الجمهورية الجزائرية الديمقراطية الشعبية
People's Democratic Republic of Algeria

Ministry of Higher Education and
Scientific Research
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جامعة اكلي محند اولحاج
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Thesis

In order to obtain the professional Master's degree in:

Formulation Engineering

Topic:

Effect of different accelerators on the characteristics of The rubber compounds

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Academic Year: ***2023/2024***

Acknowledgements

First of all, this thesis represents much more than just academic work. It signifies the culmination of five long years of study. Therefore, we would like to extend our heartfelt gratitude to all the people who supported us throughout the process of completing this thesis.

Our first thanks go to our parents, who provided us with both psychological and financial support, for their patience and unwavering belief in our academic and personal success.

We also express our gratitude to our professors for the quality of education they imparted to us during these five years at INSTITUTE OF TECHNOLOGY OF BOUIRA University.

Our gratitude also goes to our supervisor, Dr. IGGUI KAHINA, whose help, suggestions, and constructive criticism brought us this far and were the backbone to finishing this dissertation.

We would like to thank the team at IRIS TYRES, Setif, for their warm welcome, the time each of its members dedicated to us, and, more broadly, for all the information, bibliographical references, insights, corrections, etc., that each one provided and that enriched this work, particularly Mr. BOUHMILA ILYES, Mr. IMAD, MR. ANIS, MR.AHMED, MR. HAMZA, MR. HOUSSAM and many other.

Lastly, we extend our gratitude to all the members of the jury who honor us by agreeing to evaluate this work; we hope it meets their expectations.

DEDICATION 1

This thesis is dedicated to my family, especially my Mom and Dad. Without their selfless efforts and endless support, I would not be where I am right now.

I would also like to dedicate this work to my sister and my brothers, who have not stopped advising, encouraging, and supporting me throughout my studies. May Allah protect them and offer them health and happiness.

And to my best friend, DJALAL, who might insist he's done half the work at least, you did not.

With all my heart, I give thanks to Allah, the Almighty, for giving me the strength to survive and the audacity to overcome all difficulties and many graces in all areas of my life and that of my family. Also, FAYCEL was there.

Last but not least, I wanna thank me
I wanna thank me for believing in me
I wanna thank me for doing all this hard work
I wanna thank me for having no days off
I wanna thank me for never quitting

I wanna thank me for always being a giver
And tryna give more than I receive
I wanna thank me for tryna do more right than wrong
I wanna thank me for just being me at all times

CH.Noufel

DEDICATION 2

With deepest reverence and boundless gratitude, I humbly dedicate this thesis to my cherished parents, whose steadfast love, unwavering support, and unshakable belief in my potential have been the bedrock upon which I have built my academic pursuits.

Throughout the labyrinthine corridors of learning, they have been my stalwart guides, offering encouragement in moments of doubt and celebrating every triumph, no matter how small.

Their relentless dedication to my education, manifested through countless sacrifices and untold hardships, serves as an enduring testament to their profound commitment to my future.

To my entire family, whose collective wisdom and steadfast faith have provided me with a nurturing environment in which to flourish, I offer my deepest appreciation.

Additionally, I extend my heartfelt gratitude to all my friends.

Furthermore, I extend this dedication to all who champion the virtues of resilience, determination, and unwavering perseverance in the face of life's myriad challenges.

B. El Djilani.

Abstract

In recent years, the automotive industry, particularly tire manufacturing, has experienced significant development and transformation from a simple rubber strip to a complex system composed of dozens of different materials. This complexity aims to significantly enhance tire performance, with a focus on increasing longevity, durability, and adaptability to various operational conditions. These improvements require a detailed study of the materials used and their manufacturing processes

In this work, we studied the effects of different types of accelerators on the processing characteristics and mechanical properties of sulfur-cured rubber compounds. We used five different accelerator systems to analyze how each one affects the final performance of the rubber. The accelerators tested include CBS, TBBS, DCBS, DPG, and ZBEC. The study focused on providing a reliable comparison of these accelerators in terms of processing ease and final product characteristics, such as hardness, elasticity, and strength. The results aim to offer insights that help improve tire design and manufacturing to achieve the highest.

TBBS emerged as the most effective accelerator, in terms of processability, mechanical properties, and safety margin during processing.

This comprehensive analysis provides valuable insights for the rubber industry, aiding in the selection of optimal accelerators for various applications.

Keywords:

Automotive industry, Tire manufacturing, Rubber compounds, Sulfur curing, Accelerators, CBS, TBBS, DCBS, DPG, ZBEC, Processing characteristics, Mechanical properties, Hardness, Elasticity, Strength, Tire performance.

Résumé

Ces dernières années, l'industrie automobile, en particulier la fabrication de pneus, a connu un développement et une transformation significatifs, passant d'une simple bande de caoutchouc à un système complexe composé de dizaines de matériaux différents. Cette complexité vise à améliorer considérablement les performances des pneus, en mettant l'accent sur l'augmentation de la longévité, de la durabilité et de l'adaptabilité à diverses conditions de fonctionnement. Ces améliorations nécessitent une étude détaillée des matériaux utilisés et de leurs processus de fabrication.

Dans ce travail, nous avons étudié les effets de différents types d'accélérateurs sur les caractéristiques de traitement et les propriétés mécaniques des composés de caoutchouc vulcanisés au soufre. Nous avons utilisé cinq systèmes d'accélérateurs différents pour analyser comment chacun d'entre eux affecte les performances finales du caoutchouc. Les accélérateurs testés incluent le CBS, le TBBS, le DCBS, le DPG et le ZBEC. L'étude a été axée sur la fourniture d'une comparaison fiable de ces accélérateurs en termes de facilité de traitement et des caractéristiques du produit final, telles que la dureté, l'élasticité et la résistance. Les résultats visent à offrir des perspectives qui aident à améliorer la conception et la fabrication des pneus pour atteindre les plus hauts niveaux de performance.

Le TBBS s'est révélé être l'accélérateur le plus efficace en termes de processabilité, de propriétés mécaniques et de marge de sécurité pendant le traitement. Cette analyse complète fournit des informations précieuses pour l'industrie du caoutchouc, aidant à sélectionner les accélérateurs optimaux pour diverses applications.

Mots-clés

Industrie automobile, fabrication de pneus, composés de caoutchouc, vulcanisation au soufre, accélérateurs, CBS, TBBS, DCBS, DPG, ZBEC, caractéristiques de traitement, propriétés mécaniques, dureté, élasticité, résistance, performance des pneus.

الملخص

في السنوات الأخيرة، شهدت صناعة السيارات، وخصوصاً صناعة الإطارات، تطوراً وتحولاً كبيراً من شريط مطاطي بسيط إلى نظام معقد يتكون من عشرات المواد المختلفة. تهدف هذه التعقيدات إلى تحسين أداء الإطارات بشكل كبير، مع التركيز على زيادة طول العمر والمتانة والقدرة على التكيف مع مختلف ظروف التشغيل. تتطلب هذه التحسينات دراسة مفصلة للمواد المستخدمة وعمليات التصنيع الخاصة بها.

في هذا العمل، درسنا تأثيرات الأنواع المختلفة من المسرعات على خصائص المعالجة والخصائص الميكانيكية لمركبات المطاط المفلكن بالكبريت. استخدمنا خمسة أنظمة مسرعة مختلفة لتحليل كيفية تأثير كل منها على الأداء النهائي للمطاط. المسرعات التي تم اختبارها تشمل CBS و TBBS وDCBS وDPG وZBEC. ركزت الدراسة على تقديم

Abstract

مقارنة موثوقة لهذه المسرعات من حيث سهولة المعالجة وخصائص المنتج النهائي، مثل الصلابة والمرونة والقوة. تهدف النتائج إلى تقديم رؤى تساعد في تحسين تصميم وتصنيع الإطارات لتحقيق أعلى مستويات الأداء.

تبين أن TBBS هو المسرع الأكثر فعالية من حيث القابلية للمعالجة والخصائص الميكانيكية وهامش الأمان أثناء المعالجة .يوفر هذا التحليل الشامل رؤى قيمة لصناعة المطاط، مما يساعد في اختيار المسرعات الأمثل للتطبيقات المختلفة.

الكلمات المفتاحية:

صناعة السيارات، تصنيع الإطارات، مركبات المطاط، معالجة بالكبريت، المسرعات، CBS، TBBS، DCBS، DPG، ZBEC، خصائص المعالجة، الخصائص الميكانيكية، الصلابة، المرونة، القوة، أداء الإطارات.

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List of abbreviations

ASTM : American Society for Testing and Materials

BR : Butadiene Rubber

CBS : N-Cyclohexyl-2-benzothiazole sulfenamide

CR : Chloroprene Rubber

CSt : centistokes

DCBS : N.N'-dicyclohexyl-2-benzothiazole sulfenamide

DPTT : Dipentamethylene thiuram tetrasulfide

DPTU : Di-pentamethylene thiourea

EP : Polyepoxides or epoxides

EPDM : Ethylene Propylene Diene Monomer

ETU : Ethylene thiourea

ISO : International Organization for Standardization

MBS : 2-(4-Morpholinothio) -benzothiazole

MDR : Moving Die Rheometer

NR : Natural rubber

PBR : Polybutadiene Rubber

PF : Phenoplasts

Phr : Per hundred rubber

PUR : Crosslinked polyurethanes

SBR : Styrene-Butadiene Rubbers

TBBS : N-tert-butyl-2-benzothiazole sulfenamide

TBzTD : Tetrabenzyithluram Disulfide

TMTD: Tetramethyl thiuram disulfide

TMTM : Tetramethyl thiuram monosulfide

UP : Unsaturated polyesters

VE : Vinylester

ZDBC : Zinc dibutyldithiocarbamate

ZDEC : Zinc diethyldithiocarbamate

ZDMC : Zinc dimethyldithiocarbamate

ZIX : Zinc-Isopropyl Xanthate

ZnO : Zinc oxide

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General Introduction

General Introduction

Polymers, commonly known as "plastics," are inseparable from our environment and practical life. They have become essential in all areas of our activities. Most often synthetic, sometimes natural, they owe their growth to their wide range of characteristics: hard, soft, or elastic; transparent or opaque; insulating and sometimes conductive; more or less resistant to aggressive conditions of use; always lightweight **[1]**.

Elastomers, commonly known as rubber, are a type of polymer completely elastic and resist to temperature. Thanks to their properties, the use of these elastomers has become widespread in particularly for the manufacture of technical parts in the field of tires.

