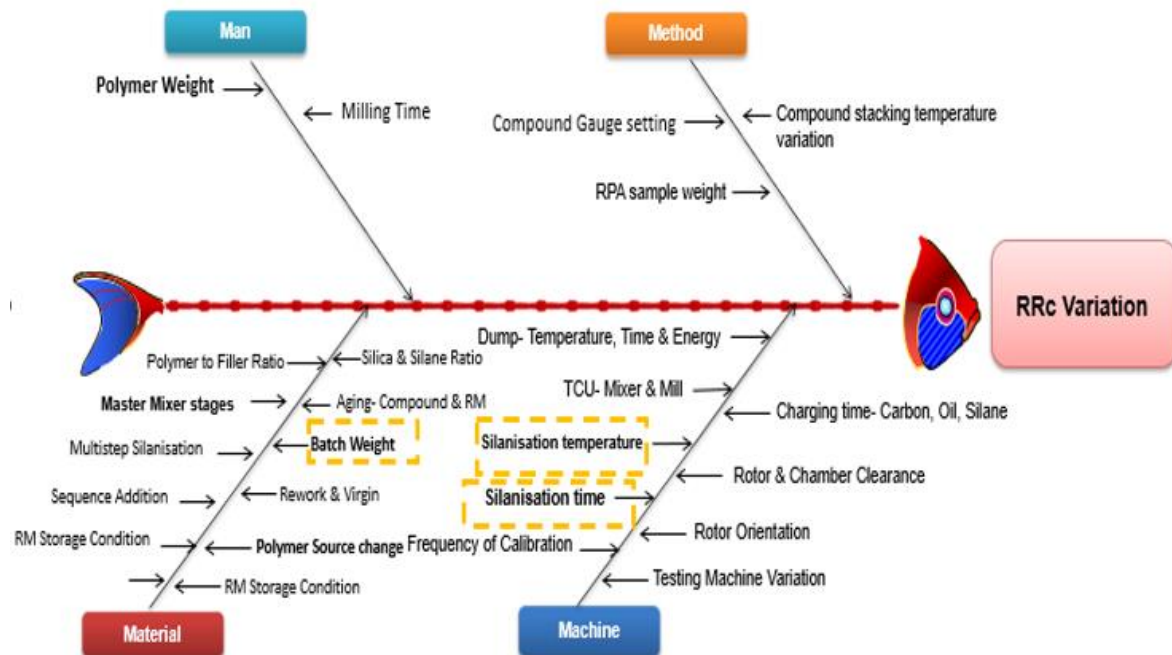
All the prepared composites show a high value of E' at low temperature (-20 °C).

4.5 METHOD

4.5.1 Brainstorming

Probable Causes- Mixing			
S.no	Input	Process	Output
1	Polymer source change	Mixing Temperature	Payne effect
2	Polymer and filler ratio	Mixing Time	Tan Delta
3	Compound ageing-Overage	Mixing Energy	Lab Machine variation
4	Compound ageing-Minimum	TCU Mixer	Specific Gravity
5	Batch Weight	Milling Time	RPA sample weight
6	Polymer Weight	Mill Temperature	Dispersion
7	RM Aging	Silanisation temperature	Rheo Property
8	Silica & Silane Ratio	Silanisation time	Frequency of Calibration
9	Rework & Virgin	Mixing stages	Physical Property- Hardness & Modulus
10	RM Storage Conditions	Charging time- Carbon, Oil, Silane	Compound Stacking Temperature
11		Sequence of Addition	Compound Gauge variation
12		Multistep Silanisation	
13		Rotor and Chamber Clearance	
14		Rotor Orientation	

4.5.2 Cause & Effect Diagram



4.5.3 Conditions for DOE as per Taguchi concept

S.no	Parameter	Tolerance	justification
1	Batch weight- Fill Factor (%)	50 to 70% or (330 – 370kg)	Below 50temp raise was difficult thereby rpm exceeds 90. Above 70 temp maintenance is difficult and increases mixing time.
2	Temp (Deg C)	135 -155	Less than 130 the silanisation reaction will not happen for TESP (silane). More than 155 for a long time (Polymer properties get deteriorated)
3	Time(sec)	90 to 270	90 to simulate a lower degree of silanisation, 270 to

The three mixing parameters were chosen, which affect the silanization as factors for DOE.

1. mixing time,
2. mixing temperature,
3. Batch weight,

We have chosen a range of values for selecting the levels as boundary conditions with the justification explained in the table above.

*To study the influence of mixing parameters on silanization efficiency and energy consumption, a masterbatch was prepared in the same mixing condition and mixing sequence (same formulation), which was further mixed and silanized in different mixing conditions by varying the several mixing parameters based on DOE in the second stage of mixing (also called as Repass / Master II).

4.5.4 Reason to adopt Design of Experiment—Taguchi method.

To study the effect of mixing variables on silanization during the mixing process, the Taguchi experimental design method is chosen. This method is a powerful tool that provides a simple, efficient, and systematic approach to optimize performance, quality, and cost designs.

Several DOE methods can be used to identify the most significant factors affecting the quality of a product and offer optimal conditions for the best quality.

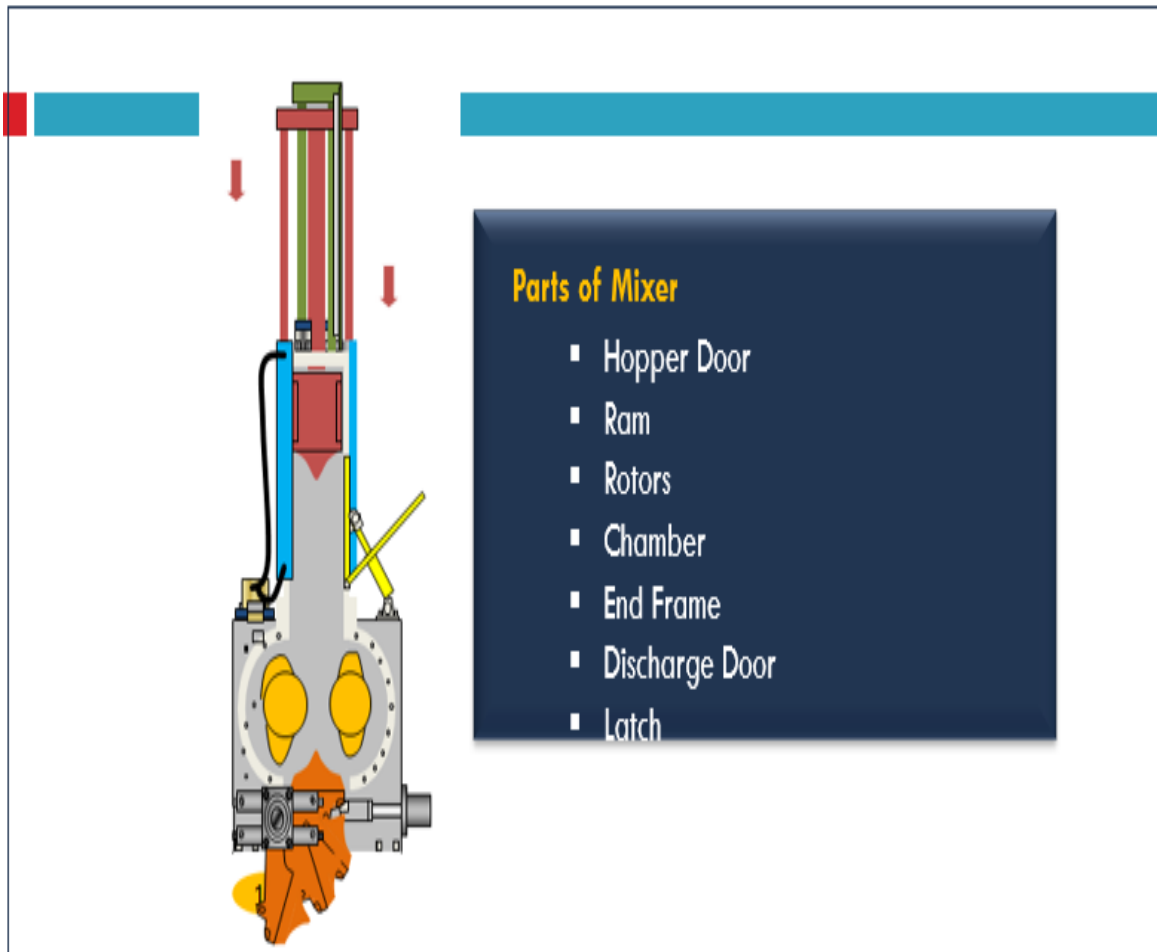
The Taguchi method uses orthogonal arrays as the basis of experiments. The benefit of using orthogonal arrays is that a large amount of information from the effects of many mixing parameters can be obtained from a few experiments.

There are three categories of quality characteristics in the analysis of the S/N ratio, i.e., "lower the better," "larger the better," and "nominal the better." Compared to Factorial and One Factor at a Time (OFAT) analysis, Taguchi has fewer runs which can efficiently provide the interaction parameter and main effect plot.

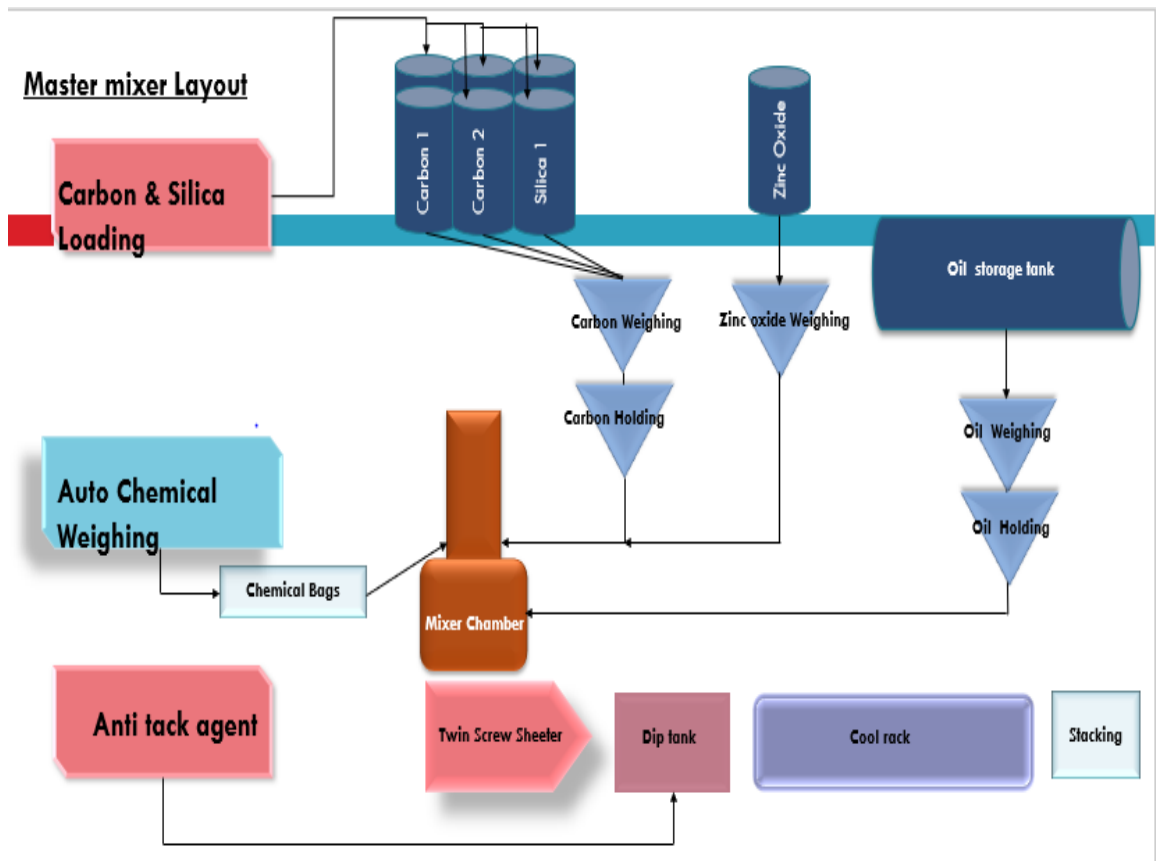
The parameters presumed to affect the degree of silanization, and compound performance are mixing time, mixing temperature, ram pressure, TCU, fill factor, and feed door condition.

In the present study, six factors with mixed three & two levels were chosen, and by these factors and levels, an appropriate O.A. was made with the Minitab software.

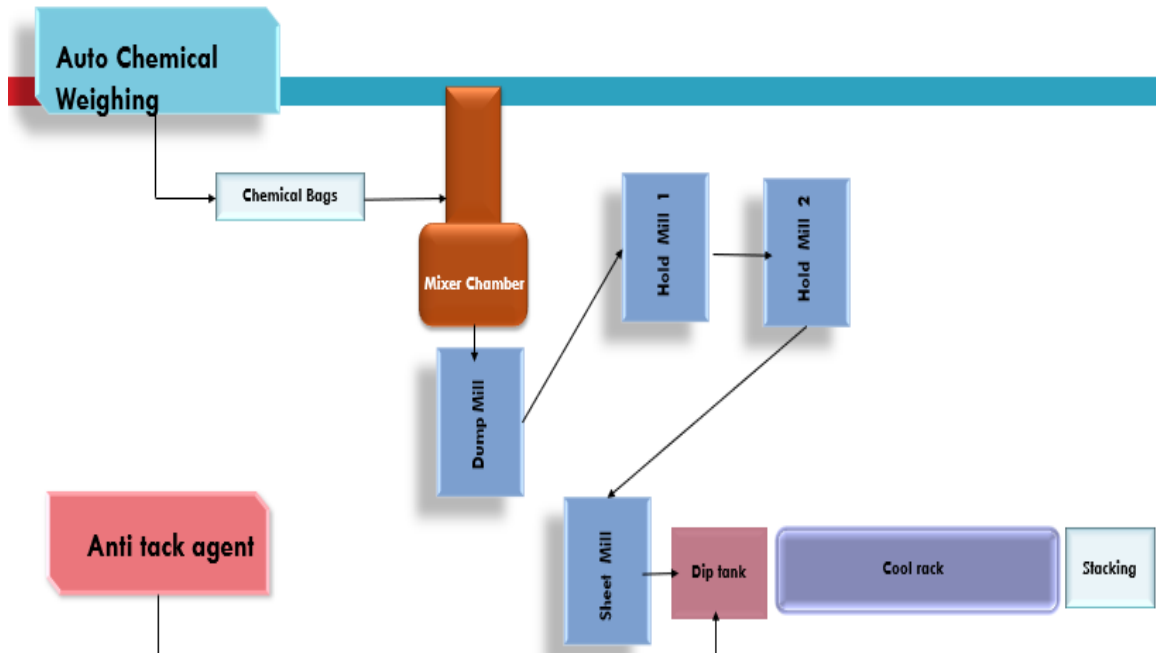
4.5.5 Tandem Mixer:



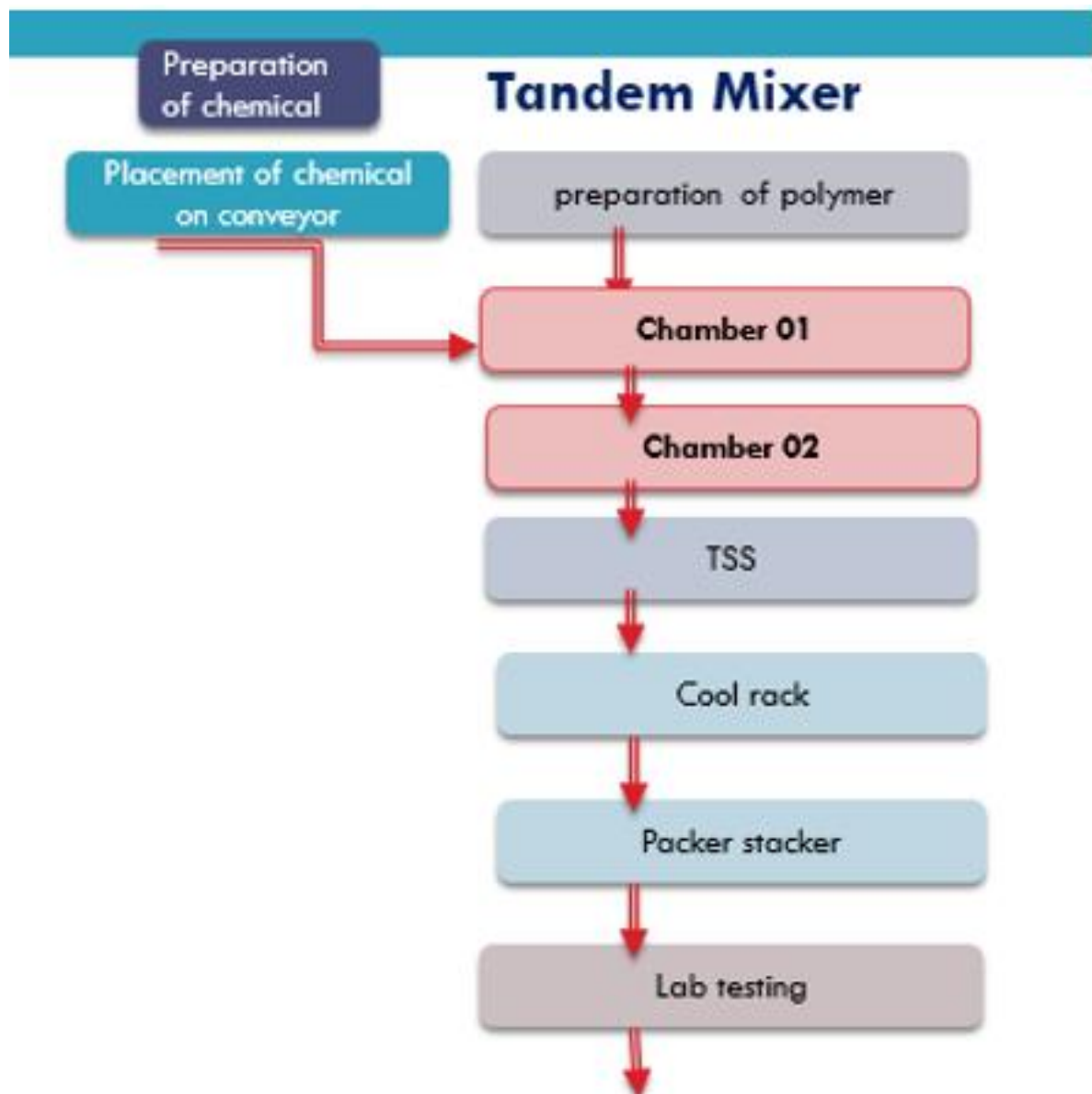
4.5.6 Master mixer Layout



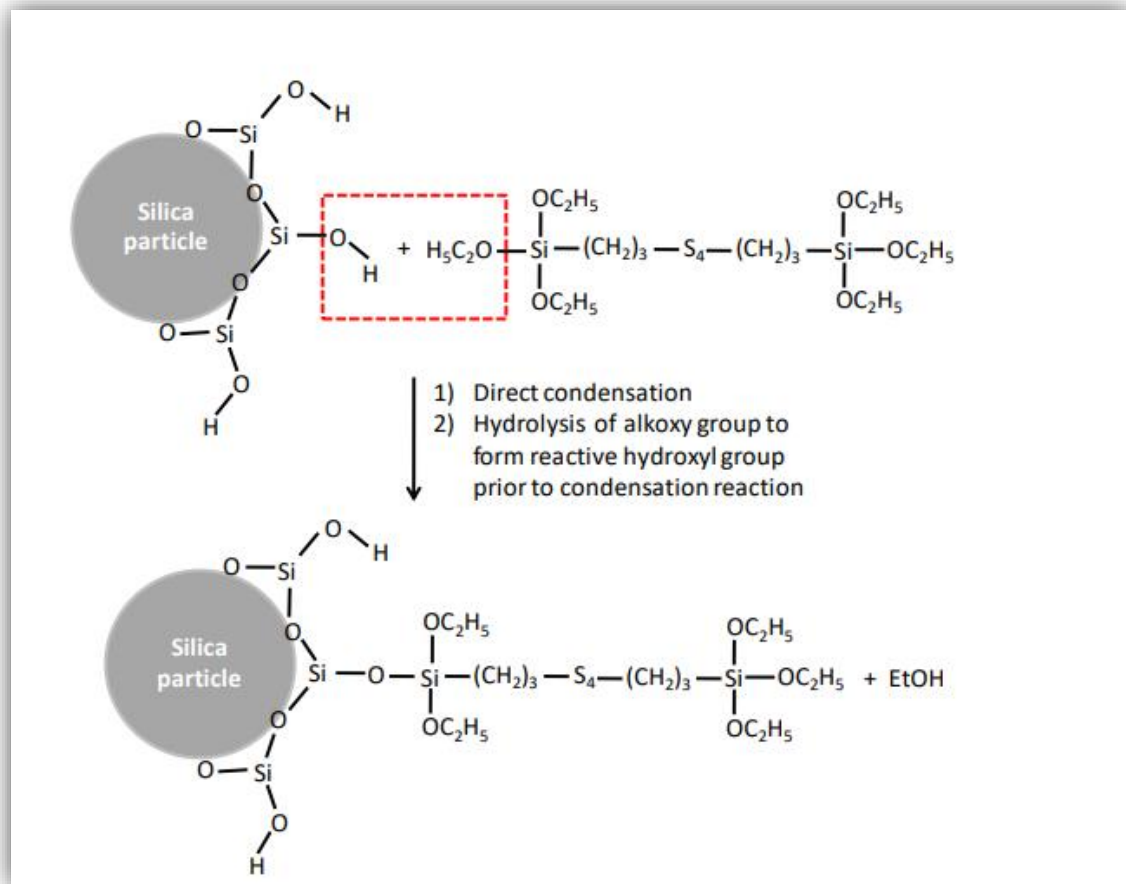
4.5.7 Final mixer Layout



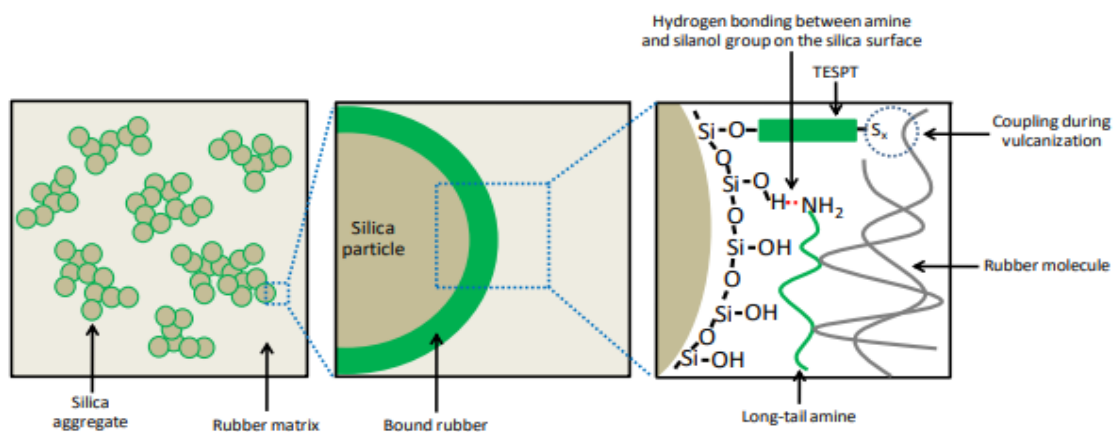
4.5.8 Process flow diagram



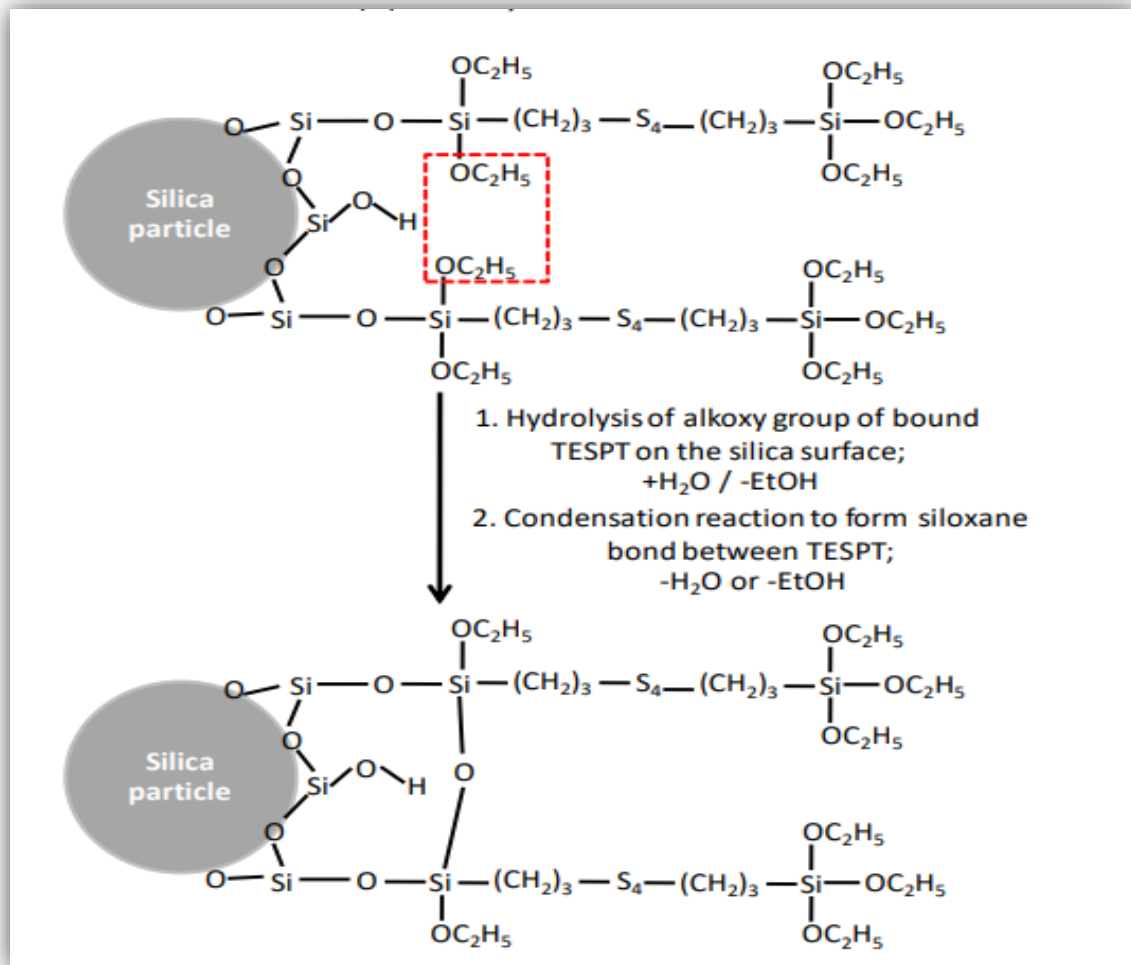
4.5.9 Silanization - Primary Reaction



The primary reaction can proceed via two pathways: either by direct condensation between the silanol groups of the silica surface and one alkoxy group of TESPT or by hydrolysis of the alkoxy groups of TESPT to form reactive hydroxyl groups before the condensation reaction



4.5.10 Silanization - Secondary Reaction



chemical reaction in mixing:

A secondary reaction often occurs between adjacent TESPT molecules on the filler surface, also releasing ethanol.

4.6 Effect of temperature on mixing

4.6.1 In masterbatch

Dump temperature is directly proportional to the thermal degradation of polymers. Hence an increase in temperature beyond the specified value will lead to excessive damage of polymer chains, and gelling.

Hence most of the polymers are hydrocarbons and being mixed with carbon black exposing them to higher temperatures beyond 170°C in the presence of atmospheric air can lead to fire catch-up.

4.6.2 In final batch

As the final batch is mixed with the master along with sulfur & accelerators, the presence of high temperature, the vulcanization reaction starts which leads to cross-linking of polymer chains by Sulphur.

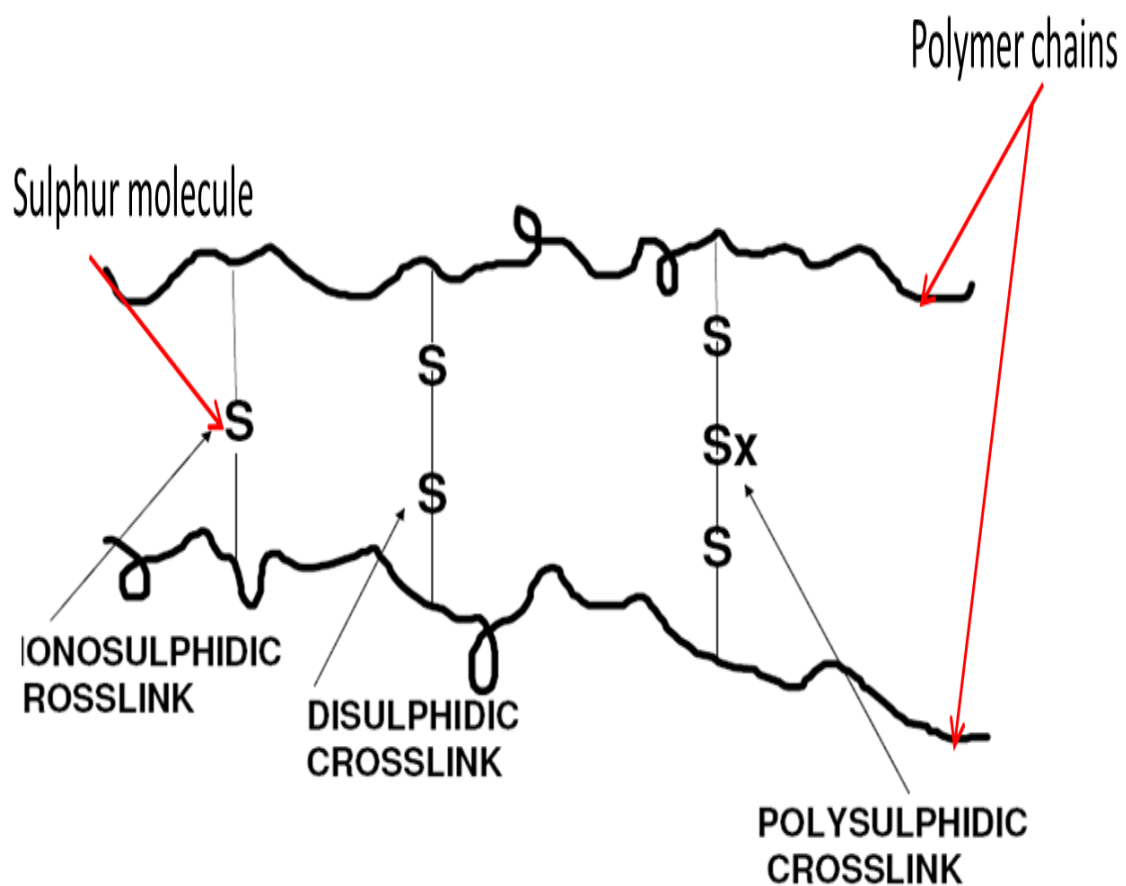


Figure 13 Silane Cross linking

4.7. DOE –Mixing trial plan

S.no	Stage	Parameter	Compound	Regular spec	Trial-1	Trial-2
1	Process	Silanisation Temperature	T392	148 deg C	130 deg C	155 deg C
2	Process	Silanisation Time	T392	150 sec	130 sec	170 sec
3	Process	Batch weight/Fill factor	T392	350 kg	335kg	365kg

4.7.1 List of Q parameters to be tracked during the project.

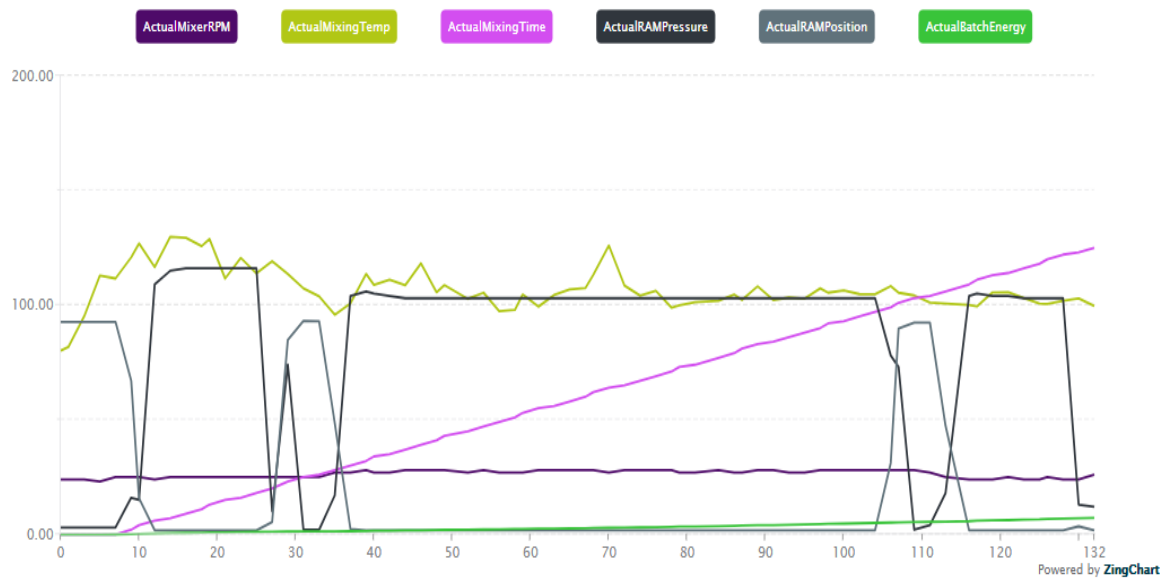
Area	Parameter	Standard
Master mixing	Payne effect	As per the lab control plan & checking condition
Final mixing	Payne effect & Tan delta	
Final mixing	Rolling Resistance	
Final mixing	DMA (Dynamic Mechanical Properties)	

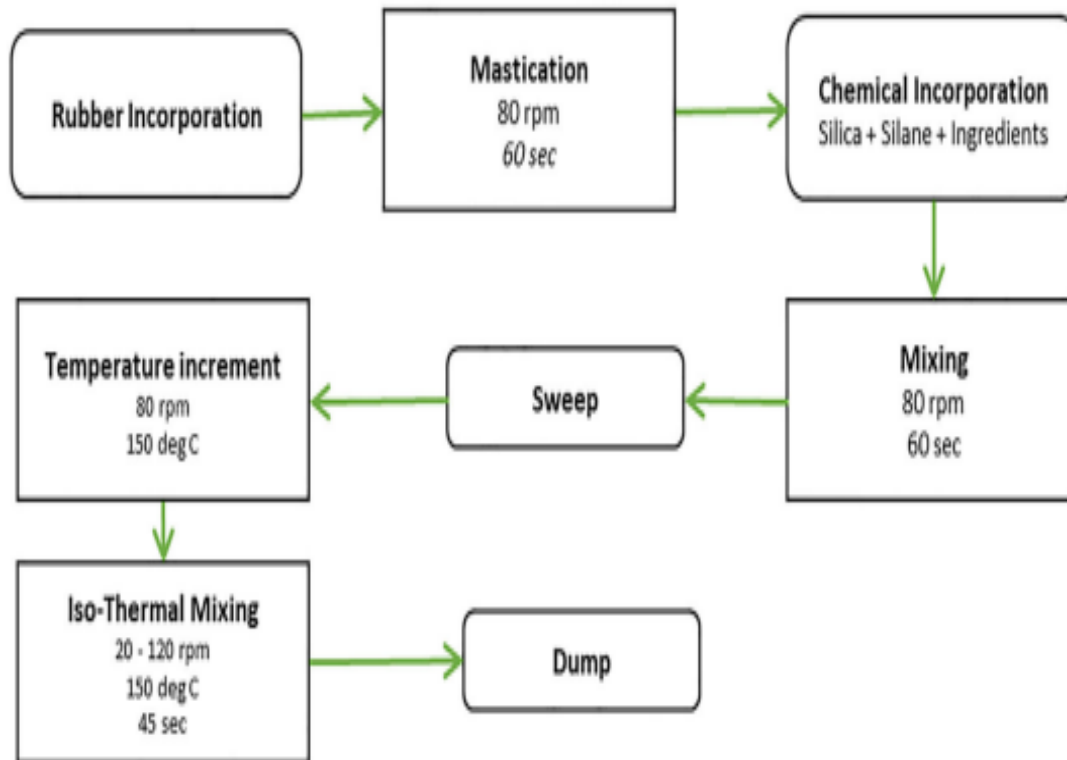
4.8 Mixing flow chart and mixing fingerprint graph.

4.8.1 Mixing sequence

Sequence No	Action	Mode	Rotor Speed	Ram Pressure	Mixing Override Time	Mixing Override Temp	Mixing Override Energy	Mixing Minimum Speed	Rotor Maximum Speed	Rotor Minimum Speed	Set Temperature(Speed Control)	Discharge Door Open Time	Ram Sweep Time	Step Time	Mixing Time	Batch Temperature	Batch Energy
1	StartMix	Null Mode	50	135	0	0	0	0	0	0	0	0	0	0	0	0	0
2	Feed Polymer and Small Bag	Null Mode	50	135	0	0	0	0	0	0	0	0	0	0	0	0	0
3	Ram Down	Null Mode	50	135	0	0	0	0	0	0	0	0	0	0	0	0	0
4	Feed Carbon and Zno	Step Time	50	135	0	0	0	0	0	0	0	0	0	20	0	0	0
5	Feed Silane2 and Oil	Null Mode	40	115	0	0	0	0	0	0	0	0	0	0	0	0	0
6	Ram Down	Null Mode	50	115	0	0	0	0	0	0	0	0	0	0	0	0	0
7	Feed Small Bag	Step Time	50	115	0	0	0	0	0	0	0	0	0	20	0	0	0
8	Ram Down	Null Mode	35	115	0	0	0	0	0	0	0	0	0	0	0	0	0
9	Ram Sweep	Mixing Time And Temperature	35	115	0	0	0	0	0	0	0	0	3	0	60	115	0
10	Ram Sweep	Mixing Time And Temperature	35	110	0	0	0	0	0	0	0	0	3	0	70	135	0
11	iram Profile(iRAM-0.2-MB01)	Step Time	23	110	0	0	0	0	0	0	0	0	0	40	0	0	0
12	Ram Sweep	Mixing Time And Temperature	30	110	0	0	0	0	0	0	0	0	3	0	80	144	0
13	Maintain Temperature_TM	Step Time	0	0	0	0	0	15	35	146	0	0	0	150	0	0	0
14	Batch Discharge with Ramp Float	Temperature And Energy	55	100	0	160	50	0	0	0	0	12	0	0	0	145	28

4.8.2 Mixer Fingerprint





Energy consumption for control silica-filled S-SBR/ BR compound for master, repass, and final stage:

The masterbatch mixing sequence and materials used in DOE are kept the same to minimize interference with external noise factors.

Significant variations of factors with different levels were carried out during the Isotherm (silanization) stage of mixing; the mixing parameters like temperature, feed door condition, time, ram pressure, and TCU were varied along with the fill factor for Master II [Repass] mixing according to the DOE table mentioned.