Indeed, in 1839, the American CHARLES GOODYEAR discovered vulcanization, which is a chemical reaction between sulfur and natural rubber, forming bridges between macromolecular chains. After this discovery, ROBERT WILLIAM THOMSON invented a first pneumatic tire in 1845, which quickly fell into oblivion. The use of solid rubber tires for bicycles became widespread in 1868. In 1888, in Belfast, the Scottish veterinarian JOHN BOYD DUNLOP, who himself made his surgical gloves, imagined and patented a flexible inflated tube to replace solid tires. Then in 1891, the wired tire invented by C.K. WELCH marked a significant breakthrough in the history of tires. That same year, the Michelin brothers patented tires that could be mounted or dismounted manually. In 1904, FIRESTONE and the GOODYEAR company developed tires with wired straight sidewalls **[2]**.

In this landscape, IRIS Tyres Company stands as a testament to the enduring spirit of innovation within the pneumatic industry. Founded in 2019, IRIS Tyres quickly established itself as the premier tire manufacturer in Algeria and one of the largest in Africa, embodying the culmination of centuries of pneumatic progress. Offering high-quality products that drive mobility and advancement across the continent, IRIS Tyres represents the vanguard of indigenous industrial success, with its commitment to excellence and 100% Algerian ownership poised to leave a lasting imprint on the global pneumatic stage.

The aim of our work is to investigate both experimental and theoretical aspects for modeling the rubbers used in the automotive industry at IRIS TYRES SETIF. To achieve this, we have divided this work into four chapters.

The first chapter explores the history, evolution, and significant contributions of 'IRIS TYRES' to the pneumatic industry. It provides a detailed exploration of the company's historical background, its localization efforts, and offers a vivid description of its state-of-the-art factory.

The second chapter will delve into a meticulous bibliographical study of polymers, laying the groundwork for a deeper understanding of these versatile materials. From elucidating the fundamental properties of elastomers to exploring their diverse applications, this chapter serves as a comprehensive primer on the subject. Additionally, this chapter will explore the world of tires, providing a nuanced exploration of their components, various types, and the underlying engineering principles driving their design and functionality.

The third chapter will delve into the meticulous process of preparing the samples for analysis, a crucial step in ensuring the reliability and accuracy of our findings. Each sample underwent rigorous preparation, with attention to detail at every stage. Notably, we prepared five distinct versions, each utilizing a different accelerator to explore the varying effects and outcomes. These accelerators, chosen for their unique properties and potential impacts on the samples, added depth to our experimentation and provided valuable insights into the materials under study. Additionally, comprehensive tests were conducted on each sample, employing a range of methodologies to scrutinize their compositions, properties, and behaviors.

The fourth chapter will delve into the comprehensive comparison of the results obtained from the five different versions prepared and tested in the previous chapter. This comparative analysis will offer valuable insights into the nuanced effects of each accelerator on the samples' properties and behaviors. Through meticulous examination and discussion, we aim to unravel the intricacies underlying these variations, providing a deeper understanding of our experimental outcomes.

Concluding our study, we will wrap up with a comprehensive general conclusion that synthesizes the key findings and insights gleaned from our experimentation and analysis.

Chapter I: Company presentation

I.1. Introduction

After investing in the fields of electronics and household appliances, this industrial hub EURL SATEREX diversified its activities and has recently ventured into tire manufacturing, a mega-industrial complex built on an area of 5.5 hectares located in the industrial zone of Setif. It aims to cover the entirety of national needs and then in a second phase, to conquer foreign markets **[3].**

This company ranks first in Algeria and third in Africa, using cutting-edge technologies to produce a wide range of tires for both passenger vehicles and various other types of rolling equipment.

EURL SATEREX Pneumatic (IRIS TYRES) is an Algerian company that utilizes a 100% local process involving several foreign technological partners, aiming to benefit from technology transfer and know-how with global standards. The designed tires are characterized by better conformity, high rolling resistance, improved vibration absorption, and reduced noise levels.

The estimated production of this complex is 2 million tires for light vehicles, utility vehicles, and semi-heavy vehicles per year during the first phase, with a considerable increase in production capacity to 4.5 million tires per year for the second phase.

The complex has implemented over 320 checkpoints for each tire. Within the research and development laboratory, daily tests are conducted using highly sophisticated equipment to provide tires that meet international standards and are completely safe and comfortable. This laboratory is a crucial structure within the complex, overseeing the choice of raw materials, control of mixed blends, and research and development of new recipes.

Currently, there are 450 workers, with plans to increase to 750 with expansion. They are also preparing for a tire factory for heavy trucks and surface construction equipment covering 20 hectares with 800 workers, ultimately reaching 4,500,000 tires per year **[3]**.

***Figure I.1**: IRIS TYRES logo*

I.2. Localization and Description of the Factory

Located in the industrial zone of Sétif, IRIS TYRES' factory is an impressive project, a vast industrial complex covering 5.5 hectares **[3]**.

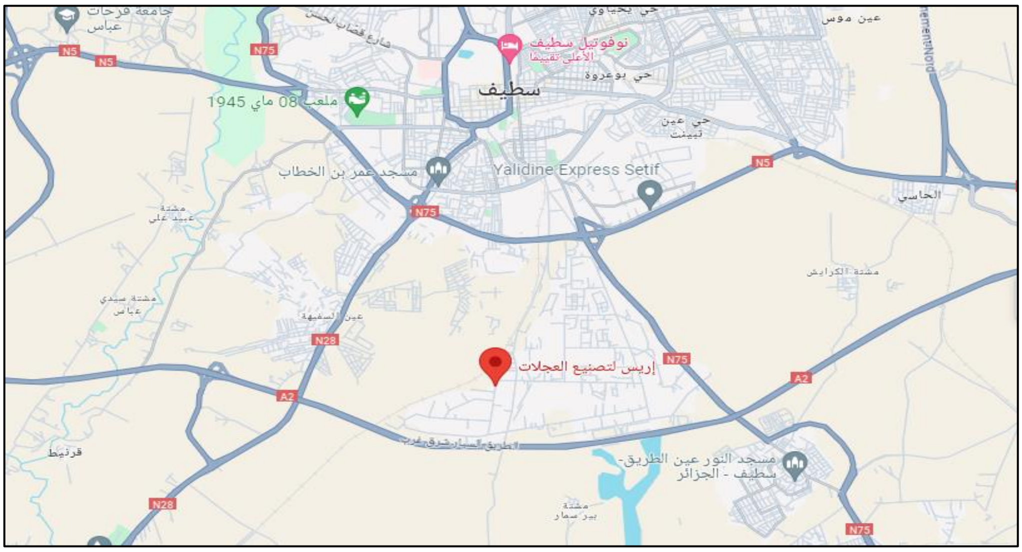


Figure I.2*: Localization of the Factory.*

The space is divided into four distinct blocks, each dedicated to a specific activity:

A: Layer assembly, baking, and final product control.

B: Layer fabrication and incorporation of reinforcing materials.

C: Storage of raw materials and layer mixing.

D: Storage area.

Figure I.3*: Factory main sectors.*

The IRIS TYRES laboratory is equipped with various equipment for rheological, physical, mechanical, and dynamic analyses for the characterization of rubber. The laboratory's objective is to approve new raw materials, test new formulations, inspect the quality of received raw materials, and semi-finished components **[3]**.

I.3. Activities

All activities of EURL SATEREX are focused on:

- Manufacturing refrigerators.
- Manufacturing air conditioners and domestic ovens.
- Manufacturing televisions.
- Plastic injection.
- Manufacturing washing machines.
- Manufacturing pneumatic products.

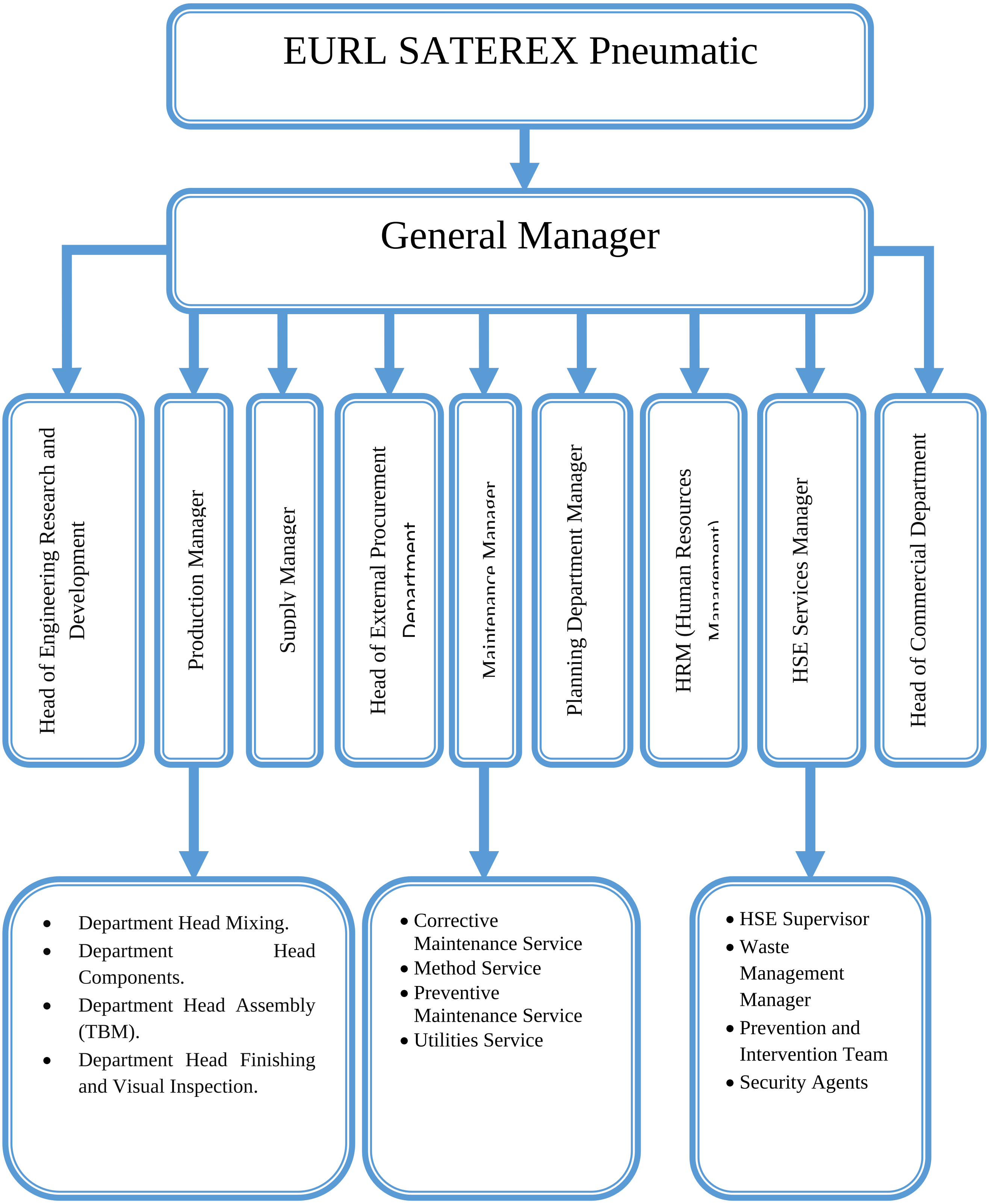
The types of tires produced: ECORIS / SEFAR / STORMY / AURES.