The masterbatch and repass mixing fingerprint graphs extracted from the Banbury mixer with a 4-litre capacity [Farrell Banbury mixer from HF Mixing group] are mentioned respectively.

During the masterbatch mixing isothermal stage with a silanization temperature of 130C and silanization time of 45 seconds is maintained via variable rpm method and then dumped. The extent of the silanization reaction is kept minimum during this stage I mixing.

For Master II [Repass] stage, the masterbatch compound is mixed without further addition of chemical ingredients; once the silanization temperature reaches the isothermal phase-mixing will be carried out automatically.

Compound temperature is controlled via variable RPM method using Farrell HF mixing Banbury mixer.

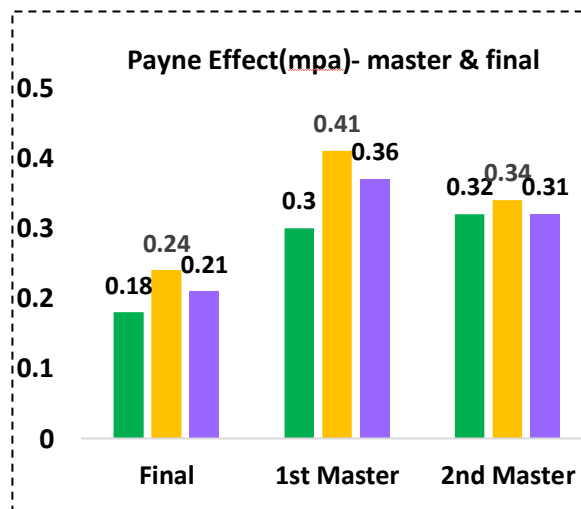
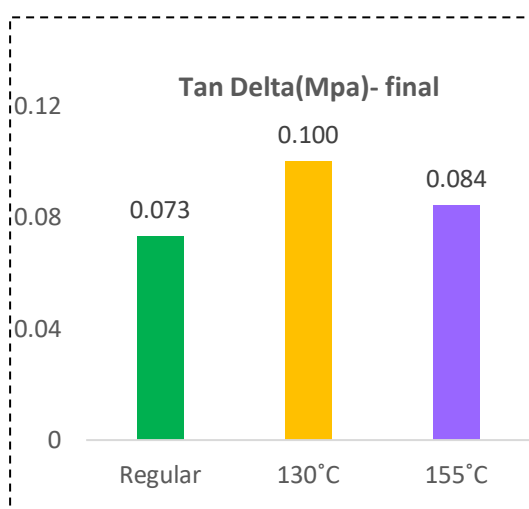
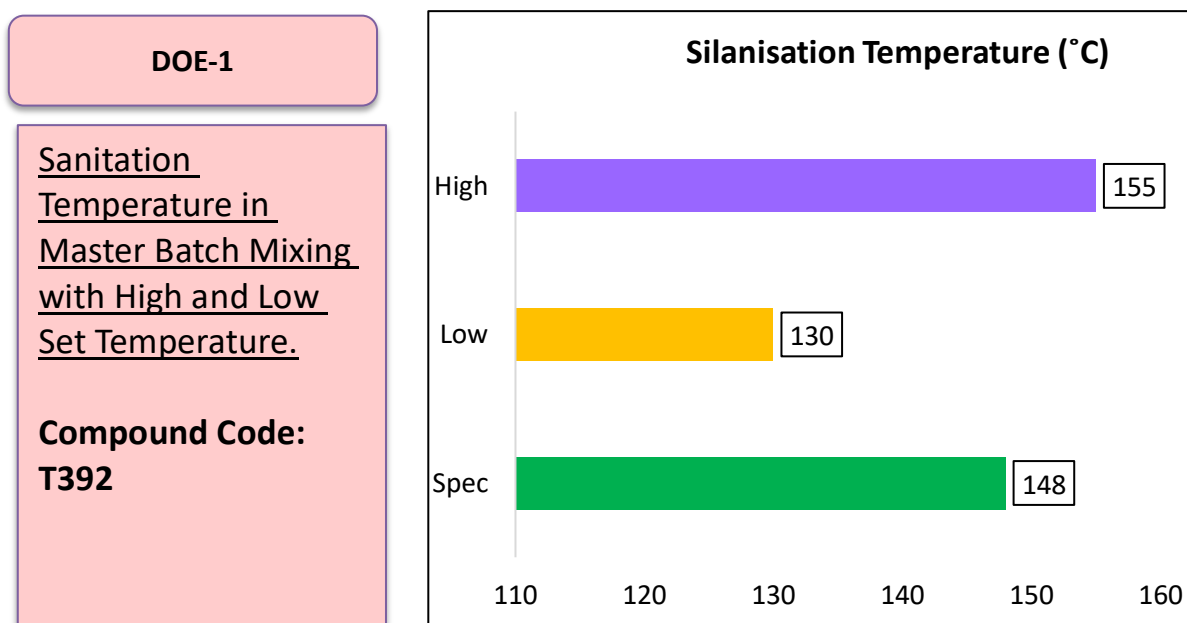
The energy input for each sequence in the master's and repass mixing stage was noted and depicted.

The mixing parameters play a vital role in energy consumption during mixing. Especially parameters like TCU, mixing temperature and mixing time. RPM directly affects energy consumption. i.e., the higher the values, the higher the energy input for the system.

CHAPTER-5

5.1 RESULTS AND DISCUSSION, PERFORMANCE

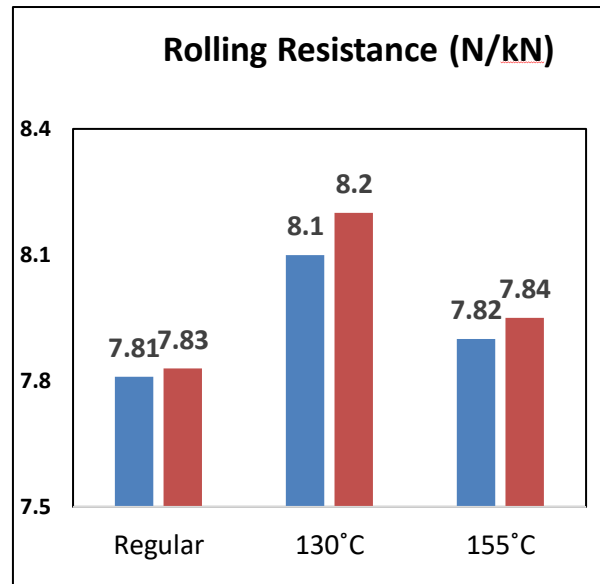
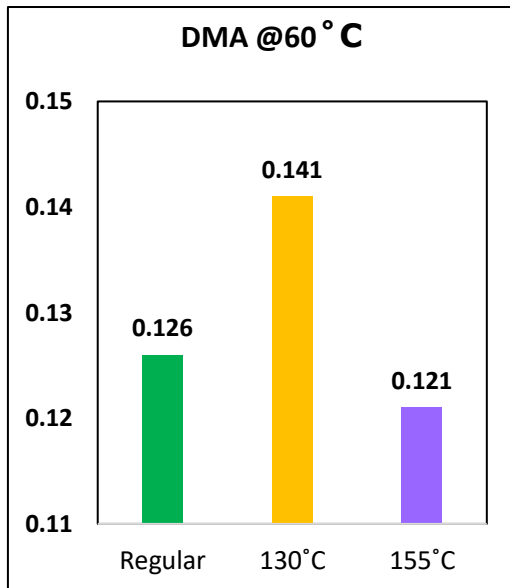
5.1.1 Silanisation Temperature



(i)@155 C temp trial observation: Payne Effect found to decrease by 0.06Mpa Unit as compared with @130 deg C in the master stage-1, and Master stage-2 found 0.01Mpa reduced. It is good result which is indicating good silanisation.

(ii)@ 155 deg C temp trial observation – In Tan delta found 0.03 Mpa reduced as compared with Regular. It is good result for proper silanisation.

- From this trial observation, 130 degC is not suitable for silanisation compared with 148 & 155 deg C.
- Establish Process specs by cross-checking the right degree of silanization



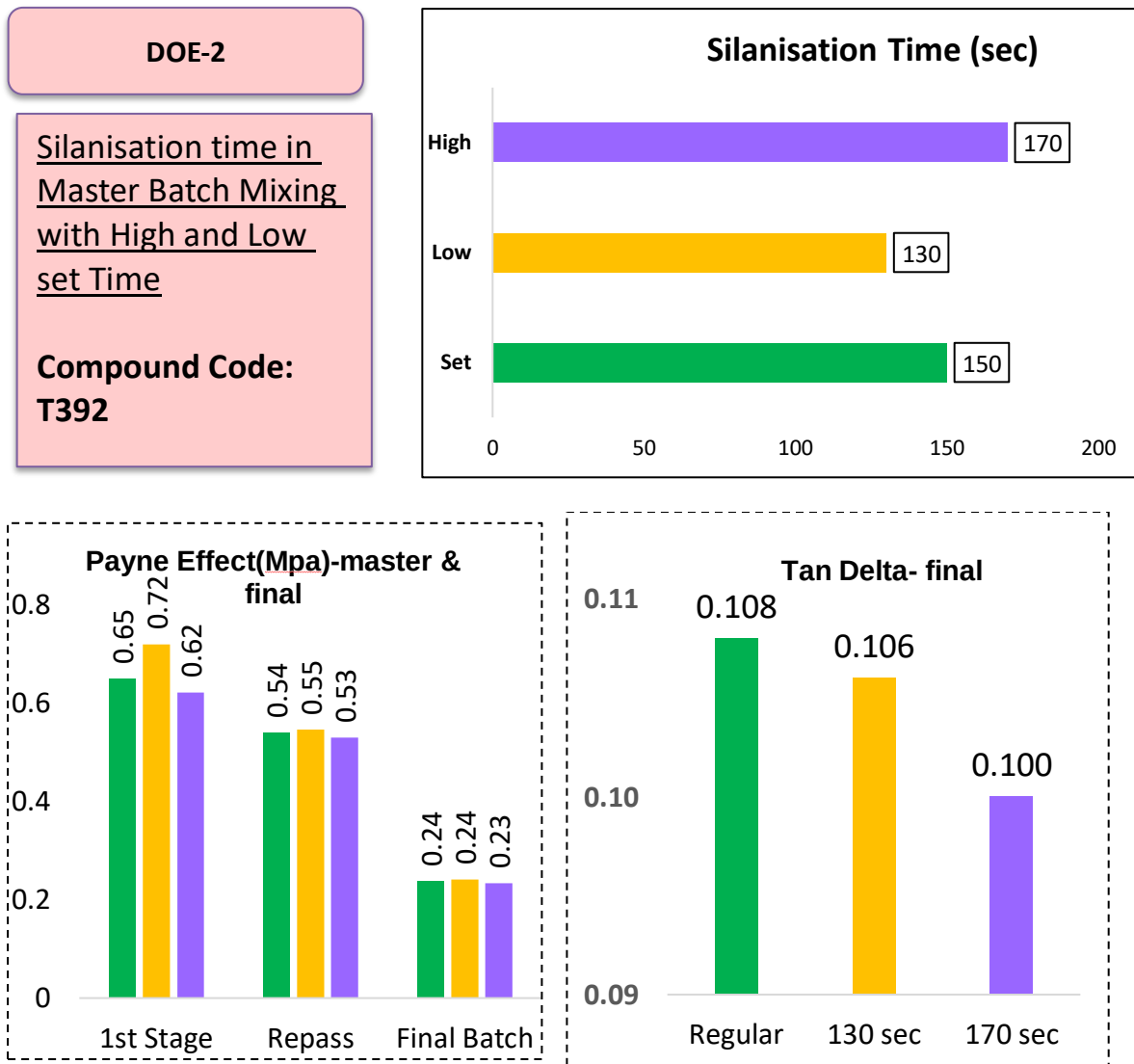
(i)DMA test result 0.121Mpa achieved from regular 0.126 Mpa with 155deg C silanisation temp condition and it is good value for the proper silanisation.

Silanisation Temperature has a profound impact on RRc, and optimized temperature is better for RRc.

(ii)Tyre RRc was found 7.82N/KN) as compared with regular value 7.83N/KN.

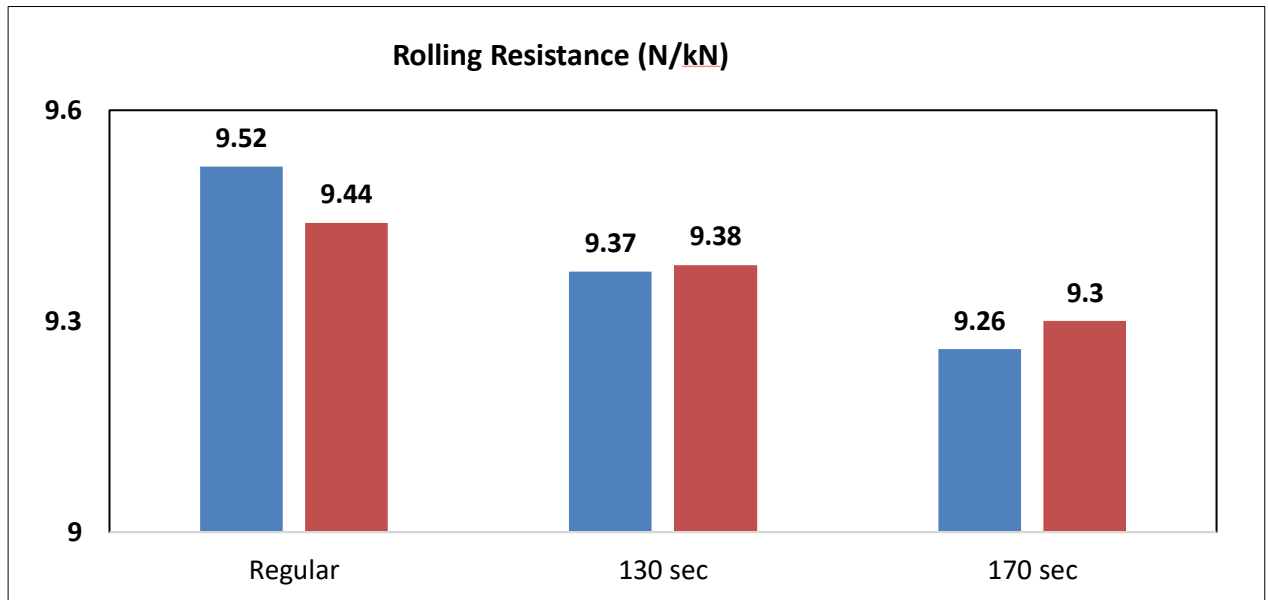
It is indicating proper silanisation happened in master1,2 stages.

5.1.2 Silanisation time



- (i)@170 sec silanisation time trial observation: Payne Effect found to decrease by 0.62Mpa Unit as compared with regular @150 sec(0.65Mpa)
- (ii)@130sec Silanisation time is not sufficient for the proper mixing, so it is not correct silanisation required in master stage-1 and Master stage-2 found similarly good with regular.
- (ii) So 170sec silanisation time must be required for the proper silanisation as per the study report.

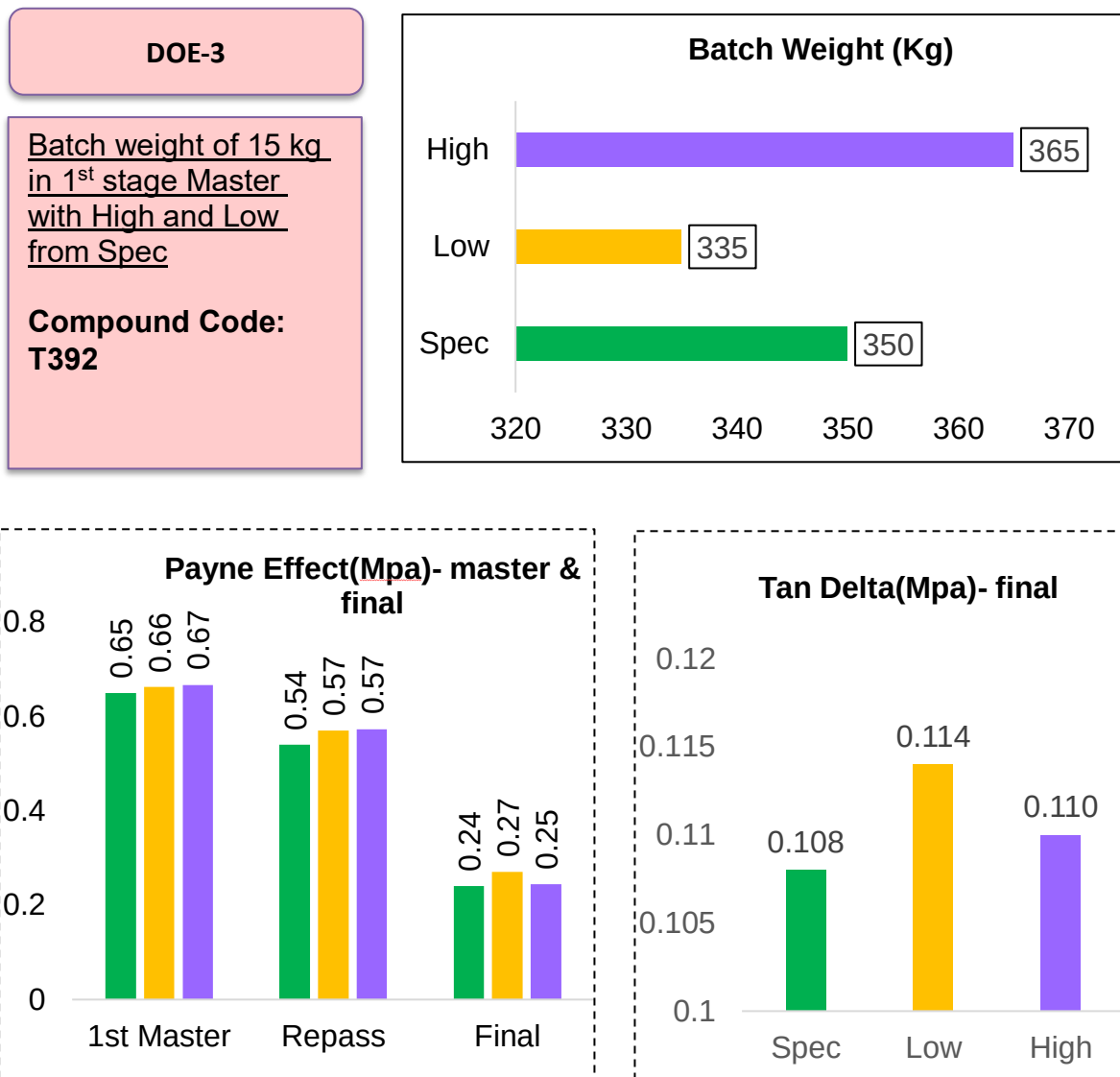
(ii)@ Tan delta trial observation – In Tan delta found 0.100 Mpa compared with Regular 0.108. It is a good result for proper silanisation. Almost 0.08 units were reduced because of proper silanisation.



(i) Tyre RRc was found 9.26N/KN) as compared with regular value 9.52N/KN Almost 0.34 units reduced with 170sec Silanisation time. And 130 sec silanisation time is also comparable with regular but not sufficient for the RRc.

(ii) So as per the trial observation 170sec is better than regular 150 sec, and 130sec is also not recommend for the proper silanisation.