I.4. Legal information

Table I.1**: Legal information of IRIS Tyres **[3].

Nature of the company	Producer (2.5 million tires in 2021)
Share Capital (in DA)	2000000000,00
Start Date of Activity	01/01/2019
Legal Form	EURL (sole proprietorship with limited liability)
Regime	Private
Number of Employees	450 employees
Certifications	ISO 9001 ISO 14001 IATF 16949 (in preparation)

I.5. Company Organizational Chart



Chapter II: Literature review

II.1. Polymers

II.1.1. *Definition*

A polymer is a large molecule with a high molecular weight, consisting of the repeated sequence of the same pattern; the monomers (from the Greek monos: one and meros: part). These monomers are connected to each other by organic or inorganic covalent bonds. The chains can get tangled up and create a 3D network either during the process or by adding crosslinks.

Most polymers used by humans are synthetic and have broad applications. However, long before humans, nature was already using natural polymers, the most well-known being rubber, cellulose, and starch. It's important to note that in this chapter, we will focus on discussing synthetic polymers.

<u>Note:</u>

The assembly of monomers to obtain polymers (or macromolecules) is called polymerization.

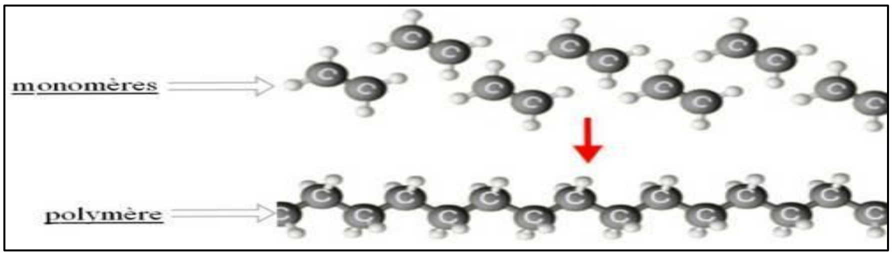


Figure II.1*: Polymerization [4].*

II.1.2. *Applications*

The advent of polymers stands as a cornerstone in the technological revolutions of the 20th century, profoundly impacting various facets of daily existence. These versatile compounds find application in an exceptional array of uses, permeating every aspect of life, from industrial processes to everyday consumer products. Their influence extends beyond material science, contributing significantly to advancements in fields such as medicine, electronics, and environmental sustainability. The table II.1 summarizes the main areas of applications polymers **[4].**

***Table II.1**: Application domains of polymers.*

Areas	Examples
Construction sector	Doors, water pipes and sanitation, painting of walls, chairs and ceilings, floor covering.
Packaging industry	Bottles, yogurt pots, mailboxes, thermal problems, video film sheathing.
Medicine and health	Blood bags, gloves, lenses, spectacle lenses, artificial organs, syringes, dental industry, prosthetics, chirurgical tools
Household items	Tupperware, trash cans, buckets, dishes.
Electrical and electronic equipment and communications	Voltage insulation, insulation, washers, computers and cameras, Radio and television, telephone.
Automobile Industry	Clear glass system, upholstery, bodywork, optics, dashboards, interior trim, television fronts, cable sheathing.
Textile industry	Clothing, natural and synthetic textile fibers, bags, imitation leather, non-wovens.
Chemical industry	Piping, tanks, coatings.
Sports-leisure	Parts of buildings, planes and boats, DVDs, magnetic tapes, fishing lines and cords used
Food sector	Food manufacturing processes, packaging (bottles, yogurt pots, milk cartons, egg cartons) or industrial (detergent bottles, bags, racks).
Home equipment	Furniture, tableware, accessories... Used in industry to protect equipment from a violent collision

II.1.3. Polymer classification

Polymers are often classified according to their thermomechanical properties into three main families:

- Thermosetting polymers;
- Thermoplastics polymers;
- Elastomers polymers.

II.1.3.1. Thermosetting Polymers

These are polymers that harden irreversibly at a temperature depending on their chemical nature. The chaining of their molecules forms a three-dimensional network that opposes any thermal mobility. The most commonly used families of thermosetting polymers are:

Aminoplasts, Phenoplasts, Polyepoxides or epoxides, Crosslinked polyurethanes, Unsaturated polyesters, Vinylester **[5].**

II.1.3.2. Thermoplastic Polymers

These are compounds that melt when heated but they set again when cool. Their materials are "moldable in the molten state," meaning they can be shaped into usable forms when in a liquid (melted) or viscous phase.

In most manufacturing processes, thermoplastics are heated, then formed by injection molding, extrusion, or thermoforming before being cooled so that the finished product retains its shape.

Currently, there are numerous types of thermoplastics offering a wide range of interesting properties. They can be made as flexible as rubber, as rigid as metal and concrete, or as transparent as glass, for use in many piping products and other components. Common examples of thermoplastics polymers include Polyethylene, Polypropylene, Polyvinyl Chloride, Polystyrene, Polybenzimidazole, Acrylic, Nylon, And Teflon **[5].**

II.1.3.3. Elastomers (Cross-linked Polymers)

Thermoplastic and especially thermosetting polymers can be cross-linked to produce elastomers. Depending on the type of cross-linking, elastomers are classified into two families:

- Thermosetting elastomers: low cross-linking with covalent bonds,
- Thermoplastic elastomers: low cross-linking with non-covalent bonds such as hydrogen bonds.

Structures of this type are generally prepared from linear or branched low molecular weight prepolymers, cross-linked under the influence of heat in the presence of a catalyst. The structure is typically three-dimensional.

Cross-linking binds polymer chains together, imparting greater elasticity and resistance to abrasion to the material.

The macromolecules of elastomers are tangled in a ball, and moreover, they are loosely connected by knots whose nature varies depending on the types of elastomers. When an elastomer is stretched, the molecules unfold and elongate. The role of the knots is to prevent them from slipping and to bring them back to their original position when released [see Figure 2]. Some examples of elastomers include natural rubber, polyurethane, polybutadiene, neoprene and silicone **[6]**.

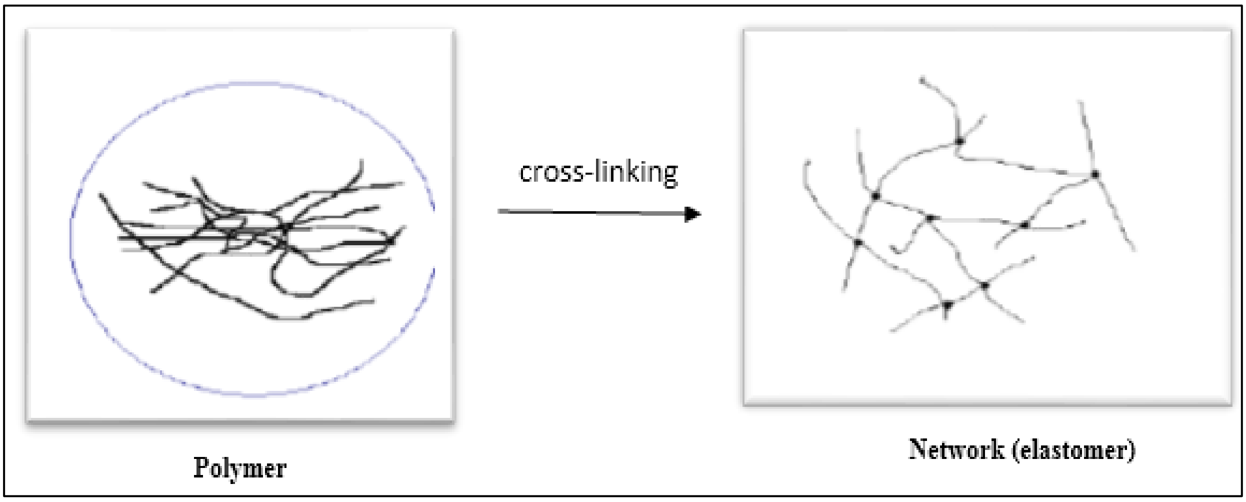


Figure II.2: *Schematic representation of polymer chains and networks (strongly cross-linked) or elastomers (weakly cross-linked)* ***[6].***

II.2. Rubber

II.2.1. *Introduction*

Rubber products play a ubiquitous role in contemporary living, touching nearly every aspect of daily life. Whether in tires, automotive parts, industrial hoses, flooring, or applications in food, medicine, and adhesives, rubber products have a pervasive presence.

On a global scale, a substantial 25 million tones (25,000,000 t) of natural and synthetic rubber are annually produced, traded, and utilized. As the world economy expands, driven by the industrialization of emerging economies, the demand for rubber products and rubber itself steadily rises **[7].**

II.2.2. *History*

- 15th-17th century: Discovery of rubber by Europeans in Central and South America;
- 1770: Production of the first erasers in Great Britain (Priestley);
- 1823: Rubber dissolution in a solvent and fabric waterproofing: creation of the first raincoats (Macintosh);
- 1839: Vulcanization by Charles Goodyear: enhancement of rubber properties (elasticity and stability) through sulfur;
- 1909: Fritz Hoffmann files the first patent for synthetic rubber manufacturing;
- 1950 - 2007: Beginning of the industrial era of "synthetic" rubbers. Boost to the tire industry **[8]**.

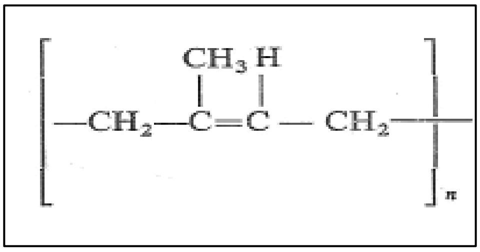
II.2.3. Types

There are approximately twenty families of elastomers, with some of these families having between ten to twenty different grades. This indicates that modern polymerization techniques increasingly enable the customization of products to address both processing requirements and desired properties. The typical classification involves dividing rubbers into natural and synthetique rubber.

II.2.3.1. Natural rubber (NR)

II.2.3.1.1. Structure and properties

Raw natural rubbers are obtained from various trees and shrubs in tropical regions such as Malaysia, Indonesia, Thailand, India, and Sri Lanka. The hevea tree is the predominant source due to its high yield. Rubber is extracted in the form of latex, not from sap but from latex vessels located between the bark and wood of the tree. To obtain latex, incisions are made in the bark, allowing the latex to flow slowly. Chemically, natural rubber is a 1,4-cis poly isoprene with the empirical formula (C_5H_8) n. It is a linear polymer with a high molecular weight, as depicted in Figure II.3 **[9] [10].**



$$\left[-CH_2-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{H}{|}}{C}-CH_2- \right]_n$$

Figure II.3: Chemical structure of poly isoprene 1,4 Cis **[11].**

The polyisoprenes found in nature are mostly in the cis form of natural rubber (Figure II.3), or the trans form of gutta-percha (Figure II.4) **[11]**.

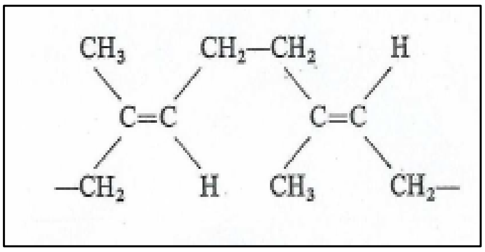


Figure II.4: Chemical structure of Trans de gutta-percha **[11].**

Hevea brasiliensis natural rubber (NR) comprises approximately94% cis-1,4-polyisoprene and 6% non-rubber components like proteins, lipids, and sugar. Despite synthetic cis-1,4-polyisoprene (IR) reaching over 98% cis-1,4 configuration **[12]**.

NR demonstrates superior mechanical properties, including tack and green strength in the unvulcanized state, as well as high tensile strength, crack growth resistance, and minimal heat build-up in the vulcanized state **[13,14]**. It tears easily, lacks elasticity, and exhibits plastic behavior, meaning it does not return to its original shape after deformation. In warmer temperatures, it becomes soft, sticky, and tacky, while in colder conditions, it becomes rigid and stiff **[15]**.

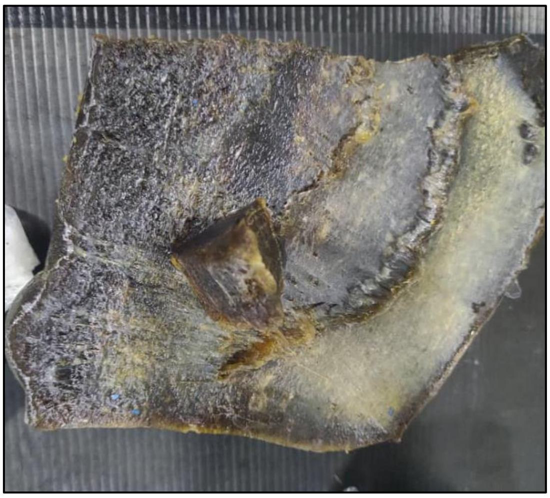


Figure II.5*: Natural rubber.*

II.2.3.1.2. Applications of natural rubber (NR)

Due to its exceptional properties, natural rubber (NR) is a vital component in various applications across six sectors:

- Tire Products: Over 70% of NR consumption is in tires, especially heavy-duty ones for trucks, buses, and airplanes. NR's ability to resist heat build-up enhances the safety of heavy-duty tires compared to those made from synthetic rubber;
- Molded Products: Produced through compression or injection into a closed mold, examples include sponges, carpet underlay, sandals, shoes, rubber bands, connectors, curing tubes, O-rings, and more;
- Extruded Products: Rubber is extruded through dies to create shapes like hoses, pipes, electric cables, refrigerator seals, window/door seals, insulators, rollers, and erasers;
- Adhesives: Solid NR in solution adhesives is used in products like pressure-sensitive adhesives, electrical insulation tapes, adhesive tapes, packaging tapes, surgical tapes, and plasters;
- naturalrubber Latex-Based Products: Produced through dipping, coating, binding, foaming, and extrusion processes, including;

- Dipped Products: Household and medical gloves, finger caps, balloons, and sporting goods;
- Coating and Binding Products: Used for carpet backings, adhesives, adhesive tapes, and self-seal envelopes;
- Foam Products: Such as cushions, seating, mattresses, and pillows;
- Extrusion Products: Elastic threads used in undergarments and socks **[16]**.

II.2.3.2. Synthetic rubber

The discovery of natural rubber in the New World dates back to the time of Columbus's voyages, yet its technological utilization only gained momentum with the onset of the 19th century during the Industrial Revolution. Despite this early awareness, attempts to synthesize rubber from basic chemical compounds did not emerge until the latter part of the 19th century.

The inception of synthetic rubber marks a pivotal milestone in macromolecular synthesis, representing the earliest developments in creating man-made polymers. Unlike other synthetic polymers in contemporary use, synthetic rubber did not arise as a novel material but rather emerged as a response to a critical need in the modern world. Notably, in the United States, the impetus for its development stemmed solely from the exigencies of World War II. The unique status of synthetic rubber is rooted in the unparalleled property of rubber, the only substance demonstrating extensive elasticity over long distances, thereby fulfilling a distinctive role in modern technology **[17]**.

➢ Styrene-Butadiene Rubbers (synthetic rubber)

Styrene-Butadiene Rubbers (SBR), are polymers formed from styrene and butadiene, constituting over half of the global production of synthetic rubber. In contrast to Natural Rubber (NR), SBR exhibits lower mechanical strength, necessitating the blending of raw gum with fillers like carbon black to enhance rigidity and mechanical resistance. While other chemical properties align with NR, SBR demonstrates improved aging resistance. Production costs of SBR are roughly comparable to those of NR **[18]**.

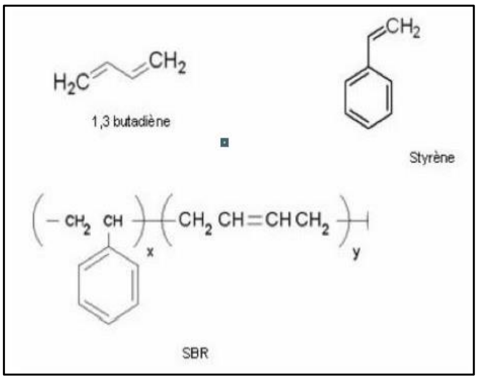


Figure II.6: Styrene-Butadiene Rubbers reaction synthesis.

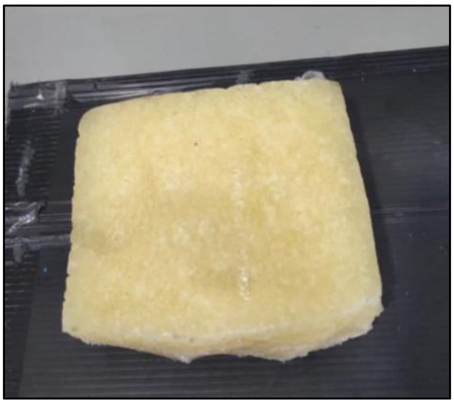


Figure II.7: Styrene-Butadiene Rubber.

II.2.4. Vulcanization

Vulcanization involves chemically crosslinking (establishing covalent bonds) between polymer chains. Unvulcanized rubber is a mass of long, entangled polymer chains similar to spaghetti. Stretching this mass causes some degree of untangling and sliding of chains relative to each other. When the stress is released, the material contracts, and the chains entangle again. Vulcanization significantly increases the material's elasticity by locking these chains relative to each other, reducing or eliminating the long-term sliding of polymer chains. This process results in a dimensionally stable and heat-resistant mass. There are primarily two types of chemical crosslinking agents: peroxides and sulfur compounds **[19,20]**.

The formation of a three-dimensional network, or vulcanization, is a crucial step in rubber processing, as many properties of vulcanized rubber depend on the crosslink density.

Common vulcanization systems include the sulfur system and the peroxide system. Recently, a combination of both sulfur and peroxide systems is employed, resulting in significant improvements in elastomer properties, such as residual deformation after compression, elastic recovery, and mechanical properties **[21,22]**.

- **The sulfur-based vulcanization**

Sulfur-based vulcanization is the first and most widely used process for crosslinking polymers. Discovered by Goodyear in 1839, this process utilizes sulfur as a crosslinking agent. At temperatures of 135-160 °C, sulfur binds the polymeric chains at the double bonds of carbon. Accelerators for crosslinking are added, in addition to free sulfur atoms, to speed up the curing process and make other sulfur atoms within the polymer molecules available **[18]**.