5.1.3 Batch weight/Fill factor

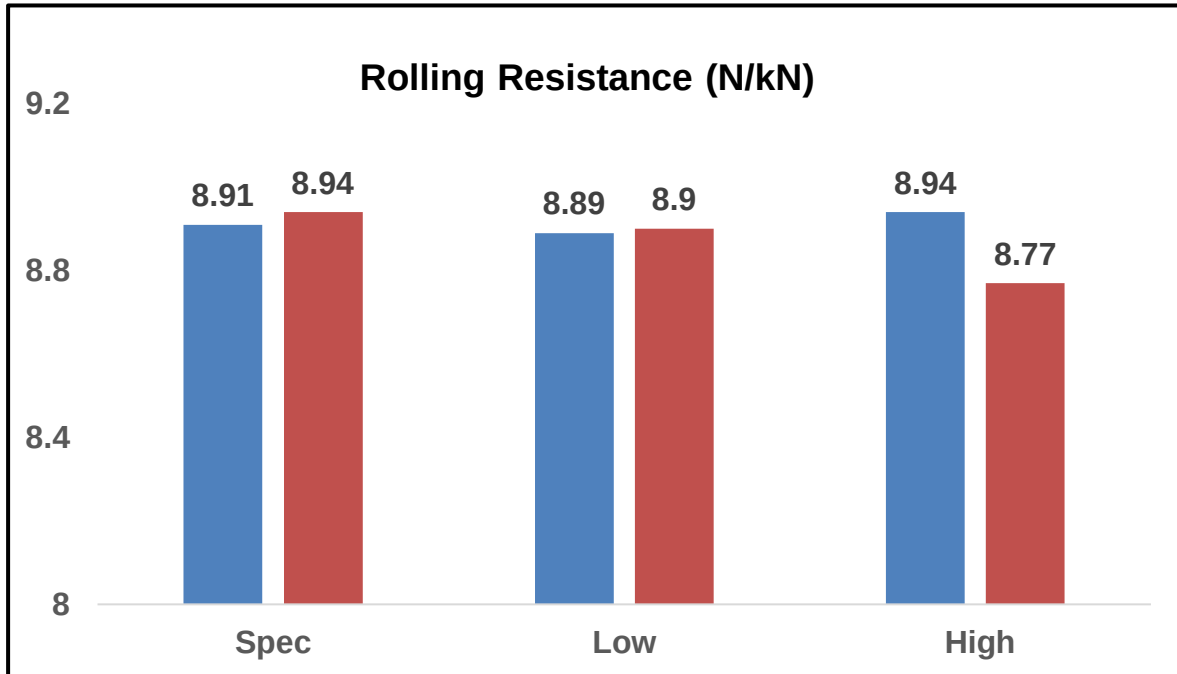


(i)@335 kg batch weight trial observation: Payne Effect found to increase by 0.66Mpa Unit as compared with regular @350kg batch weight(0.65Mpa) in master stage 1. Master stage-2 is found to be similar as regular.

(ii)@365 kg batch weight trial observation: Payne Effect found to increase by 0.67Mpa Unit as compared with regular @350kg batch weight(0.65Mpa).

(iii) Both master stages found similar as regular. No major differences observed.

(iii) So as per the above trial observation regular 350kg batch weight only suitable for the proper silanisation. So 335kg & 365kg batch weight trial is also recommended.



(i) 370kg batch weight trial observation- Tyre RRc was found 8.94N/KN) as compared with regular value 8.91N/KN. There is no major difference observed. Similar as 335kg batch weight also not more difference.

(ii) As per the trial observation RRc is normal in regular(350kg) and Trial(335kg) batch weight.

CHAPTER 6

6.1 SUMMARY AND CONCLUSIONS

DOE - Mixing Summary							
S.no	Parameters	Compound	Spec	No of Trials	Report observation	Status	Remarks
1	Batch weight/Fill factor	T392	±15kg	+15	Normal		No Influence
				-15	Normal		No influence
2	Silanisation temperature	T392	148 C	130	Not ok		Not recommended
				155	Good		Recommended
3	Silanisation time	T392	150 sec	130	Not ok		Not recommended
				170	Good		Recommended

For specified mixing conditions, actual values align with Taguchi's predicted values for Responses.

The longer the silanization time, the higher the TCU, and silanization temperature consumes more energy for mixing. The higher the filler factor results in lesser energy consumption as the fill factor increases, the less time is taken to reach fixed silanization temperature compared to the lower fill factor.

increase in silanization temperature and time lead to a better degree of silanization and filler dispersion. An increase in fill factor from 50%(335kg) to 60%(350kg) positively impacts the silanization reaction, whereas a further increase up to 70%(365kg) has a negative impact due to a reduction in devolatilization efficiency.

This work was attempted to investigate and figure out the significance of mixing parameters, such as silanization temperature, silanization time, fill factor, and temperature of TCU on the degree of silanization reaction using L18 orthogonal array for a better insight. From the main effect plot of the S/N ratio for key properties like Payne effect, $\tan \delta$ @ 60C, DMA trend is observed.

Silanisation Temperature:

(i)@155 C temp trial observation: Payne Effect found to decrease by 0.06Mpa Unit as compared with @130 deg C in the master stage-1, and Master stage-2 found 0.01Mpa reduced. It is good result which is indicating good silanisation.

(ii)@ 155 deg C temp trial observation – In Tan delta found 0.03 Mpa reduced as compared with Regular. It is good result for proper silanisation.

(iii)From this trial observation, 130 degC is not suitable for silanisation compared with 148 & 155 deg C.

(iv) Establish Process specs by cross-checking the right degree of silanization

(v)DMA test result 0.121Mpa achieved from regular 0.126 Mpa with 155deg C silanisation temp condition and it is good value for the proper silanisation.

Silanisation Temperature has a profound impact on RRc, and optimized temperature is better for RRc.

(vi)Tyre RRc was found 7.82N/KN) as compared with regular value 7.83N/KN.

It is indicating proper silanisation happened in master1,2 stages.

Silanisation Time:

(i)@170 sec silanisation time trial observation: Payne Effect found to decrease by 0.62Mpa Unit as compared with regular @150 sec(0.65Mpa)

(ii)@130sec Silanisation time is not sufficient for the proper mixing, so it is not correct silanisation required in master stage-1 and Master stage-2 found similarly good with regular.

(iii) So 170sec silanisation time must be required for the proper silanisation as per the study report.

(iv)@ Tan delta trial observation – In Tan delta found 0.100 Mpa compared with Regular 0.108. It is a good result for proper silanisation. Almost 0.08 units were reduced because of proper silanisation.

(v) Tyre RRc was found 9.26N/KN) as compared with regular value 9.52N/KN. Almost 0.34 units reduced with 170sec Silanisation time. And 130 sec silanisation time is also comparable with regular but not sufficient for the RRc.

(vi) So as per the trial observation 170sec is better than regular 150 sec, and 130sec is also not recommended for the proper silanisation.

Silanisation for Batch weight:

(i)@335 kg batch weight trial observation: Payne Effect found to increase by 0.66Mpa Unit as compared with regular @350kg batch weight(0.65Mpa) in master stage 1. Master stage-2 is found to be similar as regular.

(ii)@365 kg batch weight trial observation: Payne Effect found to increase by 0.67Mpa Unit as compared with regular @350kg batch weight(0.65Mpa).

(iii) Both master stages found similar as regular. No major differences observed.

(iii) So as per the above trial observation regular 350kg batch weight only suitable for the proper silanisation. So 335kg & 365kg batch weight trial is also recommended.

(iv)370kg batch weight trial observation- Tyre RRc was found 8.94N/KN) as compared with regular value 8.91N/KN. There is no major difference observed. Similar as 335kg batch weight also not more difference.

(v) As per the trial observation RRc is normal in regular(350kg) and Trial(335kg) batch weight.

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Silane4

by Dhinakaran Y

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CHAPTER 1

1.1 INTRODUCTION

1.1.1 TRUCK BUS RADIAL TIRE

Truck Bus Radial (TBR) tires contain body ply cords which are present radially from bead-to-bead area, it will be at a 90-degree angle to the centerline of the tread portion. More than two belts are present diagonally in the tread region to improve strength and stability.

Radial plies are that run perpendicular towards the travel direction. For this, we are getting very little heat generation and very smooth riding.

Radial tire's advantages,

- (i) Sidewalls give good flexibility.
- (ii) Fuel consumption will get less because of less rolling resistance.
- (iii) Softer while riding and vibration is also less.
- (iv) Due to less heat generation tire life can be extended.

The disadvantages of radial tires when compared to a bias ply tire include:

- (i) Difficult for transport handling.
- (ii) Sidewall bulge which could cause tire puncture and damage in the sidewall region,
- (iii) Overloading and improper air inflating may cause tire damage.
- (iv) Sometimes Belt edge filler damage may cause Belt separation on tire failure.



Figure 1 Radial Body ply & Belt

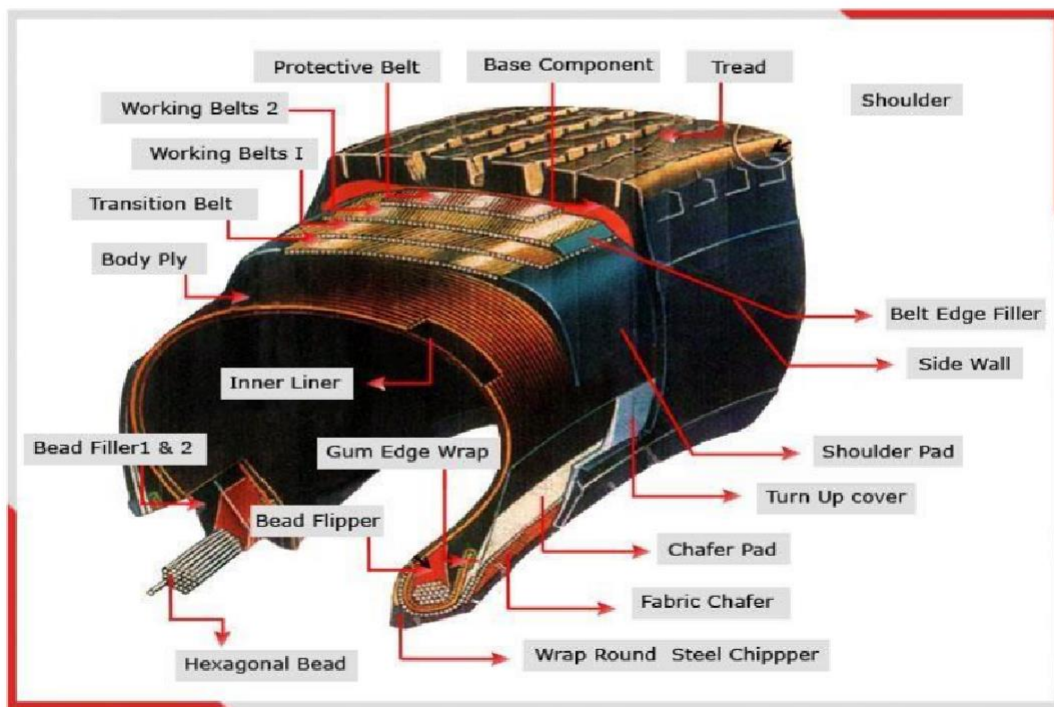


Figure 2 Truck bus radial Components

1.1.2 COMPONENTS OF RADIAL TIRE

(1) Inner liner (IL)	(11) Belt edge filler (BEF)
(2) Squeeze	(12) Belt edge gum (BEG)
(3) Transition belt 1	(13) Body ply (BP)
(4) Protection belt 1	(14) Sidewall (SW)
(5) Working belt 1(WB1)	(15) Bead seat profile
(6) Tread cushion (TC)	(16) Soft apex (SA)
(7) Tread Base (TB)	(17) Hard apex (HA)
(8) Tread Cap	(18) Steel chafer
(9) Shoulder cushion/pad	(19) Nylon chafer
(10) Flipper	(20) Bead

Tires are part of the vehicle; they help to carry the weight and move forward on the road. Our vehicles mostly pass through very harsh environments such as high and low temperatures or wet regions. That is the reason rubber is used in tires with additives and fillers to strengthen the tire; It will maintain the grip and good stable on the rough surface places.

A Radial tire is a composite material which has rotational symmetry. It contains several rubber components bound together and textile or other steel reinforcement materials give more strength to the tire.

1.1.3 TYRE TREAD ASSEMBLY

The tread is the part of the tire that contacts the road's surface and protects the inner casing from road hazards. Apart from tread pattern, tire performance depends strongly on tread properties.

Tyres were made with synthetic and natural rubber. The tread portion contains three parts si base, cap, and shoulder.

1.1.4 FUNCTION OF TYRE COMPONENTS

- (i) The Radial tire tread part must provide good wear and tear resistance and good wet grip in all the road conditions. The tread base reduces the rolling resistance and temperature.
- (ii) For driving stability multi-ply steel belt Steel cords embedded in the rubber compound Enhance and minimise the rolling resistance, which will give a long service life.
- (iii) For driving comfort steel casing Steel cord is used, which gives the tire structural strength.
- (iv) To prevent the diffusion of air and moisture in tubeless tires mostly Inner liner Rubber compounds were used.
- (v). SW compounds protect against and effects of weather-related defects.

1.4 COMPOUNDS IN THE TYRE TREAD:

The tread compound formulation comprises five materials: rubber, reinforcement materials or fillers, antioxidants and other compound protectants, processing aids, and the vulcanization system.

The selection of the elastomers will depend on the mission profile and design parameters for the tire but will, in all cases, be selected to provide wear resistance, traction under both wet and dry conditions, low rolling resistance, and contribute toward good vehicle fuel economy, and resistance to damage caused by cutting or tearing of the tread.

Tread compound development is a complex field in materials science, polymer chemistry and technology, and chemical blending to optimize the required mechanical properties.

Rolling resistance, damage resistance, and contribution to tire-vehicle handling qualities further impact formulation composition.

Silica is used as filler in the tire tread compound mixing and it results in fuel savings of 5% to 13% compared to tire tread type of compounds (contains carbon black used as filler). silica in the tire tread compounds reduce rolling resistance by up to 25%, and less greenhouse gas emission also.

Tyre tread processing conditions can impact tire performance such as RRC (Rolling resistance), WC (wet traction), and WR (wear resistance). tyres (low rolling resistance tyres), several coupling agents and high surface area silica filler were researched widely and used in rubber vulcanizate.

Highly dispersible silica enhances the degree of dispersion in the rubber compound than conventional types of silica filler. While mixing, the silane will react with silica filler leading to hydrophobization of the silica to the filler surface, thereby breaking down the agglomeration of silica fillers, **which is called a silanization reaction.** This hydrophobization can reduce the silica-to-silica bonding and makes the polar silica more than compatible with non-polar rubber materials, leading to ease of processing and reducing the flocculation and good dispersion.

During cross-linking, Sulphur available in the coupling agents creates a covalent bond between the rubber chain and forms a chemical bond linkage.

RPA- Rubber Process Analyzer machine is used to measure fluctuation rate and filler-to-filler dispersion level, it indicates the **degree of silanization.**

Some of the mixing parameters can significantly influence the silanisation reaction, and it affects the energy consumption during mixing and the final performance properties of the radial tire. Much of the research had been carried out to optimize the silanisation temp and time in both silica-filled Styrene-Butadiene Rubber (SBR) compound and Natural Rubber (NR) compound.

This project study is to statistically determine the significance of proper mixing parameters on the degree of silanization and energy consumption in an actual Tandem /Banbury mixer using the DOE (design of experiments).

*Tread strip (Rubber compound) – The tread strip must provide high wear resistance and good grip in all road conditions.

*Multi-ply steel belt (Steel cords embedded in the rubber compound) - Enhances driving stability, reduces rolling resistance, and gives the tire its long service life.

*Steel casing (Steel cord) - it gives the tire structural strength & deflection characteristics that substantially enhance driving comfort.

*Inner liner (Rubber compound)- Prevents the diffusion of air & moisture in tubeless tires.

*Sidewall (Rubber compound) – Protects from lateral scrubbing and the effects of weather.

*Bead reinforcement (Nylon, steel cord) – secures the end of the steel cord ply to the bead core and reinforces the bead against high shear forces.

*Bead core (Steel wire embedded in the rubber compound) – Ensures firm fit of the tire to the rim.

1.5 NATURAL RUBBER & SYNTHETIC RUBBER

Synthetic and natural rubbers are used in tire manufacturing.

The consumption of natural rubber in the tire industry is almost 75% of its production.

The conversion from bias to radial tires increased the genuine rubber requirement in tires. It improves the green strength, tears strength, rolling resistance, etc.

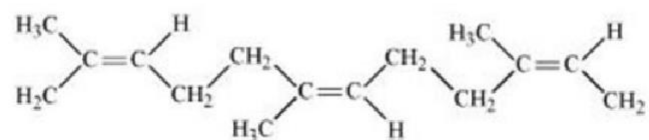
In winter tires, mostly synthetic rubbers are used, but if the requirement of load-carrying capacity is high, the tire size increases to almost 100% natural rubber.

Synthetic rubbers like SBR, Polybutadiene, and butyl rubbers were used in tire manufacturing. The introduction of SBR in tire compounds to passenger car tires leads to the improvement in the wet skid and traction properties of the tire. Adding butadiene in tread and sidewalls gives good abrasion resistance and enhances tread impression performance and resistance to cut propagation.

Table-1 Properties of natural rubber and synthetic rubber

NR (Natural Rubber)	SBR (Styrene-Butadiene rubber)
(i) Good tensile strength, Good resilience	(i) non-polar,
(iii) Lower hysteresis	(ii) Type of non-crystalline copolymer
(iv) Good tear strength	(iii) Less tensile strength
(v) Less heat generation	(iv) Good glass transition temperature High
(vi) Better fatigue resistance	(v) Good tire traction
(vii) Good cutting resistance	(vi) Well handling performance

Natural Rubber-



Natural rubber

- (i) Natural rubber occurs in almost 2000 plant species, out of which only a few are commercially important.
- (ii) The most important species is *Hevea Brasiliense* (tree).
- (iii) It is a tree which can grow up to 30m high with a main trunk of about 50cm diameter.
- (iv) It grows in tropical regions with high rainfall.
- (v) Applications in tyre- Tread, Body ply and Belts.



Figure 3 Different type of NR

1.6 FILLERS

The other important additive during compounding is fillers. Natural or synthetic rubber cannot be used in its purest form because they don't have the strength, hardness, and wear resistance. The addition of fillers will improve properties. A wide variety of fillers are used in rubber compounding. The array includes expensive reinforcing fillers to low-cost non-reinforcing fillers.

The selection of fillers depends on the requirement of the compound. Fillers improve rubber's mechanical, thermal, and electrical properties. The reinforcing fillers can increase the modulus and the elongation at break in an elastomeric compound. Mainly Silica and Carbon black were used in the tire industry. Carbon black and silica were in the category of reinforcing fillers.

1.7 CARBON BLACK

Carbon black contains elemental carbon in the form of spherical particles of colloidal size coalesced into particles of aggregates and agglomerates. Carbon black increases the strength, wear resistance, and fatigue properties of the tire. Carbon black can be produced from hydrocarbon combustion methods in different ways.

The classification includes furnace black, channel black, and thermal black; where the channel and thermal blacks are used in early times, it is not that popular. Its aggregate size and structure is directly influencing the compound properties. For a rubber compound, increase in carbon black aggregate size increases the cut and growth strength.

A reduction in particle size results in high abrasion resistance and tear strength. In the tire industry, the carbon black amount influences the properties.

(i) Minimizing carbon black loading lowers tire rolling resistance. In constant black loading, an increase in oil level will increase rolling resistance but also improve traction (at less oil levels, an increase in oil level may decrease compound hysteresis by improving carbon black dispersion).

(ii) Fineness carbon black raises both RR (rolling resistance) and traction performance.

(iii) Increased aggregate size distribution to reduce the tire RRc with constant area and DBP test may help for this analysis.

(iv) Tread-grade carbon blacks can be selected to meet defined performance parameters of rolling resistance, traction, wear, etc.

Tread compound based on a blend of Solution SBR and Butadiene rubber filled with highly dispersible (HD) precipitated silica with an optimized amount of sulfur-functional organosilane resulting in lower rolling resistance and better wet traction than the traditional tread compounds.

(v) Carbon black characterization- Particle size, Surface area, structure.

(vii) Carbon black is made by either incomplete combustion of hydrocarbon or by thermal decomposition of the hydrocarbons.

1.8 CARBON BLACK VS SILICA

Compared to carbon black, silica contains fewer permanently fused particles. But their tendency to form agglomerates is higher—more traction properties and rolling resistance. Silica does not produce greenhouse gases, which is why it is environmentally friendly, and silica tires are known as green tires.

Three significant properties of CB, these three properties can be attributed to distinguishing the features of CB as well as silica, but with modifications.

The surface area measurement determines the particle size of silica. Silica gives abrasion property are lower than carbon black. The highly dispersed silica is an excellent alternative to conventional silica, with better RRc (Rolling resistance), Better traction properties, and good abrasion resistance.

The major problem concerning carbon black is the wet reduction and increasing rolling resistance; it affects the safety of tires and increases vehicle fuel consumption. The addition of silica can overcome these disadvantages. Silica can increase the wet grip and decrease the rolling resistance. Precipitated silica contains a silanol group on the surface, interacting weaker than carbon black. It leads to more hysteresis. In higher elongation, silica compounds have less modulus due to the slippage of rubber molecules.

First letter indicates the cure rate:

S=Slow

N=Normal

The second digit indicates particle size.

Lower=Smaller

- N100 – N199: SAF (Super abrasion furnace)
- N200 – N299: ISAF (Intermediate super abrasion furnace)
- N300 – N399: HAF (High abrasion furnace)
- N400 – N499: FF (Fine furnace)
- N500 – N599: FEF (Fast extrusion furnace)
- N600 – N699: GPF (General purpose furnace)
- N700 – N799: SRF (Semi reinforcement furnace)
- N880: FT (Fine thermal)

Figure 4 Carbon black grades

The use of silica in place of carbon black leads to a comparable tan delta at lower temperatures, providing an ice and wet grip on tires. The hysteresis of silica-filled rubber increases with the temperature due to a stable covalent bond between the silica and polymer network. The influence of silica on the properties of rubber compounds has been demonstrated in literature. However, there is still scope to understand the behavior of rubber-silica compounds, especially the tear and wear properties.

1.9 SILICA

- (i) It contains natural minerals, and it is used as the second major filler after carbon black.
- (ii) Silica – as a sustainable filler.
- (iii) Highly dispersible type of silica material can significantly enhance the degree of dispersion % and so lead to good filler-rubber interaction.
- (iv) Silica is an inorganic filler.
- (v) The particle size of silica ranges from 1-30 nanometers

Uses- Excellent winter properties, Low rolling resistance, Excellent wet grip, Extension of the magic triangle,

Types- Precipitated silica, Ground silica, Fumed silica.

If considering cristobalite which has an open network and instead of silica Al, Na, and Ca be in the system but, still 95% SiO_2 can still be produced from it.

Tire-containing silica fillers have been popular because of reducing rolling resistance and improve the frictional force on wet and snow-covered roads. However, silica's polar nature makes it challenging to blend with non-polar rubber.

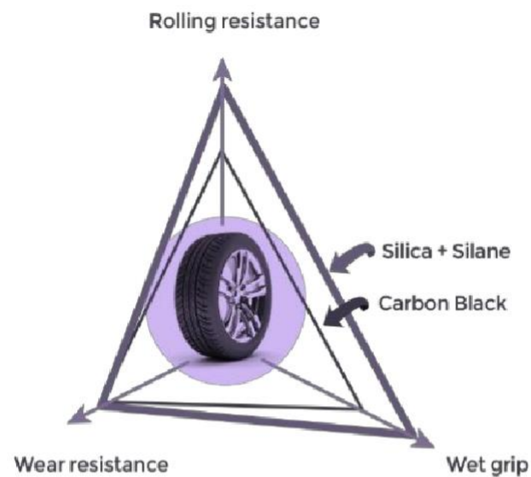


Figure 5 Tire Magic Triangle

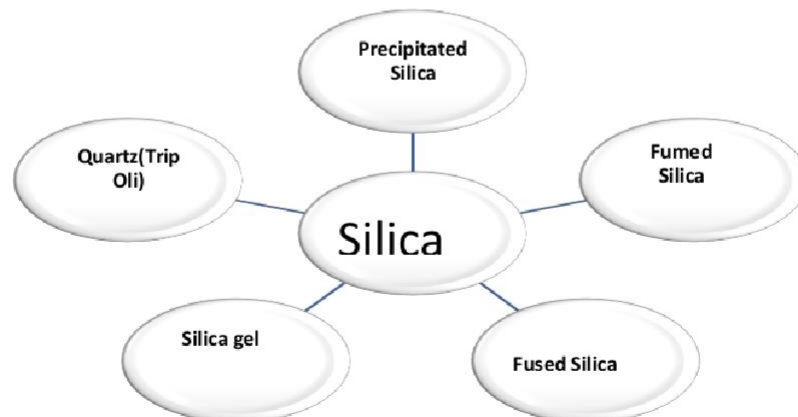


Figure 6 Classification of silica

1.9.1 PRECIPITATED SILICA

Precipitated silica is a form of synthetic amorphous silicon dioxide derived from quartz. The synthesis of precipitated silica is from the reaction of water glass and mineral acids. Precipitated silica is produced by four steps, precipitation, filtration, drying, and granulation. The precipitated silica's surface contains hydroxyl groups with active hydrogen atoms for reaction.

The surface area of silica is very high; it possesses a filler-filler solid network. This will directly influence the adhesion and tear resistance properties. However, the processability of the material is affected inversely. This will directly influence the curing efficiency. As a result, longer cure time and fewer sulfur crosslinks can be seen in the vulcanized rubber compound. Glycol or an active amine ingredient can be added to silica-filled compounds to tie up the active silica surface and reduce its affinity for curative chemicals.

Silica is hygroscopic; moisture remains after mixing and can interfere with non-sulfur cure systems, including peroxides. The reinforcement mechanism of silica- the silane system in the rubber compound. Three significant properties that directly influence silica mixing are Surface area, Structure, and surface chemistry.

1.9.2 COUPLING AGENT

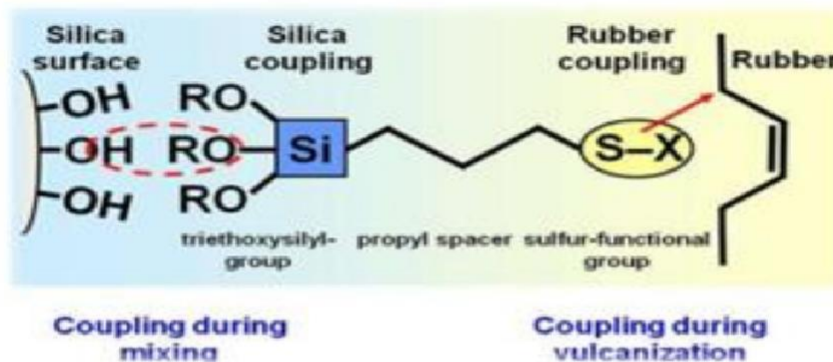


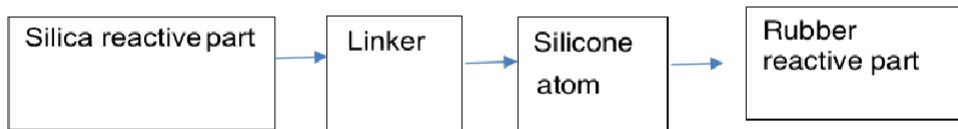
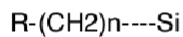
Figure 7 Silane coupling agent.

"Silane coupling agent: It will act as a bridge between the rubber and silica which results in the desired reinforcement of silica-filled rubber."

(i) Silica-polar

(ii) Rubber -Nonpolar

Examples: TESPT, TESP, Mercapto propyl trimethoxy silane.



1.1.5 PROCESS OIL

These materials can improve processability and reduce cost without affecting physical properties. Different types of rubber are used based on the product applications; Different types of rubber process oils are selected. For this compound paraffin oils were chosen as the process oils.

- | | | |
|------------------|---|--------------------------|
| (a) Butyl rubber | - | Paraffinic type oil |
| (b) NR | - | Aromatic type oil |
| (c) BR | - | Aromatic type oil |
| (c) SBR | - | Highly Aromatic type oil |

1.1.5 ACTIVATORS-STEARIC ACID

Stearic Acid is also called Fatty acids, it contains long molecules of Hydrocarbon Chains. It is used mainly in the activator system of the Rubber mixing compounding and is specific for the Curing process based on the vulcanization agent (Sulfur) in the accelerator-activator network bond. because of this Dual nature of hydrophilic and hydrophobic nature of the Stearic Acid, It is very helpful in the activator system of the rubber compounding as this will help Zinc Oxide to convert into a soluble form - rubber in effective dispersions of Zinc Oxide into the rubber matrix.

1.1.6 RESIN & MBTS

It is also called a tackifying agent. It increases adhesive and tack properties. Resins modify the optical and mechanical properties of polymer blends. Aromatic

500 resins offer better compatibility with Natural Rubber (NR), (BR) butyl rubber, and polybutene rubber.

MBTS (2'-Dibenzothiazole Disulfide) is used as a retarder. It is easily dispersed in mixed rubber compounds. MBTS are given below 3.2 phr dosage level to avoid blooming. MBTS is non-discoloring and non-staining but can turn yellow on exposure to light. It will not bloom at normal dosage.

1.1.7 SULPHUR & ZNO

Zinc Oxide (ZnO) and sulfur together are utilized as the curing method or agent. The oldest vulcanization agent still in use today for unsaturated rubbers is sulfur. It requires accelerators and activators to generate cross-links with rubber macromolecules, which is an efficient and quick process. Unsaturated rubbers are first vulcanized with sulfur in three phases.

Zinc oxide (ZnO) operates as a cross-linking agent for rubbers that contain carboxyl or halogen groups, in addition to triggering sulfur cures. Rubbers such as carboxylate nitrile (XNBR), bromo butyl elastomer (BIIR), and chloroprene rubber.

1.1.8 SILANISATION BENEFITS

- * Improved fuel economy and performance by the proper silanization.
- * Amorphous precipitated silica is utilized as a filler in the tyre tread and gives fuel savings of 3% to 15% compared to carbon black as a filler.
- * Incorporating silica into tyre tread compounds can reduce rolling resistance, and wear resistance, reducing heat buildup by up to 30%, resulting in decreased greenhouse gas emissions.
- * The chemical formulation of tyre tread compounds and their processing conditions can significantly impact tyre performance like rolling resistance, wet traction, and wear resistance.
- * Highly dispersible silica enhances the degree of dispersion in the rubber compound than conventional silica filler.
- * During mixing, the silane reacts with silica leading to hydrophobization of the silica surface, thereby breaking down the agglomeration of silica fillers, which is called as "Silanization reaction".

CHAPTER-2

2.1 LITERATURE REVIEW

Silica has polar nature rubber has a non-polar nature; during processing, it is difficult to interact with the whole amount of silica with the rubber matrix. Non-uniform dispersion causes negative results on fuel efficiency. Compared to weak filler-filler interaction, the strong filler-polymer interaction results in difficulties in silica mixing. Processing aids known as dispersing agents are introduced during compounding to overcome these difficulties.

The dispersant is a processing aid that lowers the viscosity to improve the surface roughness. As filler dispersion in the polymer, mixing consumes significant power and is time-consuming. Poor distribution can result in inferior physical and dynamic properties, mainly increased heat buildup and hysteresis.

To improve silica dispersion, it is conventional to use coupling an agent with the silica to couple or polymer-polymer-collection. Such coupling agents are conventionally silica silane-based compounds with a silane-based which is reactive with hydroxyl groups such as silanols, found on the surface of silica and having another moiety, such as a polysulfide bridge, which may interact with a conjugated diene-based elastomer.

Examples:

bis(3-triethoxysilylpropyl)disulphide (TESPD)

Mercapto-type silane coupling agents,

3-mercaptopropyl tri methoxy silane,

3-mercaptopropyl triethoxysilane,

2-mercaptoethanol tri methoxy silane,

and mercaptoethanol triethoxysilane etc.

2.2 LITERATURE SURVEY

LITERATURE-1

S. H. Song, "Study on silica-based rubber composites with epoxidized natural rubber and solution styrene butadiene rubber," Polym. Compos., vol. 29, no. 9, pp. 1422–1429, Nov. 2021, doi: 10.1177/0967391120971391

LITERATURE-2

S. Maghami, "Silica-filled tire tread compounds: an investigation into the viscoelastic properties of the rubber compounds and their relation to tire performance," University of Twente, Enschede, The Netherlands, 2016. doi: 10.3990/1.9789036541282

LITERATURE-3

"Compounding with carbon black and oil" By **S. Laube, S. Monthey, M-J. Wang** Pg No-308 [2]

LITERATURE-4

A new Cabot carbon black for improved performance in peroxide cured injection moulded compounds [2] Presented by **S.Bussolori, S.Laube** at ACS rubber division meeting, 2000 Paper no 98

2.3 CONCLUSION OF LITERATURE SERVEY

From all the above literature we can conclude that the use of semi-reinforcing, low structure and high particle size carbon black as filler can reduce the air permeability of the compound. The reason for this can be due to

- (i) High filler loading in the rubber compound.
- (ii) High dispersion of the filler
- (iii) The gases get absorbed onto a carbon-black surface.

Some of the advantages of using such carbon black are,

- (i) High load ability in halo butyl inner liner compounds compared to using only GPF grades.
- (ii) Reduction of permeability in inner liners at high carbon black loading.
- (iii) Reduction of compound cost due to high black loading.
- (iv) Possibility for reduction of inner gauge providing cost savings.

Some of the advantages of using such Silica are,

* Silica and silica coupling agents are typically used in passenger car tire treads. The silica/silane coupling agent system improves tire tread wear and enhances abrasion resistance).

It can improve the dynamic property of rubber vulcanizate; in particular, it reduces hysteresis, which can be translated into better rolling resistance and leads to fuel-saving without affecting the wet grip.

* However, whether the product is compounded with a known coupling agent, the optimum dispersion can still not be attained. Furthermore, as a result of using a silane coupling agent, the reaction between the silane and hydroxyl group on the surface of synthetic amorphous silica results in the release of alcohol (ethanol). Which escapes from rubber compositions represents an environmental issue.

* In addition, reducing the amount of silica coupling agent is desired. Since use in a conventional amount significantly adds to the cost of the rubber. The release of alcohol can be avoided by adding other silanes than those of TESPD or TESPT.

* Most of them have been appropriately selected depending on the composition and use of rubber, contributing to productivity improvement such as improving the dispersion of fillers, shortening the mixing time, and increasing the extrusion speed.

* These dispersants are effective in carbon black rubber compositions that use carbon black as fillers. But it doesn't act as a dispersant in silica. If the dispersing agent is added, the silica as filler is utilized to improve dispersion, shorter mixing time, and extrusion. The speed will increase, but the dispersant can lower the viscosity, reducing physical properties.

* The silica content of tire rubber is increased; silica contains many hydrophilic, and rubber includes a small hydrophobic group that re-agglomerates after dispersing. So, a lot of energy wastage happens in silica dispersion.

* The dispersant is added to the rubber matrix with the silica for better silica dispersion. Silica dispersant reduces the viscosity of the rubber during compounding. It reduces the time and energy required to disperse the rubber by bonding with the hydrophilic group on the silica surface not connected to the silane coupling agent.

* Most rubber compositions contain a reinforcing filler such as carbon black and silica or a combination of both. Silica is an amorphous white filler, Silica also known as silicate. Raw rubber composition comprises a relatively large amount of silica in the tire tread, generally known as green tire. These rubber compositions typically do not contain carbon black or a lesser amount of carbon black (ranges from 5 to 20 phr).

CHAPTER-3

3.1 AIM & SCOPE

- (I) To study the effect of parameters, influencing silanization and its optimization in Rubber compounding.
- (II) Screening of mixing parameters based on their significance on the extent of silanization and filler to filler to interaction, Filler to rubber incorporation.
- (III) In this paper, a design of experiments (DOE) is carried out to screen the factors that significantly affect the silanization reaction during mixing.

3.2 PROBLEM STATEMENT

"The rising demand for fuel-saving tires with low rolling resistance, minimal heat build-up, and enhanced wear resistance highlights the need for optimizing the mixing of silica filler in tire compound mixing to meet these increasingly stringent requirements".

- (i) Silanization temperature and time were identified as the most influencing factors in the Silanization process using the contribution plot.
- (ii) Tan delta and Payne effect properties are used as the monitoring parameters to find effective silanization.

3.3 OBJECTIVES

*Silica dispersibility in a silica-rubber compound is essential in determining an automobile tire tread's braking performance, wear resistance, and rolling resistance, low heat resistance.

*To study the effect of mixing variables on silanization during the mixing process to reduce the Payne effect and tan delta variation for achieving better performance.

CHAPTER 4

4. EXPERIMENTAL (Materials & Methods)

4.1 MATERIALS

- (i) Sulfur & Accelerator
- (ii) Synthetic Rubber
- (iv) Carbon black & Silica
- (v) Activators & Antioxidants
- (vii) Processing oil
- (viii) Coupling agent
- (ix) Sulphur & Silane
- (xii) Ozone-protecting wax.
- (xiii) Terpene phenolic resin

4.2 FORMULATION

INGREDIENTS	PHR
SSBR	80
PBD- HIGH CIS BR Nd	20
SILICA	86
N339 CARBON BLACK	5
RAE PROCESS OIL	10
TESPD -SILANE	7.5
TERPENE PHENOLIC RESIN	25
ZINC OXIDE	3
STEARIC ACID	2
TMQ ANTIOXIDANT	1
6PPD	6
WAX	2
SULPHUR	2
DPG ACCELERATOR	2.25
CBS ACCELERATOR	1.80
TBZD ACCELARATOR	0.45
Total	254

4.3 MIXING & COMPOUNDING

4.3.1 Mixing

- * Mixing refers to the process of combining different ingredients or raw materials to create a homogeneous mixture.
- * In the rubber industry, mixing involves blending various rubber polymers, fillers, plasticizers, curatives, and other additives to produce a uniform rubber compound.
- * The mixing process aims to distribute the ingredients evenly throughout the compound to ensure consistent properties and performance.

4.3.2 Compounding

- * Compounding, on the other hand, refers to the overall process of formulating a rubber compound by selecting and proportioning the appropriate ingredients.
- * It involves determining the specific recipe or formulation for a particular rubber product, considering factors such as the desired properties, processing requirements, end-use application, and cost considerations.

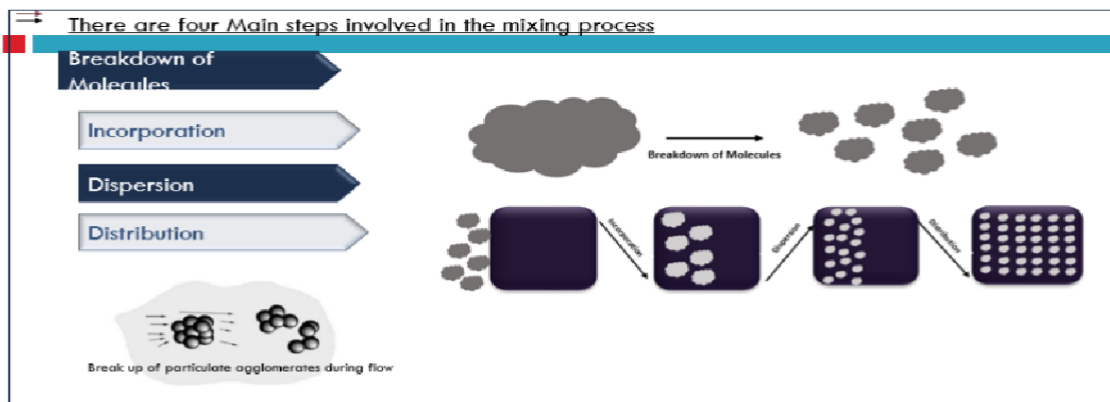


Figure 8 Mixing mechanism.