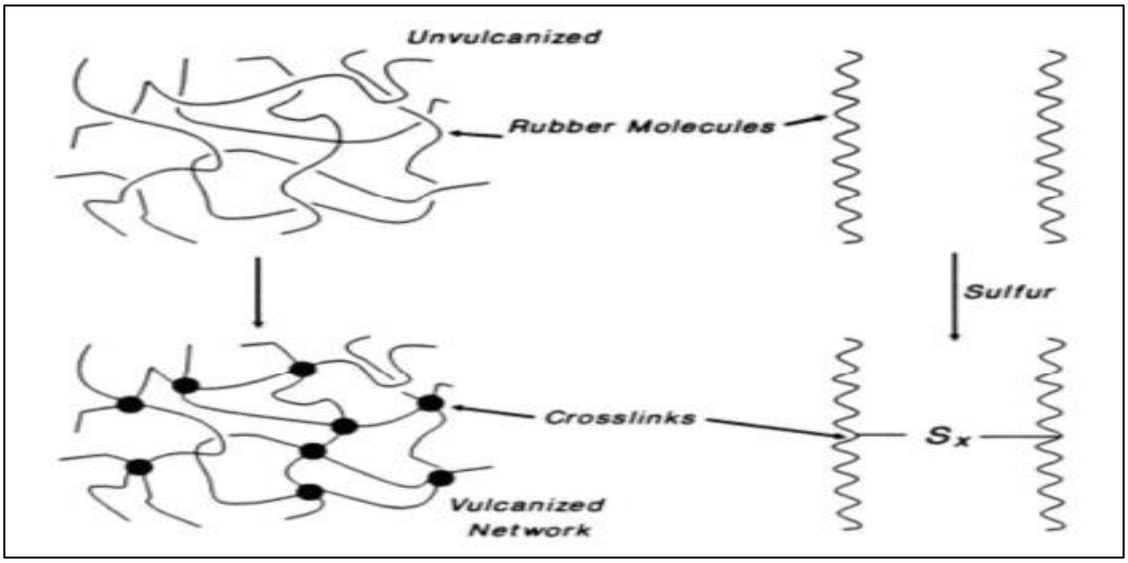


Figure II.8**: Vulcanization of rubber chains by creation of sulfur bridges between the chains* ***[23].

- **Peroxide-based vulcanization**

This represents a different category of crosslinking agents, eliminating the need for double bond reactivity or the use of cure accelerators. Peroxides interact with elastomers, extracting hydrogen atoms from the polymer chain, generating highly reactive free radicals. These radicals form bonds with each other through a carbon-carbon linkage, which is stronger and thermally more stable than the sulfur-carbon linkage **[18]**.

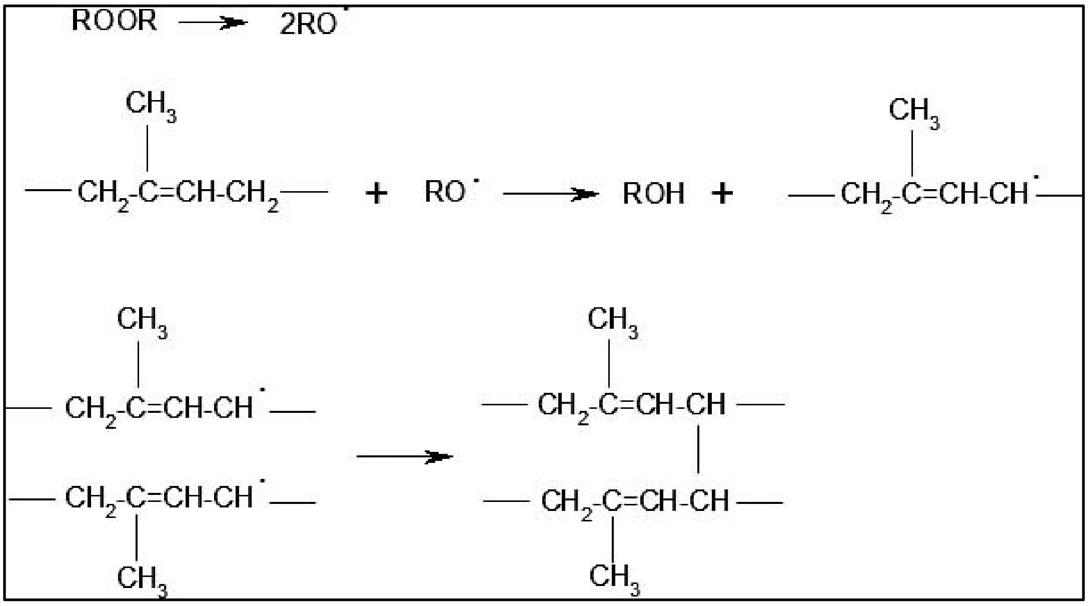


Figure II.9: Peroxide cross-linking of NR ***[18].***

II.3. Pneumatic

II.3.1. Introduction

A pneumatic tire is a flexible, toroidal container filled with compressed gas (normally air), mechanically attached to the outer circumference or rim of a vehicle wheel. Its name comes from 'attire,' indicating a protective covering or coat. In this sense, the American spelling 'tire' is closer to the original than the British 'tyre.' This covering, still referred to as a 'cover' in the rubber industry, serves essential functions in various modes of transportation, including airplanes, that cannot be matched by alternative systems. These functions include providing passenger comfort, reducing fatigue and overall shock within vehicles, offering reliable steering control, and transmitting braking and traction forces across diverse surface terrain and weather conditions. Additionally, reduced resistance to motion is a significant benefit **[24].**

II.3.2. History

The concept of a solid wheel dates back over 5000 years, but it was a Scotsman, Richard Thompson (1822-1873), who first patented the idea of a pneumatic tire in 1845. His invention aimed to reduce power usage and noise by fitting an elastic bearing around a carriage wheel, which could be filled with springs, horsehair, or air. Although Thompson's idea was initially forgotten, it was reinvented in 1888 by another Scottish inventor, John Boyd Dunlop, who designed a smoother-rolling bicycle tire. Dunlop patented a system where air was contained within a rubber and fabric tube attached to the wheel's edge. Despite initial concerns about air loss, pneumatic tire technology was successfully applied to four-wheeled vehicles as a commercial product by the Michelin brothers in 1895. Since then, tire evolution has been gradual, with occasional significant advancements such as the radial ply tire in 1948 and early run-flat technology attempts in the mid-1970s. Despite their seemingly unchanged appearance, modern tires have undergone significant improvements in performance, with various compounds and components tailored to specific needs and future developments continually under consideration **[25]**.

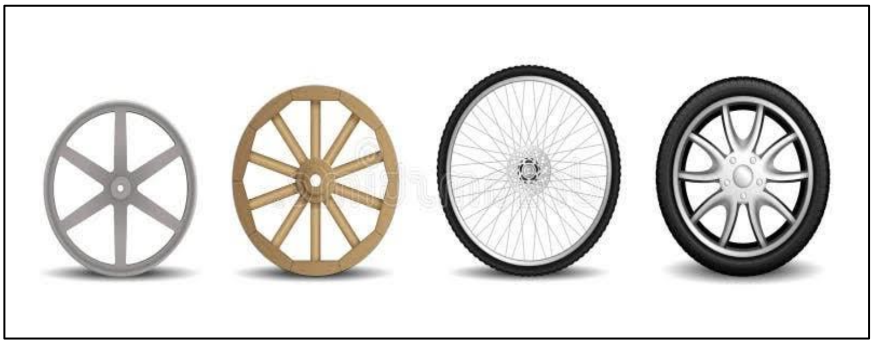


Figure II.10: Tire evolution **[26].**

II.3.3. Functions of Tires

Irrespective of the vehicle type they're designed for, tires must perform several essential functions, summarized as follows **[27,28]**:

- Transmit driving forces, including steering and braking;
- Provide damping and vibration reduction;
- Minimize noise and vibrations;
- Support load capacity;
- Resist wear and tear;
- Ensure durability and safety over their lifespan;
- Have minimal rolling resistance;
- Maintain proper grip on wet surfaces.

II.3.4. The main layers of a tire

The complexity of manufacturing this object stems not only from its composition but also from the number of layers it contains. A tire consists of 9 distinct layers, each with its own characteristics **[29]:**

II.3.4.1. tread

Tread Made from a blend of synthetic and natural rubber, the tread provides substantial mileage, excellent road grip, and efficient water dispersal on a new tire. This ensures safe driving in all conditions. The tread, linking the road and sidewall, is subdivided into three zones:

- **The screed**

This component of the tire has the most contact with the road, providing traction on all surfaces, wear resistance, and directional stability.

- **The ply**

Situated beneath the screed, the ply minimizes rolling resistance and safeguards the tire's internal structure – the carcass.

- **The shoulder**

Located at the edges of the tread, this area provides an optimal transition between the tread and the sidewall of the tire.

II.3.4.2. Belt ply

Situated directly beneath the tread, this component facilitates high-speed driving. Constructed with a durable nylon cord embedded in rubber, the cord wraps around the tire's circumference from one side to the other without overlapping.

II.3.4.3. Steel Belt

The tire is strengthened with steel belts composed of woven steel wire sheets encased in rubber to enhance rigidity resulting in **[30]:**

- Improved shape retention and directional stability;
- Decreased rolling resistance;
- Enhanced tire mileage performance.

II.3.4.4. Textile Ply

This layer of textile, made of rubber-coated rayon or polyester, regulates the internal pressure of the tire and helps maintain its shape.

II.3.4.5. Inner calendering

It consists of a rubber layer that prevents air diffusion and serves as a replacement for the inner tube in the tire. Usually made of a synthetic rubber known as butyl or a type of polyisoprene rubber. This inner liner effectively retains air within the tire **[31].**

II.3.4.6. Sidewall

The sidewall is the lateral section of the tire, linked to the tread via the shoulder, primarily composed of rubber. The suppleness of this rubber on this tire segment aids in maintaining vehicle grip during turns and smoothing out some road irregularities **[32],** thus shielding the carcass from external damage and weather conditions.

II.3.4.7. Strip

Made from nylon or aramid - a durable synthetic fiber known for its heat resistance.

II.3.4.8. Apex

A stabilizing element crafted from synthetic rubber. The apex fulfills similar roles as the heel reinforcement while offering extra steering comfort.

II.3.4.9. Bead

At the core of the heel, the bead is composed of steel wires embedded in rubber. The bead ensures a secure attachment to the rim edge.

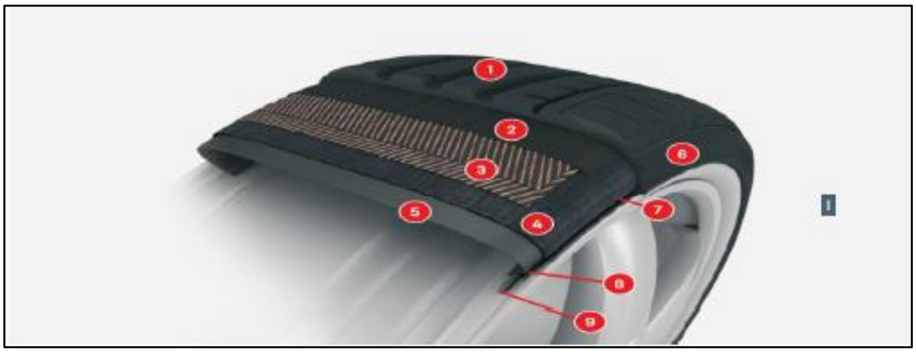


Figure II.11: different tire layers **[33].**

II.3.5. The constituents of tires

The tire is composed of multiple distinct components, each serving its specific function in achieving a high-quality tire. These include:

- Natural rubber;
- Styrene-Butadiene Rubbers (synthetic rubber);
- Carbon Black;
- Oil;
- Steric acid;
- Zinc oxide (ZnO);
- Sulfur;
- Accelerator.

II.3.5.1. Accelerator

1. introduction

Using only sulfur for curing is both time-consuming and ineffective. A typical curing process with sulfur alone involves 5-20 parts per hundred rubber (phr) sulfur and takes 5-15 hours to complete at temperatures between 130-160C^0. This prolonged duration is attributed to the slow reaction between the rubber and a large quantity of sulfur atoms necessary for crosslink formation. Certainly, the addition of accelerators could improve the efficiency of sulfur curing by expediting crosslink formation **[34]**.

An accelerator is defined as the chemical added into a rubber compound to increase the speed of vulcanization and to permit vulcanization to proceed at lower temperature and with greater efficiency.

Accelerator also Decreases the Quantity of Sulphur necessary for vulcanization and thus improving 'aged' properties of the rubber vulcanizates.

Accelerators are categorized as Primary and/or Secondary accelerators based on their role in a given compound.

Typically, Thiazoles and Sulfenamide accelerators act as Primary Accelerators due to their characteristics, including good processing safety, a broad vulcanization plateau, optimum cross-link density, and desired reversion delay.

Primary Accelerators are typically employed at dosages of 0.5 to 1.5 phr in most rubber compounds.

Basic accelerators like Guanidines, Thiurams, and Dithiocarbamates serve as Secondary accelerators to activate the primary accelerators. While the use of secondary accelerators significantly increases the speed of vulcanization, it comes at the expense of scorch safety. Dosages of the secondary accelerators generally range between 10-40% of the primary accelerator **[35]**.

Compounders have access to a diverse range of accelerators. To facilitate comprehension, these accelerators can be classified based on their chemical structure:

2. Classification of accelerators

- Thiazoles (Mercapto);
- Sulfenamides;
- Guanidines;
- Dithiocarbamates;
- Thiurams;
- Specialty Accelerators.

This discussion will primarily focus on four primary accelerator types: thiazoles, sulfenamides,Guanidines and Dithiocarbamates **[34]**.

Thiazole Class Accelerators

This category of accelerators includes commercially available and widely utilized ones like MBT, MBTS, and ZMBT. (NaMBT, the sodium salt of MBT, is also utilized in certain latex goods manufacturing applications) **[35]**.

Thiazoles serve as medium-fast primary accelerators with moderate processing safety. Widely employed in the rubber industry, thiazoles are crucial for producing a wide range of goods such as cycle tires and tubes, footwear, belts, hoses, and various molded and extruded products.

Thiazoles are activated by a combination of zinc oxide and stearic acid, resulting in a flat cure and vulcanizates with excellent resistance to reversion

The performance of thiazole accelerators in relation to curing characteristics can be outlined as follows:

1. Scorch Safety →Longer (MBT < MBTS < ZMBT)
2. Cure Rate → Faster (ZMBT < MBTS < MBT) **[35].**

- **Sulfenamide Class Accelerators**

Sulfenamide class accelerators like CBS, TBBS, MBS, and DCBS are highly favored in the tire industry for their combination of delayed action and faster cure rate during the vulcanization process of rubber compounds containing furnace blacks.

These accelerators result from the reaction of 2-Mercaptobenzothiazole with basic amines such as Cyclohexylamine, Tert-Butylamine, Morpholine, and Dicyclohexyl amine **[35]**.

They offer a wide range of crosslink densities, influenced by the type and dosage of accelerator used, and demonstrate a flat and reversion-resistant cure. Increasing the dosage of sulfenamide accelerator progressively enhances scorch delay, cure rate, and overall state of cure.

Vulcanizates containing sulfenamide accelerators typically possess an 'aminic' odor and demonstrate enhanced stress-strain properties, resilience, and flex-fatigue resistance compared to thiazoles.

Sulfenamide accelerators rapidly decompose in the presence of steam, making them preferred for manufacturing open steam-cured rubber products, resulting in faster cure onset for improved shape retention. However, this advantage is nullified in the case of hot air-cured products.

Sulfenamide accelerators are typically added to rubber compounds towards the end of the mixing cycle, when the temperature exceeds the melting point of the accelerator, to ensure proper dispersion. Excess heat generation is avoided to prevent sulfenamide accelerator decomposition. If the sulfenamide accelerator needs to be added at a later stage, incorporation in the form of a sulfenamide rubber master batch is recommended **[35].**

The function of sulfenamide accelerators can be summarized as follows:

1. Scorch safety →Longer (CBS < TBBS < MOR < DCBS}

2. Cure Rate →Faster (DCBS < MOR < CBS < TBBS)

Sulfenamide accelerators exhibit restricted storage stability, with degradation rate heavily impacted by factors like humidity and heat. Therefore, they should be stored strictly on a first in, first out basis, in a cool and dry environment (below 30°C and 60% RH (relative humidity)), away from acidic substances or fumes to mitigate rapid degradation **[35]**.

- **Guanidines**

The main varieties of guanidine accelerators include: accelerator DPG, DOTG, BG, TPG, etc..., for natural rubber and synthetic rubber. They initiate vulcanization gradually, ensuring operational safety with a moderate speed. Notably, they yield high degrees of vulcanization, resulting in elevated hardness and constant elongation stress **[36].**

Their prolonged promotion effect allows for extended vulcanization periods, making them suitable for thick rubber products like rollers. However, they are prone to aging, cracking, discoloration, and pollution, making them unsuitable for white products.

Due to their slow vulcanization speed and limited heat aging resistance, guanidine accelerators are typically used in combination with thiazoles and sulfenamides. This synergistic effect enhances activation, although they can be used alone in hard rubber products **[36]**.

- **Dithiocarbamates**

The dithiocarbamate class comprises accelerators like ZDMC, ZDEC, ZDBC, ZBDC, etc. These accelerators are extensively utilized as ultra-fast accelerators for NR latex-based compounds and are also employed as primary or secondary accelerators in most dry rubber-based sulfur-cured compounds. Activation of dithiocarbamate class accelerators necessitates Zinc oxide and Stearic acid, resulting in rapid vulcanization **[35]**.

Dithiocarbamates display minimal scorch safety, accelerate curing quickly, increase crosslink density, allowing rubber products to vulcanize rapidly at lower temperatures (115 -

120°C). However, their accelerated compounds have a narrow curing plateau, making them prone to rapid reversion from over-curing.

Dithiocarbamate accelerators, due to their restricted solubility in rubber compounds, often cause excess material to bloom on the surface of vulcanized products. However, they are non-staining and non-discoloring, even when exposed to light, making them suitable for producing transparent items.

In assessing the cure characteristics of dry rubber compounds, the effectiveness of different dithiocarbamate accelerators can be summarized as follows:

1. Scorch Safety →Longer (ZDMC < ZDEC < ZDBC)

2. Cure Rate →Faster (ZDBC = ZDEC = ZMDC) **[35].**

3. Selection of Accelerators for Rubber Compounds:

When choosing an accelerator system for producing a specific rubber product, several factors must be considered:

- Solubility in rubber (high solubility is necessary to prevent bloom and enhance dispersibility),
- Processing operations and their temperatures that the rubber compound will undergo,
- Desired scorch time for 'scorch-free' processing and storage stability,
- Cure rate requirements,
- Desired reversion characteristics (delayed reversion upon over-cure),
- Vulcanization method to be used (mode of heat transfer),
- Maximum vulcanization temperature available,
- Desired cure cycle at the available vulcanization method and temperature,
- Requirements of vulcanizate properties (to determine the type and state of cure),
- Effectiveness over a wide range of cure temperatures and suitability for use with different polymer blends,
- No adverse effects on other properties/materials (e.g., bonding, aging, adhesion, non-rubber components in the rubber product),
- No known health hazards during usage as a chemical or its decomposition products, and easy handling with dust-suppressed physical form.

- No adverse effects during the end-use of the rubber product (e.g., accelerators used in the manufacture of rubber articles intended for food contact/surgical use),
- Stability of the accelerator as a chemical (e.g., issues with the use of decomposed sulphenamide accelerators) **[35]**.

II.3.6. The evaluation criteria of tires

The evaluation of a tire depends on various factors such as rolling resistance, noise,abrasion and wet grip:

II.3.*6.1.* Rolling Resistance

The primary factor emanating from friction is commonly referred to as rolling resistance, signifying the energy needed to propel a tire along a road under a specified vehicle load. The rolling resistance coefficient is determined by dividing the drag force by the applied load. As a vehicle is in motion, energy dissipates in the engine, transmission, and vehicle aerodynamics. Notably, a consequential portion of energy loss occurs through the deflection of the tire. Consequently, tires, encompassing their compounds and structures, have become a focal point for curtailing fuel consumption in vehicles.

The rolling resistance force is typically expressed as a percentage of the vertical load, hovering around 1% for most tires on smooth roads. Michelin's introduction of the silica-filled 'green tire' in 1992 marked a significant milestone, promising a potential fuel saving of approximately 0.5 liters per 100 km of travel. This event spurred a consistent shift towards tires labeled as 'Green,' 'Energy,' 'Fuel Saver,' etc. **[37]**.

Rolling resistance values for car tires have now dipped below 1%, with truck tires featuring natural rubber-based treads consistently maintaining levels around 0.5%.

II.3.*6.2. *Noise

Environmental noise pollution is gaining increased attention from advocacy groups and legislative bodies. In 2001, a European Parliament directive (2001/43/EC) established limits for coast-by noise produced by tires on a smooth road surface as per ISO10844, 1994. Although mechanisms for noise generation and transmission have been extensively studied, the sound pressure level primarily hinges on how the tire tread pattern interacts with the road surface to eliminate water. This process involves rubber impacting the road, air escaping from sealed chambers between the pattern and road surface texture, and the elastic recovery of tread blocks as they rebound from the contact area, collectively contributing to airborne and structural noise. Designing tires with reduced noise involves considering factors such as randomized, open tread patterns, tire structural stiffness, and compound modulus or damping. However, noise reduction should not compromise tire safety, a crucial factor addressed in the new noise directive.