4.3.3 Principle of Mixing

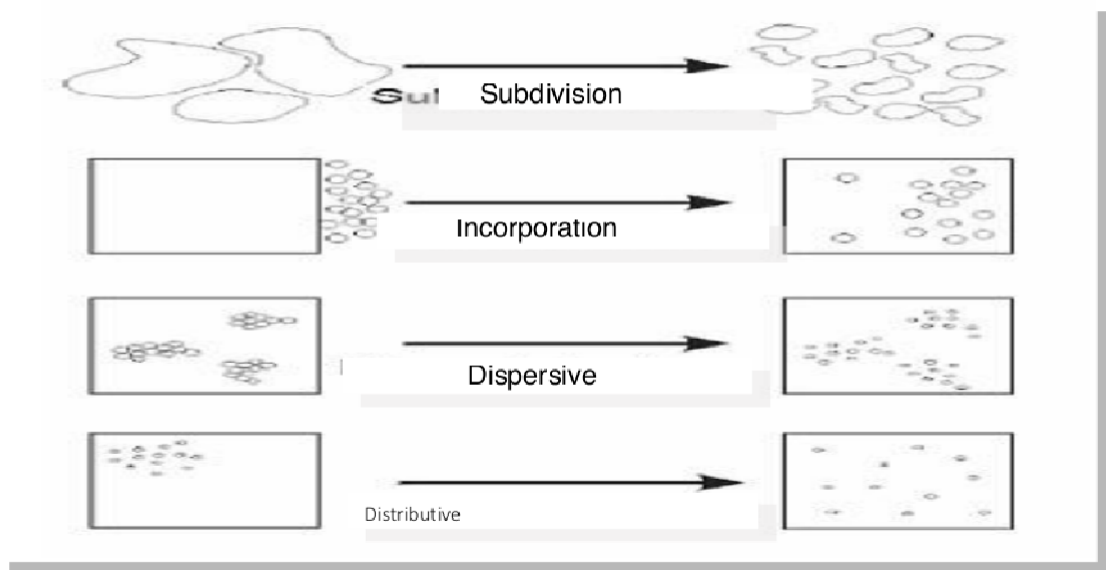


Figure 9 Principle of mixing

4.3.4 Four basic steps are involved in the mixing operation.

(i) **Incorporation:** is the first stage of mixing during which the previously separate ingredients form a coherent mass.

(ii) **Dispersion:** is the process during which the carbon black agglomerates are reduced to their ultimate size.

(iii) **Distribution:** is simple homogenization, during which the various ingredients are randomly distributed throughout the mass of the mix.

(iv) **Plasticization:** during this operation, the mix reaches its final viscosity as plasticizers effectively lubricate the mix.

4.3.5 Banbury (tangential 4 wing rotor mixer)

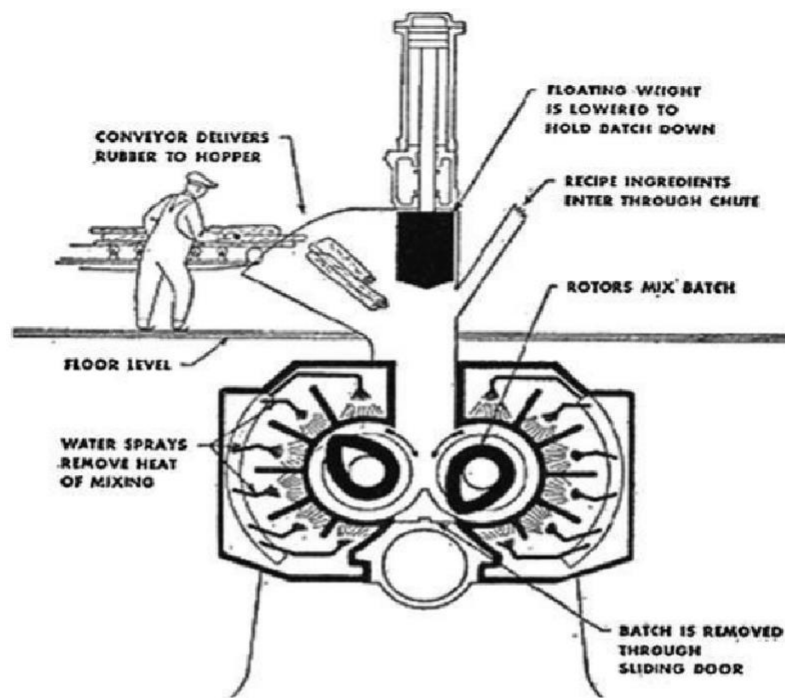
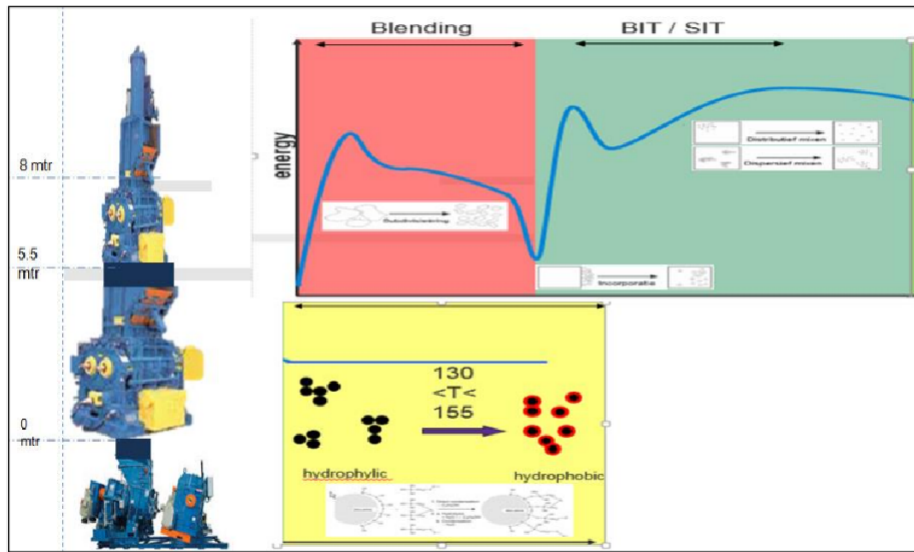


Figure 10 Banbury normal Mixer



Figure 11 Mixer blade

4.3.6 Tandem mixer Process



Tandem technology separates the two main tasks called *dispersion and distribution*.

Dispersion means the breaking down of solid materials such as fillers.

Distribution involves achieving homogeneity within a rubber mix compound with its different chemicals added.

(i) In Tandem technology two mixers are interconnected in series where a type mixer does dispersion well while ram less tandem mixer does the task of distribution.

(ii) Between the two mixers is a discharge flap and chute which would be always closed except when the lower tandem mixer receives the master batch dump from above.

(iii) The Rubber, chemicals, Fillers, oil, and silane are added in the first mixer, and it gets mixed for a fixed time after that it is dumped into the bottom mixer where the chemical reaction takes place.

(iv) In the meantime, the next batch will start in the first mixer and then it is dumped into the second mixer before that the second mixer completes its mixing and dumps the batch into TSS.

Advantages & Disadvantages

- (i) Effective Shear is high.
- (ii) Poor material intake behaviour
- (iii) Cooling efficiency is High.
- (iv) Spiral Cooling
- (v) Less productivity
- (vi) Less fill volume
- (vii) Both Dispersive and Distributive

4.3.7 Normal Mixing

Normal mixing is the process in which the raw materials are blended and mixed using Physical Reaction.

- (i) Mechanism:
- (ii) Breakdown of molecules
- (iii) Incorporation
- (iv) Dispersion

4.3.8 Silica Mixing

In Silica mixing the raw materials will undergo the physical blending process as well as which also includes the chemical reaction between the raw materials silica and silane called *Silanization*. This type of mixing is also called Reactive Mixing.

The reaction will start at a temperature around 120°C and the temperature should be maintained constantly. This reaction is Temperature sensitive.



Figure 12 Tandem Mixer blade

Mixing is a process by which two or more components are converted to a homogenous dispersion. Rubber has to be mixed with compounding ingredients like carbon black, sulphur, accelerators etc

First, we have to calculate the weight of every ingredient.

$$\text{Weight of an ingredient} = \frac{\text{weight of the ingredient in formulation} \times \text{BW}}{\text{Total weight of ingredients in formulation}}$$

Batch weight (BW)= chamber volume*s.g*fill factor

Then we have to design the mixing cycle. Mixing is mainly done in two stages. First, we will prepare a masterbatch, then the final mix. The master batch will have every ingredient except curing agents, accelerators, and retarders.

Masterbatch is mainly prepared at higher mixing speeds(40-60rpms).

Dumping is based on temperature and energy.

The variables fixed for the master batch are.

- (i) Rotor rpm
- (ii) Ram pressure
- (iii) Oil addition temperature and energy
- (iv) Ram up temperature
- (v) Dumping temperature and energy.

For final batch compounds, we set 2 energy limits and a temperature for ram up and down. Two energy limits and a temperature for dumping

Three parameters are considered for dumping.

Temperature, Energy and Time.

4.4 CHARACTERISATION

(i) Rubber processing analyzer - Payne effect & Tan delta

(ii) Dynamic Mechanical Analysis (DMA)

(i) Payne Effect (Standard: ASTM D 6204)

Condition: Temperature- 100°C, Time – 10 minutes, Frequency- 0.01Hz

It is a low-amplitude dynamic test, performed on filled rubber compounds. This test is a strainsweep with the stress measured in the elastic modulus.

Payne effect test data describe the stress-strain behaviour of a filled rubber compound, precisely the filler network's strength. In the test a drop in storage modulus characterizes the test as the sinusoidal oscillation amplitude increases, reflecting the filler network's weakening. Filled rubber is a candidate for a vital part of mechanical energy during deformation.

This behavior is the character behavior drop of elastic modulus G' when shear strain amplitude increases while the loss modulus G'' passes through a maximum. The loss tangent increases quickly, revealing a significant amount of emancipation process.

The strength of the filler network comes from the Vander Waals force in the case of carbon black and hydrogen bonding in the case of silica filler. Depending on the compound, filler networks are held together by either or both.

The amount of softening in a compound from increased strain can be attributed to mixing conditions.

Dynamic mechanical analysis (DMA),

Standard: ASTM D 7028

The viscoelastic behaviour of a material can be identified by analyzing the dynamic property.

Dynamic Modulus: The ratio of stress to strain under vibratory conditions. It is usually expressed in pascals or pounds per square inch for unit strain.

A set of consistent testing procedures has also been formulated. Measured values of dynamic properties of rubber may be influenced by the apparatus and method used, so it is not sufficient to specify a specific dynamic modulus, for example unless the details of its measurement are also limited.

The tests can generally be classified as impact rebound, forced vibration in both resonance and non-resonance conditions, and free vibration.

The dynamic mechanical analysis (DMA) of the SBR compound was studied using XPANDER DMA in tension mode from -80 to 80 °C at a testing frequency of 10 Hz. The heating rate of 3 °C/min was applied to the samples with a dimension of $15 \times 6 \times 2$ mm³. A DMA analysis is conducted to investigate the microstructure, viscoelastic properties, and rubber-filler interaction of the SBR compound.

The results of the DMA analysis are summarized. The variation of storage modulus (E'), loss modulus (E''), and loss tangent ($\tan \delta$) with temperature. The E' is the energy stored in the material. $D2 < \text{Control} < D1 < D3$.

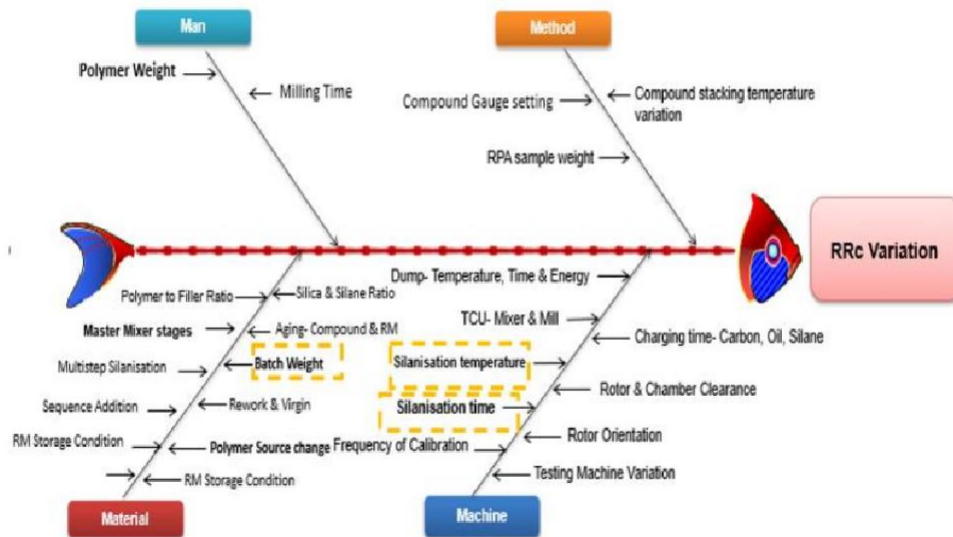
All the prepared composites show a high value of E' at low temperature (-20 °C).

4.5 METHOD

4.5.1 Brainstorming

Probable Causes- Mixing			
S.no	Input	Process	Output
1	Polymer source change	Mixing Temperature	Payne effect
2	Polymer and filler ratio	Mixing Time	Tan Delta
3	Compound ageing-Overage	Mixing Energy	Lab Machine variation
4	Compound ageing-Minimum	TCU Mixer	Specific Gravity
5	Batch Weight	Milling Time	RPA sample weight
6	Polymer Weight	Mill Temperature	Dispersion
7	RM Aging	Silanisation temperature	Rheo Property
8	Silica & Silane Ratio	Silanisation time	Frequency of Calibration
9	Rework & Virgin	Mixing stages	Physical Property- Hardness & Modulus
10	RM Storage Conditions	Charging time- Carbon, Oil, Silane	Compound Stacking Temperature
11		Sequence of Addition	Compound Gauge variation
12		Multistep Silanisation	
13		Rotor and Chamber Clearance	
14		Rotor Orientation	

4.5.2 Cause & Effect Diagram



4.5.3 Conditions for DOE as per Taguchi concept

S.no	Parameter	Tolerance	justification
1	Batch weight- ¹ Fill Factor (%)	50 to 70% or (330 – 370kg)	Below 50temp raise was difficult thereby rpm exceeds 90. Above 70 temp maintenance is difficult and increases mixing time.
2	Temp (Deg C)	135 -155	Less than 130 the silanisation reaction will not happen for TESPd (silane). More than 155 for a long time (Polymer properties get deteriorated)
3	Time(sec)	90 to 270	90 to simulate a lower degree of silanisation, 270 to

The three mixing parameters were chosen, which affect the silanization as factors for DOE.

1. mixing time,
2. mixing temperature,
3. Batch weight,

We have chosen a range of values for selecting the levels as boundary conditions with the justification explained in the table above.

*To study the influence of mixing parameters on silanization efficiency and energy consumption, a masterbatch was prepared in the same mixing condition and mixing sequence (same formulation), which was further mixed and silanized in different mixing conditions by varying the several mixing parameters based on DOE in the second stage of mixing (also called as Repass / Master II).

4.5.4 Reason to adopt Design of Experiment—Taguchi method.

To study the effect of mixing variables on silanization during the mixing process, the Taguchi experimental design method is chosen. This method is a powerful tool that provides a simple, efficient, and systematic approach to optimize performance, quality, and cost designs.

Several DOE methods can be used to identify the most significant factors affecting the quality of a product and offer optimal conditions for the best quality.

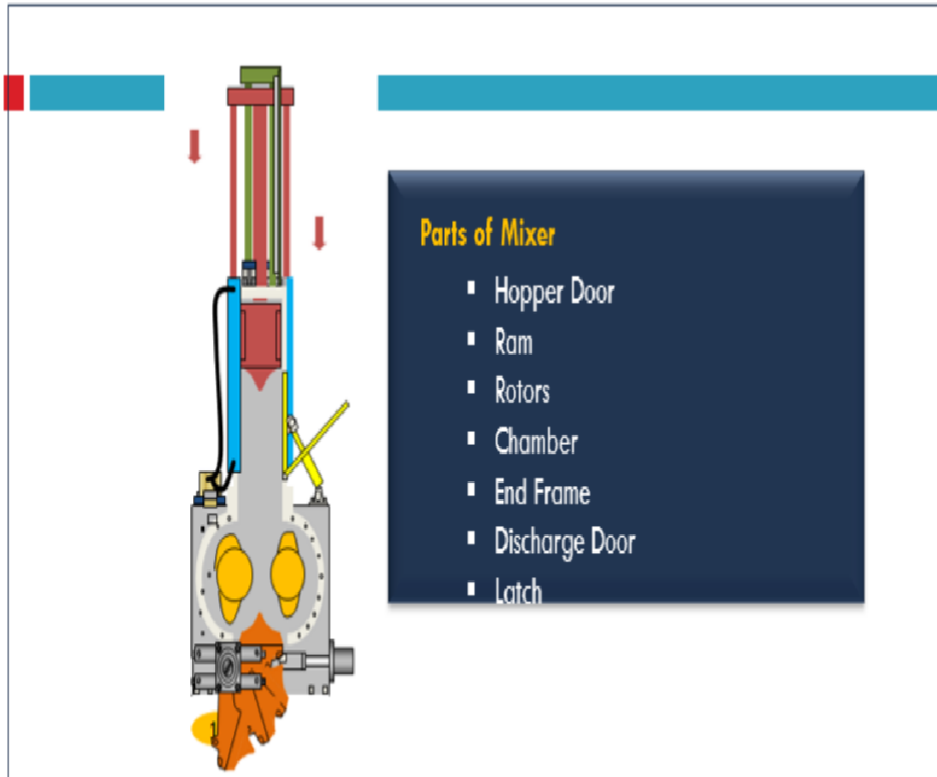
The Taguchi method uses orthogonal arrays as the basis of experiments. The benefit of using orthogonal arrays is that a large amount of information from the effects of many mixing parameters can be obtained from a few experiments.

There are three categories of quality characteristics in the analysis of the S/N ratio, i.e., "lower the better," "larger the better," and "nominal the better." Compared to Factorial and One Factor at a Time (OFAT) analysis, Taguchi has fewer runs which can efficiently provide the interaction parameter and main effect plot.