Conversely, the characteristics of road surfaces exert a more pronounced influence on noise generation, as well as grip and rolling resistance **[38].**

Roads exhibit substantial variability in texture, roughness, and overall condition, resulting in pass-by noise differences that exceed those observed between various tire patterns. The notion of porous road surfaces not only presents advantages in noise reduction but also enhances water drainage. This improvement can be advantageous for both enhancing wet grip and suppressing spray. Despite these benefits, porous road surfaces have garnered only limited acceptance in many countries thus far.

II.3.6.3. Abrasion

Rubber abrasion is fundamentally a mechanical tearing process that correlates with the rate of cut growth, determined by the dissipation of tearing energy in the contact area between rubber and the track.

This process inevitably leads to significant temperature increases at stress concentration points, where mechanical detachment of abraded particles is most likely to occur. Such thermal escalation triggers important secondary mechanisms, such as thermal degradation and oxidation, which can decisively impact a compound's performance relative to a reference, surpassing the influence of mechanical properties.

To assess abrasion performance across various conditions, a laboratory method utilizing the LAT 100 test equipment has been devised. This method evaluates energy dissipation and slip speeds in the contact area of a rubber sample wheel rotating under slip. The resulting equations can be employed to directly test the correlation between laboratory and road test results, which is generally favorable within a limited range. Alternatively, they can be incorporated into a road test simulation program, providing compound ratings and tire life predictions.

However, these outcomes are notably sensitive to the chosen test conditions, reflecting the complexities of real-world scenarios **[39]**.

II.3.6.4. Wet grip

Since 2012, the Korean and EU governments have implemented a tire labeling system, mandating all tires sold in Korea to bear a label showcasing information on two key performance criteria: rolling resistance and wet grip.

The grading of a tire's fuel efficiency is determined by its rolling resistance, while the wet grip rating indicates its braking safety. To ensure fair comparisons among tires from different suppliers, wet grip measurements must be reproducible, yielding consistent results across different laboratories testing the same tires.

Achieving good reproducibility not only promotes fairness but also prevents market surveillance authorities from obtaining conflicting results when testing identical tires. Presently, a standardized laboratory alignment procedure for wet grip measurements is lacking, leading to variations in test results across global laboratories. A proposed procedure aims to enhance the reproducibility of wet grip testing, prompting five laboratory alignment tests between KATECH and five other global test laboratories to assess the effectiveness of this new approach **[40]**.

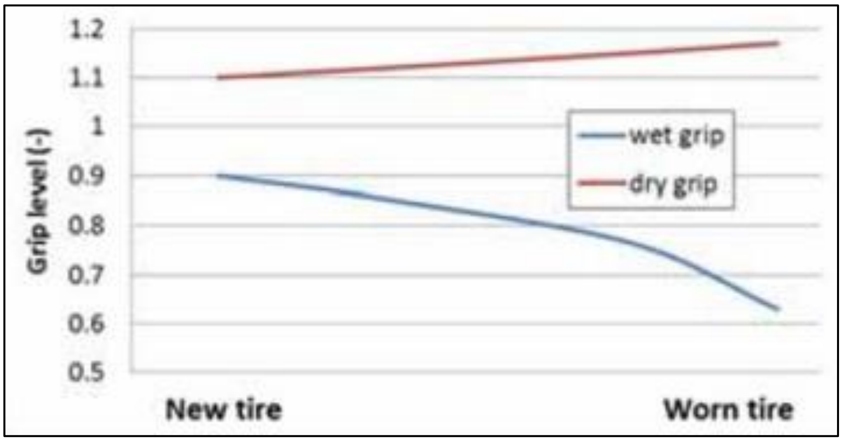


Figure II.12**: Evolution of grip through tire life (representative average value)* ***[41].

II.3.7. Impact on the environment and health

When left unattended, tires can pose significant risks to both the environment and public health due to their potential negative impacts:

II.3.7.1. Environmental concerns

Disposal of waste tire rubber has become a major environmental issue in all parts of the world. Every year millions of tires are discarded, thrown away or buried all over the world, representing a very serious threat to the ecology. It is estimated that every year almost 1000 million tires end their useful life and more than 50% are discarded without any treatment. Land filling with tires occupies lot of space, and these spaces provide the potential sites for the breeding of rodents **[42].**

Figure II.13: *Tire pollution.*

II.3.7.2. Health concerns

Initially, discarded or dumped used tires become highly resistant waste that pollutes the air and poses health risks to individuals.

Moreover, when these tires are left stacked outdoors, they create ideal habitats for rats and mosquitoes. These pests can cause significant health issues for local populations, with mosquitoes, for example, breeding in stagnant water collected within tires and potentially spreading diseases like chikungunya.

Additionally, the heat-absorbing nature of black tires can create an environment conducive to mosquito breeding, further exacerbating health concerns.

Lastly, chemical compounds such as carbon black, which is carcinogenic to both humans and animals, add to the health risks associated with tire pollution. Stressing the importance of tire recycling is crucial not only for environmental preservation but also for safeguarding public health by mitigating the potential spread of diseases **[42]**.

CHAPTER III: Materials and Methods

III.1. Introduction

To obtain a good tire meeting the standards, we conduct a characterization of the properties during the production before and after the vulcanization as well as the finished product (the tire) through mechanical and physical tests. These tests are carried out at the quality control laboratory at IRIS TYRES.

In this chapter, we will explain in detail the methodology used to conduct our study, in addition to the materials and tools necessary for data collection and analysis. A precise description of our methodological approach is essential to ensure the transparency of our results. We will also provide the conceptual framework that forms the basis of our research, providing a theoretical context for interpreting our conclusions.

III.2. Preparation of the samples

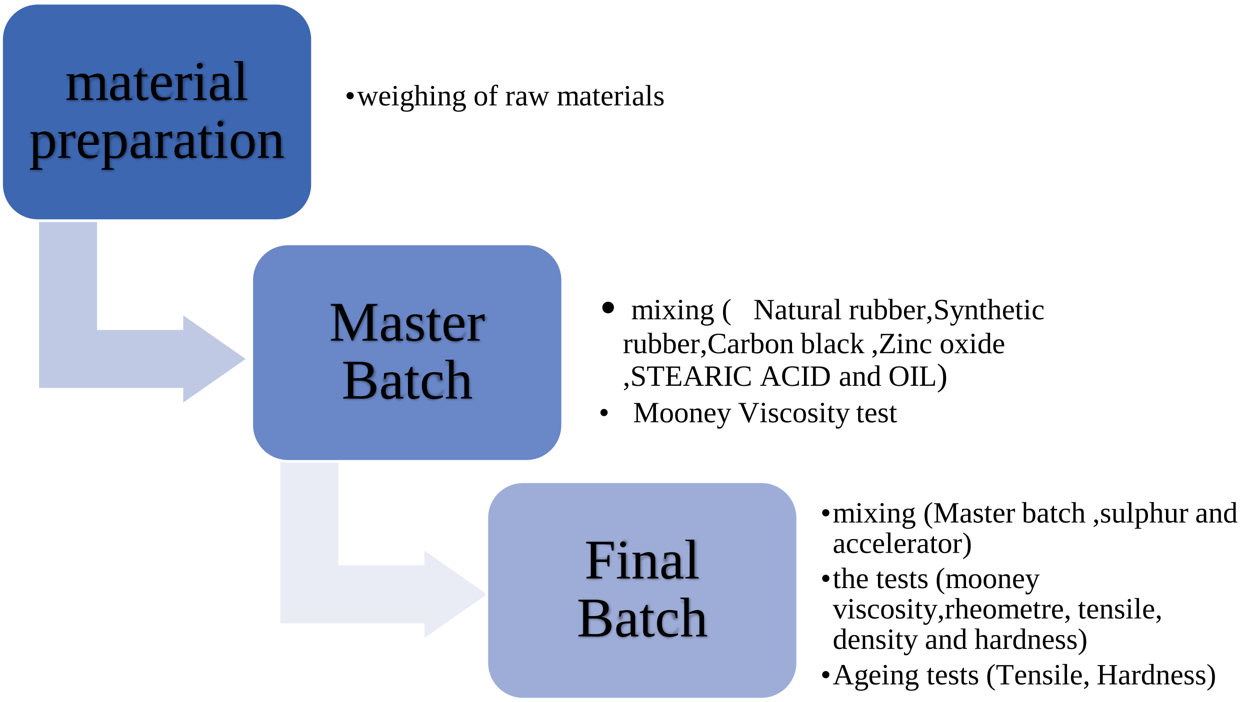
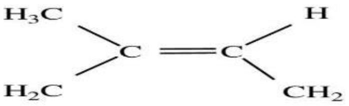
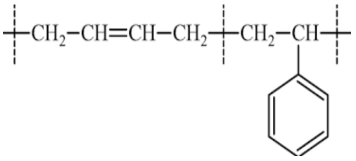
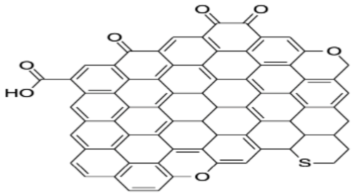
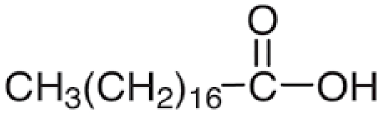
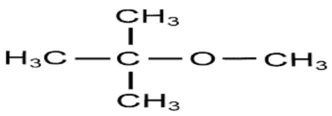
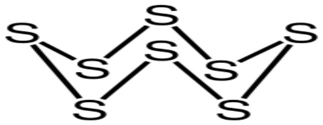


Figure III.1*: Explanatory diagram of operating procedure.*

Table III .1*: Recipe Composition.*

	Version 01 (CBS)	**Version 02 (TBBS)**	**Version 03 (DCBS)**	**Version 04 (DPG)**	**Version 05 (ZBEC)**
Natural rubber (TSR 10)	65	65	65	65	65
Synthetic rubber (ESBR 1502)	35	35	35	35	35
Carbon black (CB-N375)	55	55	55	55	55
Zinc oxide (ZnO 99)	5	5	5	5	5
STEARIC ACID	2	2	2	2	2
TDAE OIL	4	4	4	4	4
SULPHUR	2.5	2.5	2.5	2.5	2.5
CBS	1.9	-	-	-	-
TBBS	-	1.9	-	-	-
DCBS	-	-	1.9	-	-
DPG	-	-	-	1.9	-
ZBEC	-	-	-	-	1.9
Total quantity	170.4 phr	170.4 phr	170.4 phr	170.4 phr	170.4 phr

Table III.2: *Chemical structure and properties of each product.*

	Chemical formula	viscosity	density(g/cm³)	appearance	color
Natural rubber (TSR 10)		**50/70 (MU) at 100 C⁰**	**0.94/0.96**	**Solid**	**Light yellow**
Synthetic rubber (ESBR 1502)		**46/58 (MU) at 100 C⁰**	**0.92/0.94**	**solid**	**black**
Carbon black (CB-N375)			**0.35/0.38**	**Fine powder**	**black**
Zinc oxide (ZnO 99)	$O=Zn$		**5.47/5.68**	**Fine powder**	**white**
STEARIC ACID	 $CH_3(CH_2)_{16}-C(=O)-OH$		**0.84**	**granules**	**white**
TDAE OIL	 $H_3C-C(CH_3)_2-O-CH_3$	**70/140 (cSt) at 40 C⁰**	**0.87/0.92**	**liquid**	**Dark brown**
SULPHR			**2.07**	**Fine powder**	**yellow**

Note :

We prepare the recipe five times, using a different type of accelerator each time altering the accelerator type with each repetition.