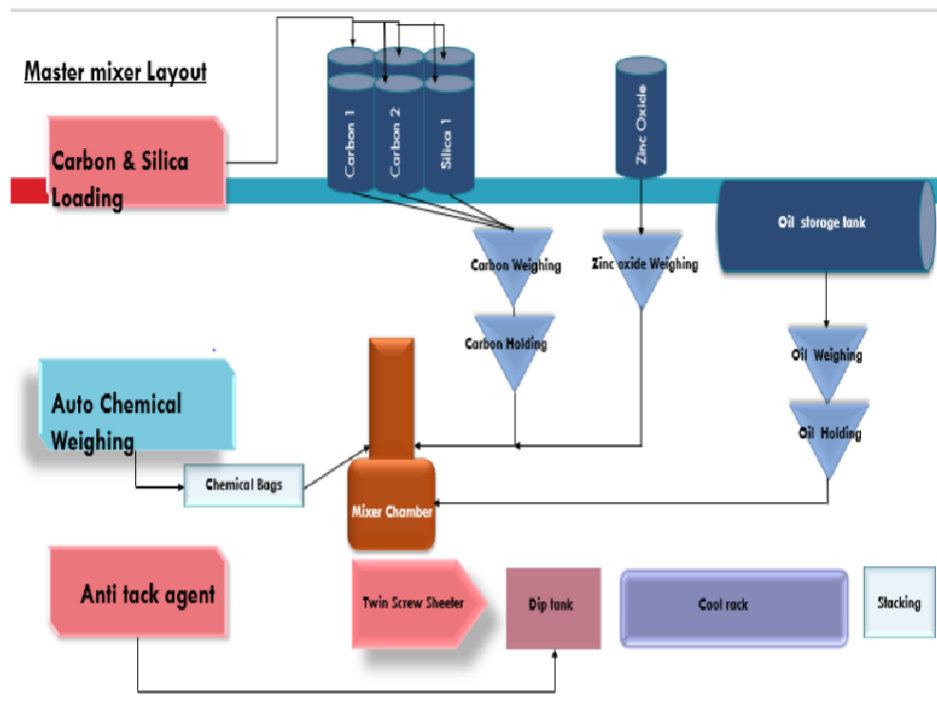
The parameters presumed to affect the degree of silanization, and compound performance are mixing time, mixing temperature, ram pressure, TCU, fill factor, and feed door condition.

In the present study, six factors with mixed three & two levels were chosen, and by these factors and levels, an appropriate O.A. was made with the Minitab software.

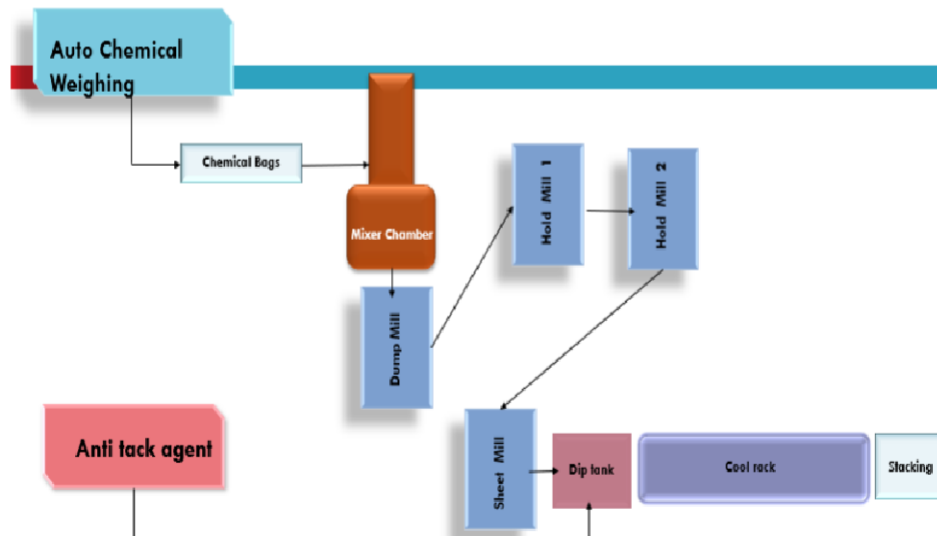
4.5.5 Tandem Mixer:



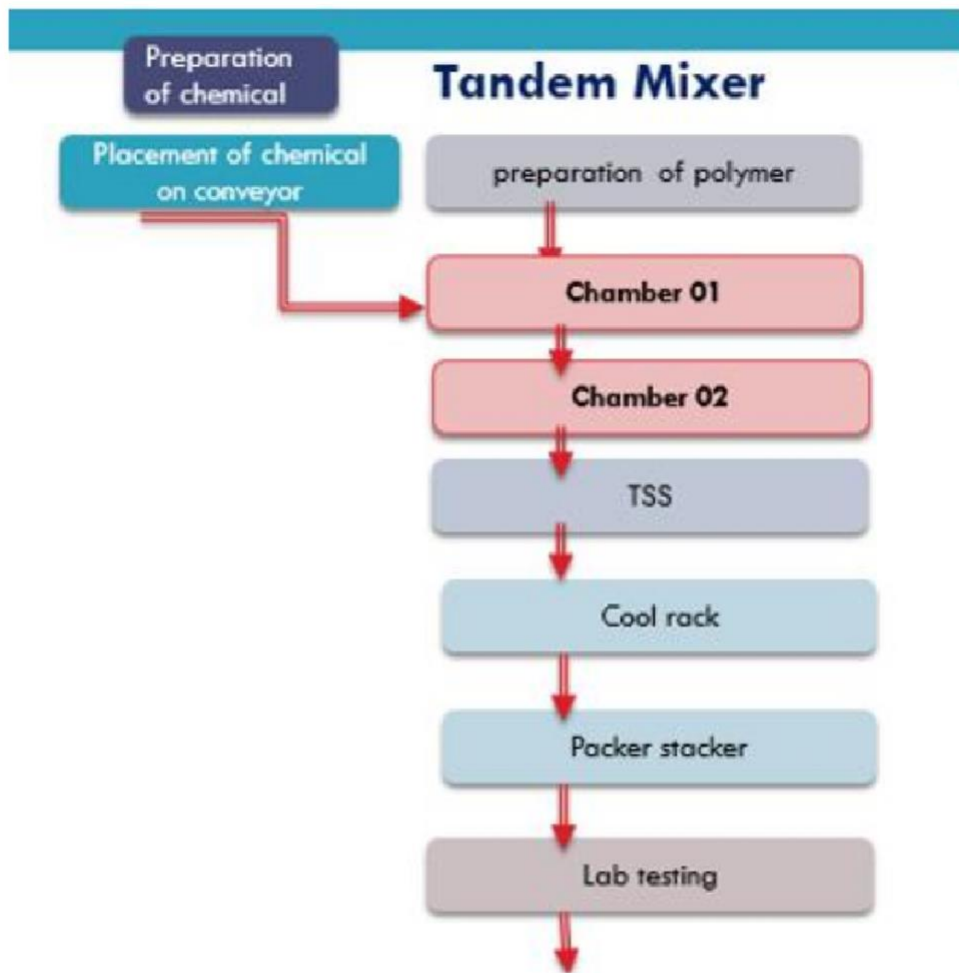
4.5.6 Master mixer Layout



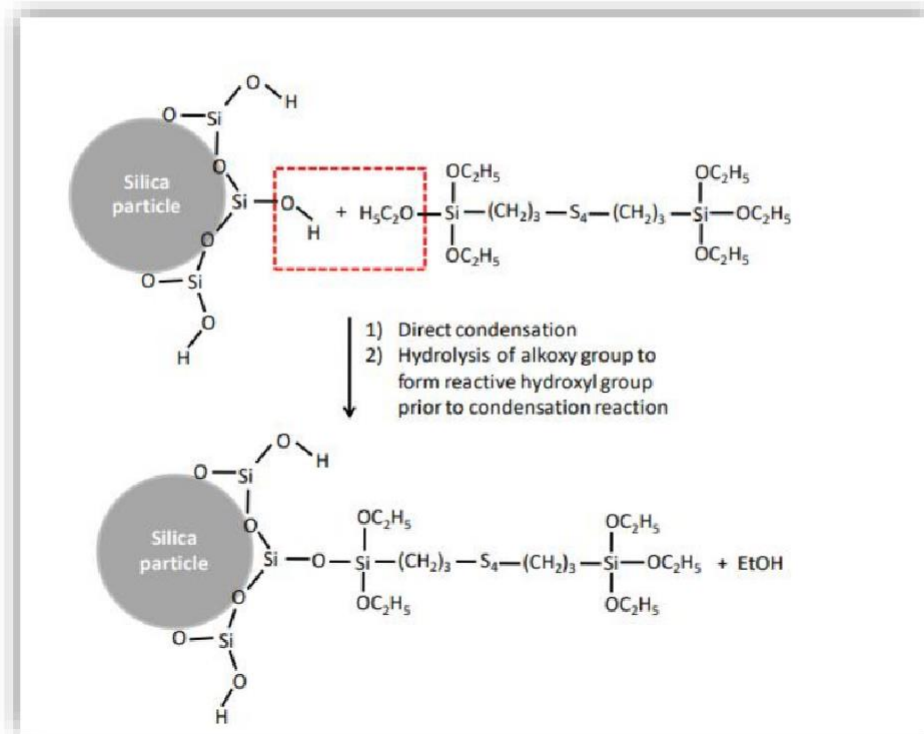
4.5.7 Final mixer Layout



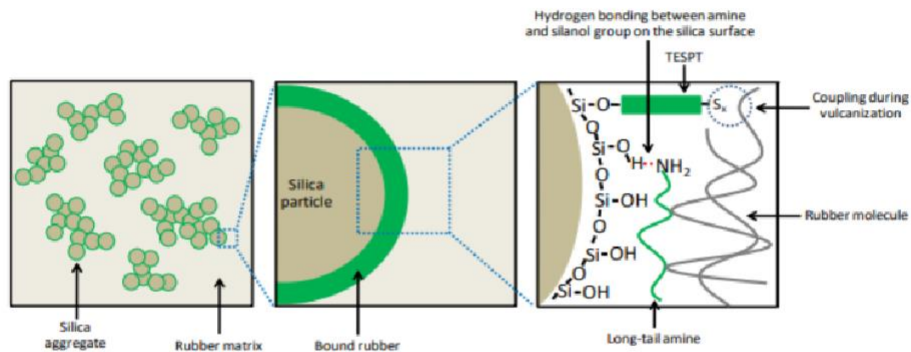
4.5.8 Process flow diagram



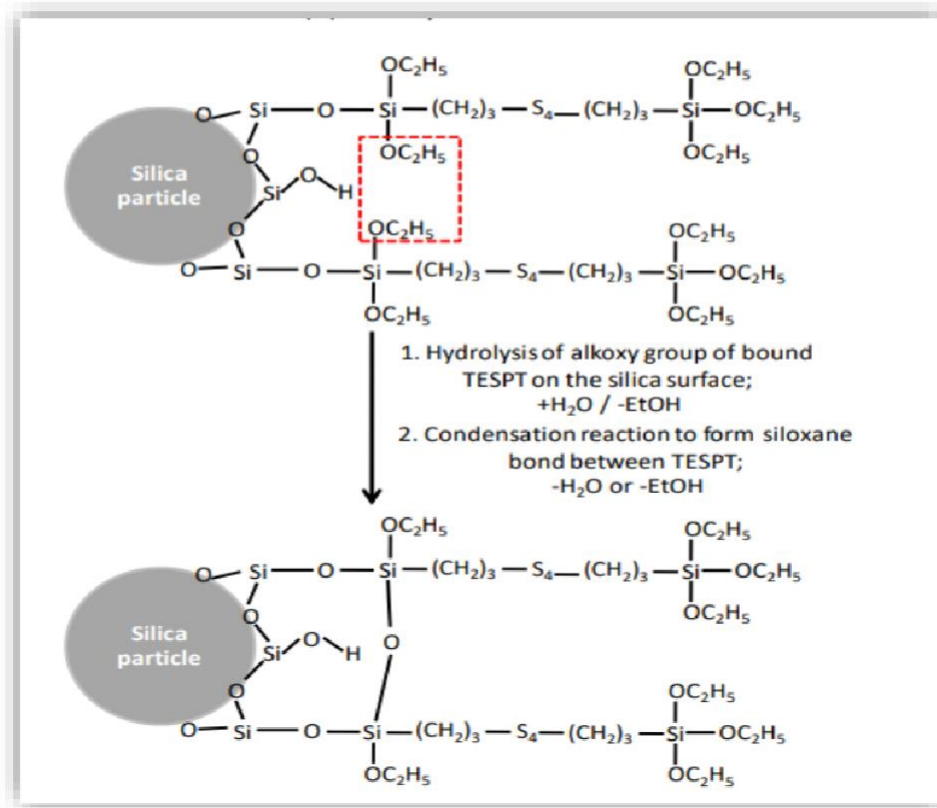
4.5.9 Silanization - Primary Reaction



The primary reaction can proceed via two pathways: either by direct condensation between the silanol groups of the silica surface and one alkoxy group of TESPT or by hydrolysis of the alkoxy groups of TESPT to form reactive hydroxyl groups before the condensation reaction



4.5.10 Silanization - Secondary Reaction



chemical reaction in mixing:

A secondary reaction often occurs between adjacent TESPT molecules on the filler surface, also releasing ethanol.

4.6 Effect of temperature on mixing

4.6.1 In masterbatch

Dump temperature is directly proportional to the thermal degradation of polymers. Hence an increase in temperature beyond the specified value will lead to excessive damage of polymer chains, and gelling.

Hence most of the polymers are hydrocarbons and being mixed with carbon black exposing them to higher temperatures beyond 170°C in the presence of atmospheric air can lead to fire catch-up.

4.6.2 In final batch

As the final batch is mixed with the master along with sulfur & accelerators, the presence of high temperature, the vulcanization reaction starts which leads to cross-linking of polymer chains by Sulphur.

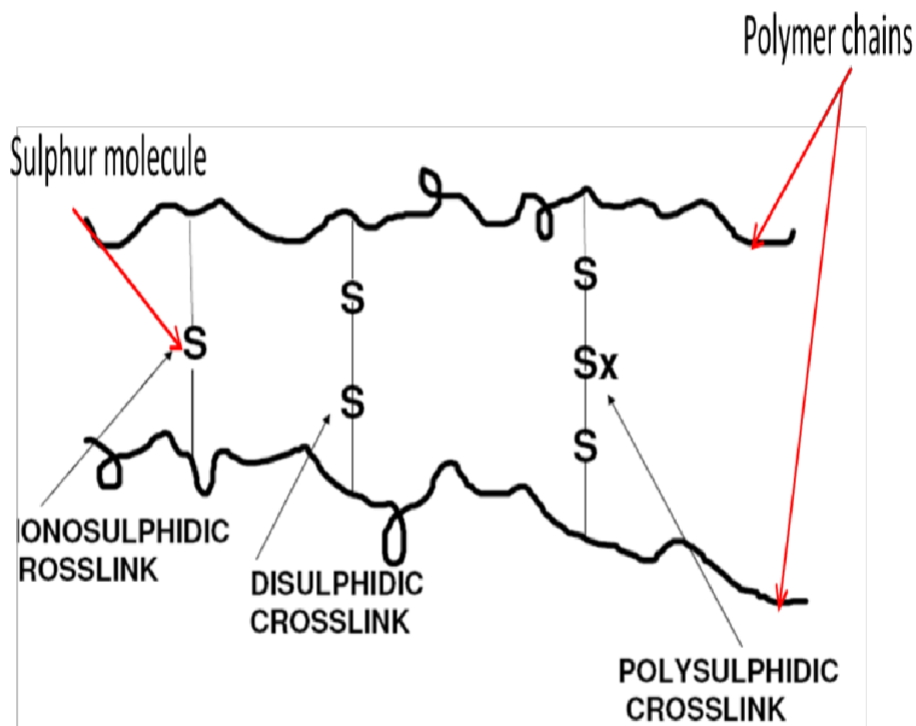


Figure 13 Silane Cross linking

4.7. DOE –Mixing trial plan

S.no	Stage	Parameter	Compound	Regular spec	Trial-1	Trial-2
1	Process	Silanisation Temperature	T392	148 deg C	130 deg C	155 deg C
2	Process	Silanisation Time	T392	150 sec	130 sec	170 sec
3	Process	Batch weight/Fill factor	T392	350 kg	335kg	365kg

4.7.1 List of Q parameters to be tracked during the project.

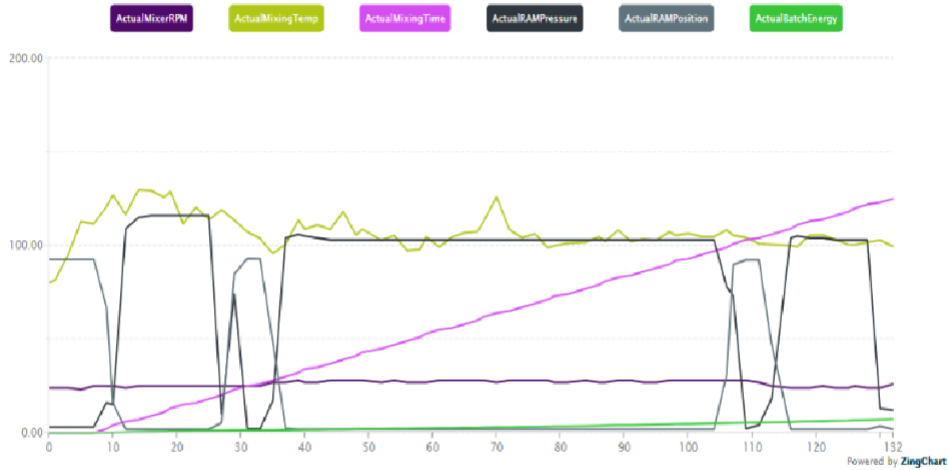
Area	Parameter	Standard
Master mixing	Payne effect	As per the lab control plan & checking condition
Final mixing	Payne effect & Tan delta	
Final mixing	Rolling Resistance	
Final mixing	DMA (Dynamic Mechanical Properties)	

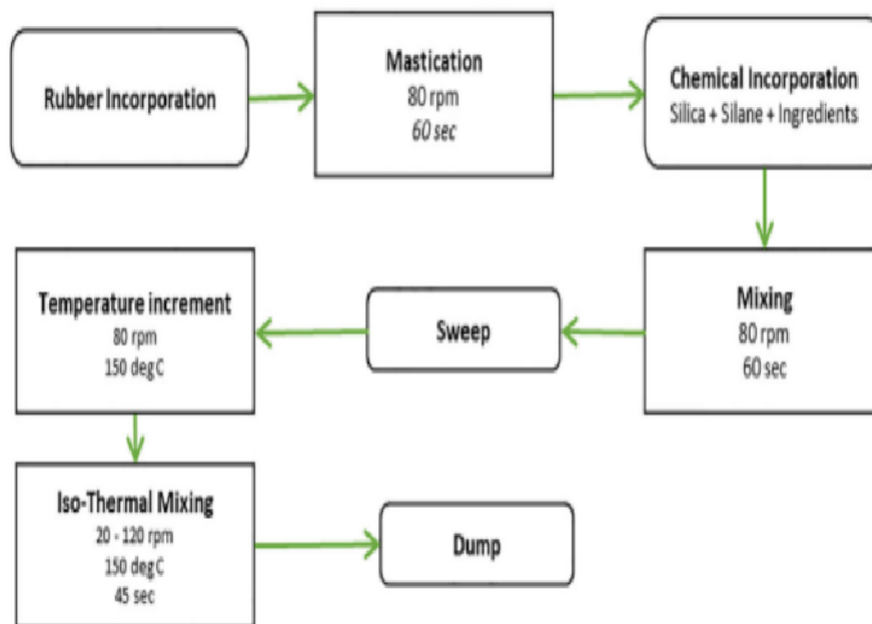
4.8 Mixing flow chart and mixing fingerprint graph.

4.8.1 Mixing sequence

Sequence No	Action	Mode	Rotor Speed	Ram Pressure	Mixing Overide Time	Mixing Overide Temp	Mixing Overide Energy	Rotor Minimum Speed	Rotor Maximum Speed	Batch Temperature Control	Set Temperature (5 speed)	Discharge Door Open Time	Ram Pump Time	Stop Time	Mixing Time	Batch Temperature	Batch Energy
1	StartMix	Null Mode	50	135	0	0	0	0	0	0	0	0	0	0	0	0	0
2	Feed Polymer and Small Bag	Null Mode	50	135	0	0	0	0	0	0	0	0	0	0	0	0	0
3	Ram Down	Null Mode	50	135	0	0	0	0	0	0	0	0	0	0	0	0	0
4	Feed Carbon and Zn	Stop Time	50	135	0	0	0	0	0	0	0	0	0	20	0	0	0
5	Feed Silane2 and Oil	Null Mode	40	115	0	0	0	0	0	0	0	0	0	0	0	0	0
6	Ram Down	Null Mode	50	115	0	0	0	0	0	0	0	0	0	0	0	0	0
7	Feed Small Bag	Stop Time	50	115	0	0	0	0	0	0	0	0	0	20	0	0	0
8	Ram Down	Null Mode	35	115	0	0	0	0	0	0	0	0	0	0	0	0	0
9	Ram Sweep	Mixing Time And Temperature	35	115	0	0	0	0	0	0	0	0	3	0	60	115	0
10	Ram Sweep	Mixing Time And Temperature	35	110	0	0	0	0	0	0	0	0	3	0	70	135	0
11	iram Profile(RAM-D.2-MB01)	Stop Time	23	110	0	0	0	0	0	0	0	0	0	40	0	0	0
12	Ram Sweep	Mixing Time And Temperature	30	110	0	0	0	0	0	0	0	0	3	0	80	144	0
13	Maintain Temperature TMI	Stop Time	0	0	0	0	0	15	35	146	0	0	0	150	0	0	0
14	Batch Discharge with Ramp Float	Temperature And Energy	55	100	0	160	50	0	0	0	0	12	0	0	0	145	28

4.8.2 Mixer Fingerprint





Energy consumption for control silica-filled S-SBR/ BR compound for master, repass, and final stage:

The masterbatch mixing sequence and materials used in DOE are kept the same to minimize interference with external noise factors.

Significant variations of factors with different levels were carried out during the Isotherm (silanization) stage of mixing; the mixing parameters like temperature, feed door condition, time, ram pressure, and TCU were varied along with the fill factor for Master II [Repass] mixing according to the DOE table mentioned.

The masterbatch and repass mixing fingerprint graphs extracted from the Banbury mixer with a 4-litre capacity [Farrell Banbury mixer from HF Mixing group] are mentioned respectively.

During the masterbatch mixing isothermal stage with a silanization temperature of 130C and silanization time of 45 seconds is maintained via variable rpm method and then dumped. The extent of the silanization reaction is kept minimum during this stage I mixing.

For Master II [Repass] stage, the masterbatch compound is mixed without further addition of chemical ingredients; once the silanization temperature reaches the isothermal phase-mixing will be carried out automatically.

Compound temperature is controlled via variable RPM method using Farrell HF mixing Banbury mixer.

The energy input for each sequence in the master's and repass mixing stage was noted and depicted.

The mixing parameters play a vital role in energy consumption during mixing. Especially parameters like TCU, mixing temperature and mixing time. RPM directly affects energy consumption. i.e., the higher the values, the higher the energy input for the system.

CHAPTER-5

5.1 RESULTS AND DISCUSSION, PERFORMANCE

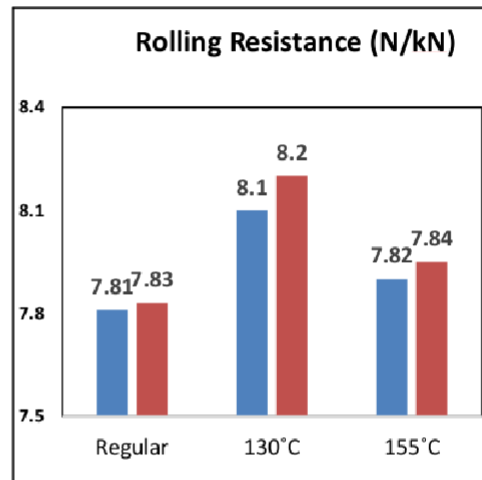
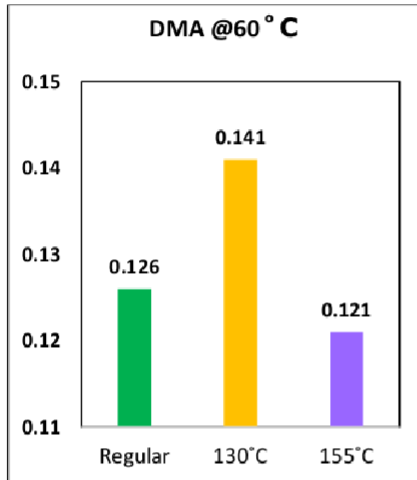
5.1.1 Silanisation Temperature



(i)@155 C temp trial observation: Payne Effect found to decrease by 0.06Mpa Unit as compared with @130 deg C in the master stage-1, and Master stage-2 found 0.01Mpa reduced. It is good result which is indicating good silanisation.

(ii)@ 155 deg C temp trial observation – In Tan delta found 0.03 Mpa reduced as compared with Regular. It is good result for proper silanisation.

- From this trial observation, 130 degC is not suitable for silanisation compared with 148 & 155 deg C.
- Establish Process specs by cross-checking the right degree of silanization



(i)DMA test result 0.121Mpa achieved from regular 0.126 Mpa with 155deg C silanisation temp condition and it is good value for the proper silanisation. Silanisation Temperature has a profound impact on RRC, and optimized temperature is better for RRC.

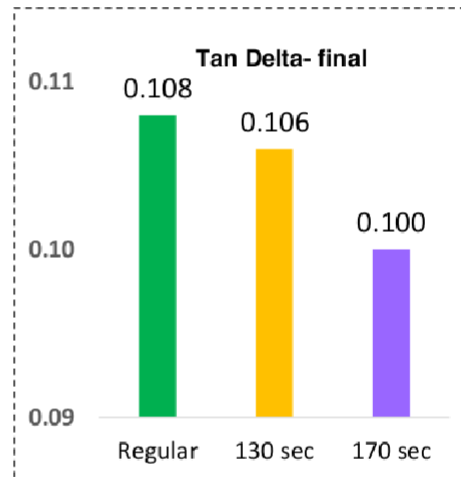
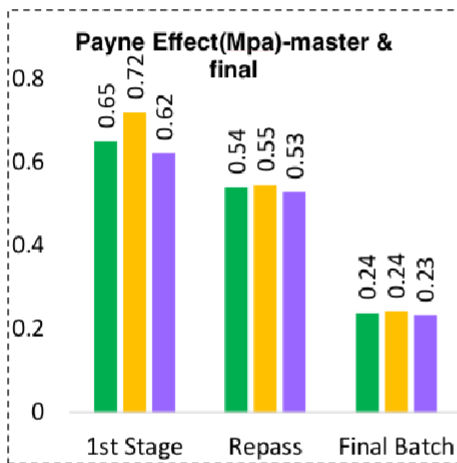
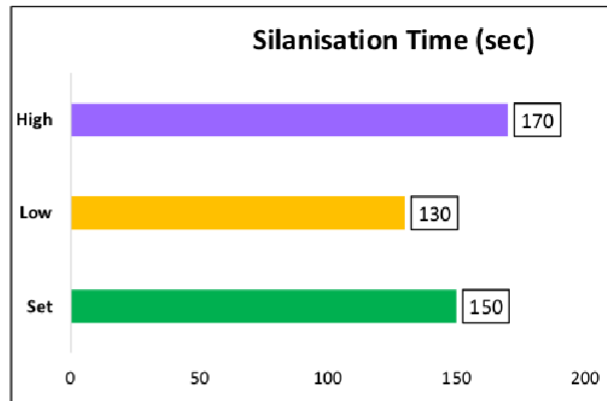
(ii)Tyre RRC was found 7.82N/KN) as compared with regular value 7.83N/KN. It is indicating proper silanisation happened in master1,2 stages.

5.1.2 Silanisation time

DOE-2

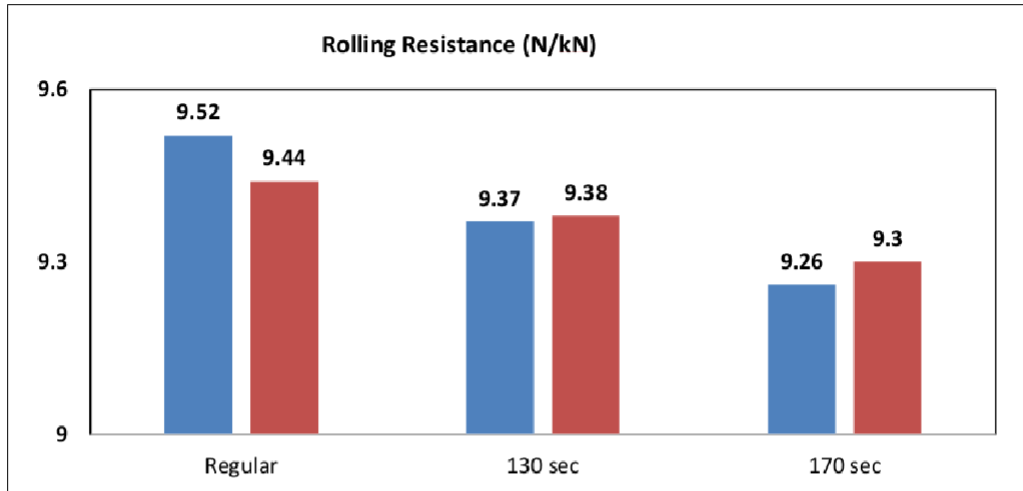
Silanisation time in Master Batch Mixing with High and Low set Time

Compound Code: T392



- (i)@170 sec silanisation time trial observation: Payne Effect found to decrease by 0.62Mpa Unit as compared with regular @150 sec(0.65Mpa)
- (ii)@130sec Silanisation time is not sufficient for the proper mixing, so it is not correct silanisation required in master stage-1 and Master stage-2 found similarly good with regular.
- (ii) So 170sec silanisation time must be required for the proper silanisation as per the study report.

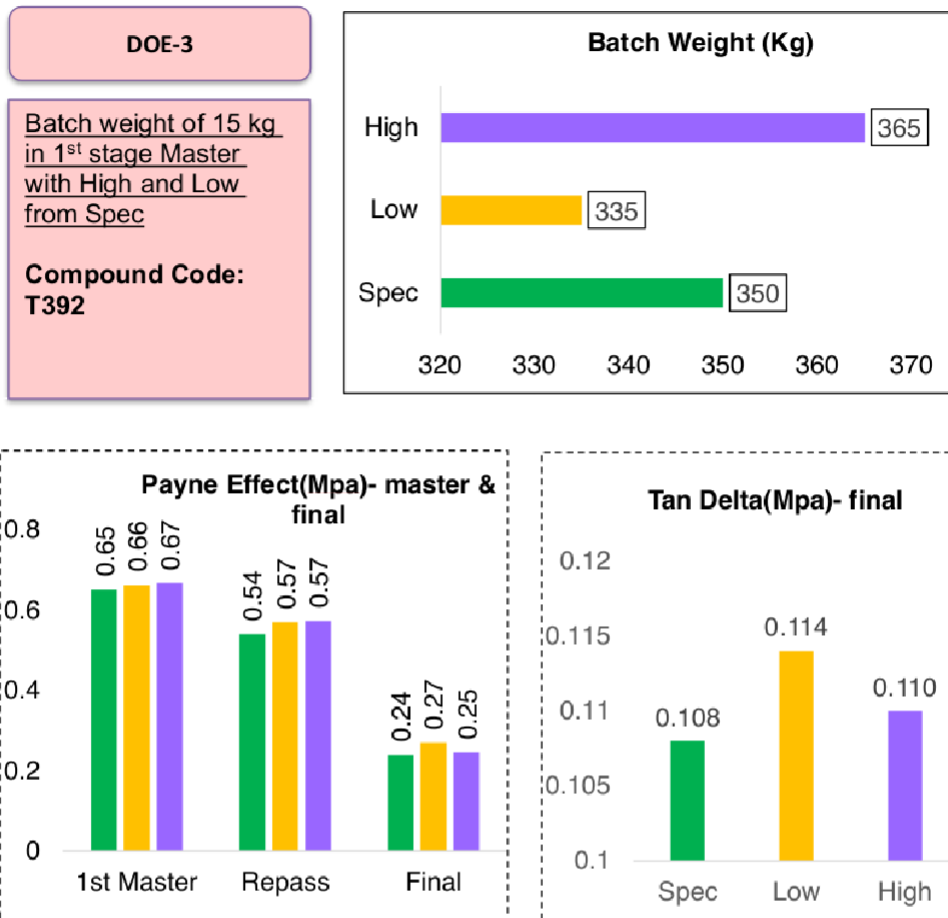
(ii)@ Tan delta trial observation – In Tan delta found 0.100 Mpa compared with Regular 0.108. It is a good result for proper silanisation. Almost 0.08 units were reduced because of proper silanisation.



(i) Tyre RRC was found 9.26N/KN) as compared with regular value 9.52N/KN Almost 0.34 units reduced with 170sec Silanisation time. And 130 sec silanisation time is also comparable with regular but not sufficient for the RRC.

(ii) So as per the trial observation 170sec is better than regular 150 sec, and 130sec is also not recommend for the proper silanisation.

5.1.3 Batch weight/Fill factor

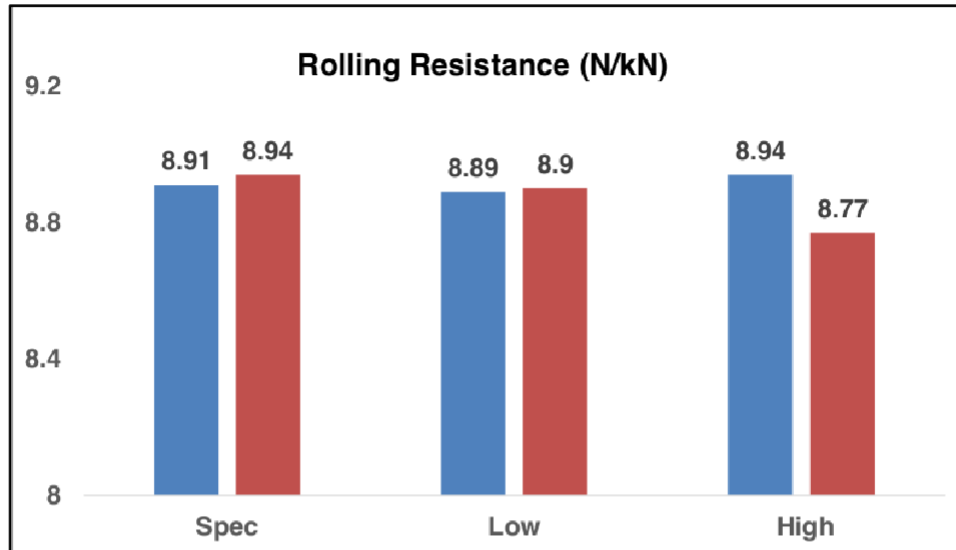


(i)@335 kg batch weight trial observation: Payne Effect found to increase by 0.66Mpa Unit as compared with regular @350kg batch weight(0.65Mpa) in master stage 1. Master stage-2 is found to be similar as regular.

(ii)@365 kg batch weight trial observation: Payne Effect found to increase by 0.67Mpa Unit as compared with regular @350kg batch weight(0.65Mpa).

(iii) Both master stages found similar as regular. No major differences observed.

(iii) So as per the above trial observation regular 350kg batch weight only suitable for the proper silanisation. So 335kg & 365kg batch weight trial is also recommended.



(i) 370kg batch weight trial observation- Tyre RRc was found 8.94N/KN) as compared with regular value 8.91N/KN. There is no major difference observed. Similar as 335kg batch weight also not more difference.

(ii) As per the trial observation RRc is normal in regular(350kg) and Trial(335kg) batch weight.

CHAPTER 6

6.1 SUMMARY AND CONCLUSIONS

DOE - Mixing Summary							
S.no	Parameters	Compound	Spec	No of Trials	Report observation	Status	Remarks
1	Batch weight/Fill factor	T392	±15kg	+15	Normal		No Influence
				-15	Normal		No influence
2	Silanisation temperature	T392	148 C	130	Not ok		Not recommended
				155	Good		Recommended
3	Silanisation time	T392	150 sec	130	Not ok		Not recommended
				170	Good		Recommended

For specified mixing conditions, actual values align with Taguchi's predicted values for Responses.

The longer the silanization time, the higher the TCU, and silanization temperature consumes more energy for mixing. The higher the filler factor results in lesser energy consumption as the fill factor increases, the less time is taken to reach fixed silanization temperature compared to the lower fill factor.

increase in silanization temperature and time lead to a better degree of silanization and filler dispersion. An increase in fill factor from 50%(335kg) to 60%(350kg) positively impacts the silanization reaction, whereas a further increase up to 70%(365kg) has a negative impact due to a reduction in devolatilization efficiency.

This work was attempted to investigate and figure out the significance of mixing parameters, such as silanization temperature, silanization time, fill factor, and temperature of TCU on the degree of silanization reaction using L18 orthogonal array for a better insight. From the main effect plot of the S/N ratio for key properties like Payne effect, Tan δ @ 60C, DMA trend is observed.

Silanisation Temperature:

(i)@155 C temp trial observation: Payne Effect found to decrease by 0.06Mpa Unit as compared with @130 deg C in the master stage-1, and Master stage-2 found 0.01Mpa reduced. It is good result which is indicating good silanisation.

(ii)@ 155 deg C temp trial observation – In Tan delta found 0.03 Mpa reduced as compared with Regular. It is good result for proper silanisation.

(iii)From this trial observation, 130 degC is not suitable for silanisation compared with 148 & 155 deg C.

(iv) Establish Process specs by cross-checking the right degree of silanization

(v)DMA test result 0.121Mpa achieved from regular 0.126 Mpa with 155deg C silanisation temp condition and it is good value for the proper silanisation.

Silanisation Temperature has a profound impact on RRc, and optimized temperature is better for RRc.

(vi)Tyre RRc was found 7.82N/KN) as compared with regular value 7.83N/KN.

It is indicating proper silanisation happened in master1,2 stages.

Silanisation Time:

(i)@170 sec silanisation time trial observation: Payne Effect found to decrease by 0.62Mpa Unit as compared with regular @150 sec(0.65Mpa)

(ii)@130sec Silanisation time is not sufficient for the proper mixing, so it is not correct silanisation required in master stage-1 and Master stage-2 found similarly good with regular.

(iii) So 170sec silanisation time must be required for the proper silanisation as per the study report.

(iv)@ Tan delta trial observation – In Tan delta found 0.100 Mpa compared with Regular 0.108. It is a good result for proper silanisation. Almost 0.08 units were reduced because of proper silanisation.

(v) Tyre RRc was found 9.26N/KN) as compared with regular value 9.52N/KN Almost 0.34 units reduced with 170sec Silanisation time. And 130 sec silanisation time is also comparable with regular but not sufficient for the RRc.

(vi) So as per the trial observation 170sec is better than regular 150 sec, and 130sec is also not recommend for the proper silanisation.

Silanisation for Batch weight:

(i)@335 kg batch weight trial observation: Payne Effect found to increase by 0.66Mpa Unit as compared with regular @350kg batch weight(0.65Mpa) in master stage 1. Master stage-2 is found to be similar as regular.

(ii)@365 kg batch weight trial observation: Payne Effect found to increase by 0.67Mpa Unit as compared with regular @350kg batch weight(0.65Mpa).

(iii) Both master stages found similar as regular. No major differences observed.

(iii) So as per the above trial observation regular 350kg batch weight only suitable for the proper silanisation. So 335kg & 365kg batch weight trial is also recommended.

(iv)370kg batch weight trial observation- Tyre RRc was found 8.94N/KN) as compared with regular value 8.91N/KN. There is no major difference observed. Similar as 335kg batch weight also not more difference.

(v) As per the trial observation RRc is normal in regular(350kg) and Trial(335kg) batch weight.

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