III.2.1. Cleaning Batch

After preparing the five recipes, we initiate the mixing process:

Initially, we operate the mixer while gradually increasing its temperature to 50 degrees Celsius. Then, we introduce natural rubber to cleanse the machine of impurities.

III.2.2. Master Batch

- Following the cleaning phase, we proceed to create our samples with various accelerators to commence the master batch.
- We commence the mixing process by combining a portion of natural rubber with synthetic rubber, along with half of the prescribed amount of carbon black. Subsequently, we incorporate chemical additives such as stearic acid and zinc oxide (ZnO).
- After a designated duration of mixing, we introduce the remaining portion of carbon black, dividing its quantity to ensure thorough blending.
- Once the mixer reaches a temperature of 100 degrees Celsius, we introduce the oil.
- Upon completion of the mixing process, we transfer the final product into a cylindrical mixer to shape it into sheets for subsequent testing.
- A portion of these sheets is then use to perform the Mooney viscosity test to determine the rubber's viscosity.
- Upon completion of the second step, we proceed to the subsequent step, wherein we:

III.2.3. Final Batch

- We start the mixer(**V=1.78 l, RPM =100 t/min**), and when the temperature reaches 42 degrees Celsius, we add a specified amount of the mixture obtained from the previous process (master batch), along with the required quantity of sulfur and a selected accelerator (varied for each test).

***Figure III.2**: TECHNOLAB mixer (intermix IM 1.5E).*

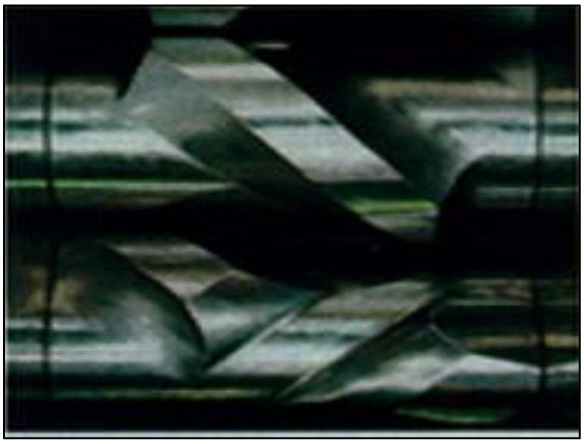


***Figure III.3**: intermeshing rotor.*

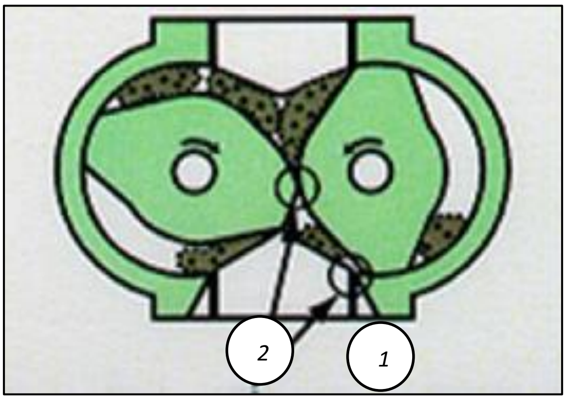


***Figure III.4**: mixing mechanism (1) Between rotor and chamber Wall, (2) Between rotor and rotor).*

- When the mixer's temperature reaches 93 degrees Celsius, the operation terminates automatically.

- Subsequently, we transfer the resulting mixture to a mixer mill (**RPM= 33.6 t/min and power of the motor =5.5 KW**).

Figure III.5**: mixer mill **[43].

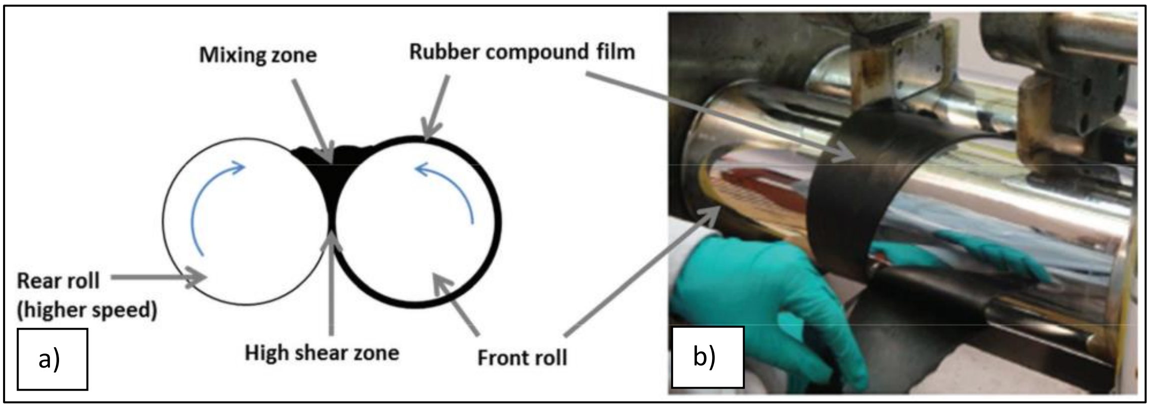


***Figure III.6**: a) Side and b) Front view of the two-roll mill used for incorporation of vulcanization agents.*

- Next, we obtain rubber sheets and cut them into squares. These samples are then left to rest in ambient air for 30 minutes to reduce their temperature and allow them to relax.

Figure III.7:*sample before vulcanization.*

- Following this, we insert the samples into a curing press (heating at rate 15 K^0 /min and its pressure 597 KN) and apply a force of 100 bars at a temperature of 150 degrees Celsius. This initiates the vulcanization process, which takes a specific duration (Tc 90), derived from the moving die rheometer test, indicating the time at which 90% of the vulcanization process is complete.

Figure III.8*: curing press.*

Note:

time in the curing press = 1.8 ×Tc90+5= … min

Figure III.9: *vulcanized samples.*

- After preparing the samples, we subject them to testing at three stages: immediately after removal from the oven, after three days, and after seven days. This allows for the evaluation of sample properties at various aging stages.

Figure III.10: *ageing machine.*

Finally, we conduct the following tests on these samples:

- Moving Die Rheometer
- Mooney Viscosity
- Tensile Strength
- Density
- Hardness

III.3. Quality control tests

III.3.1. Mooney Viscosity

The Mooney Viscosity test stands as the foremost method for characterizing rubber materials. As delineated in international standards (ISO 289-1).

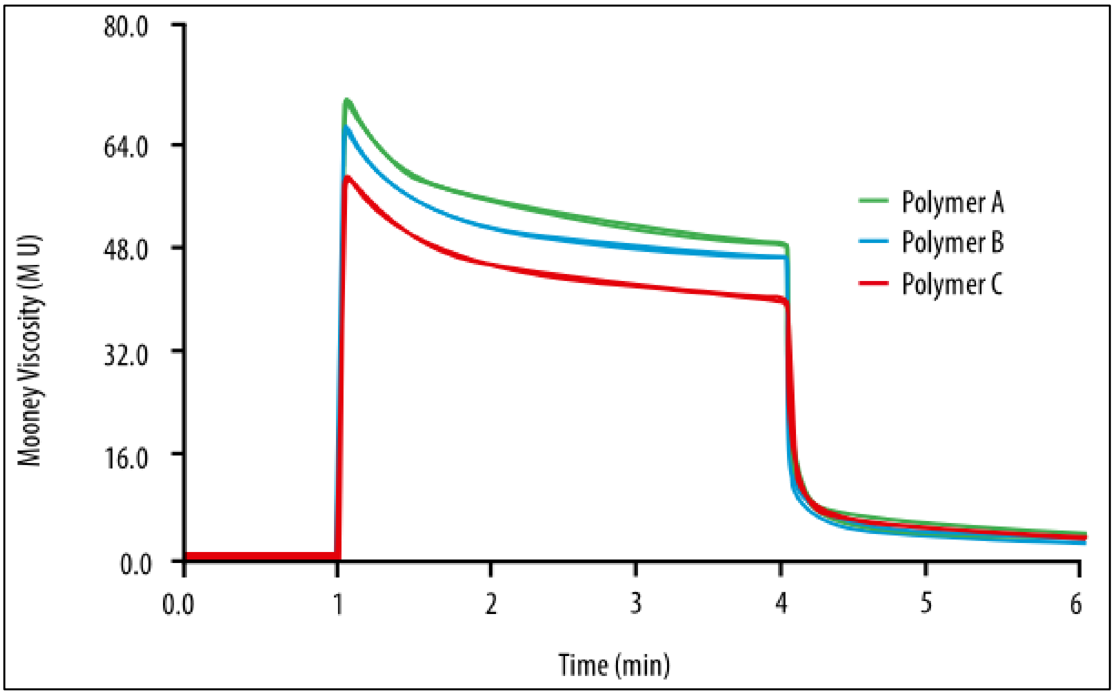


***Figure III.11**: example of a Mooney viscosity test curve.*

III.3.1.1. Principle

The torque required to rotate a metal disc within a cylindrical chamber made from mating dies filled with rubber is measured under specific conditions. This resistance from the rubber is expressed in arbitrary units as the Mooney viscosity of the test piece.

III.3.1.2. Preparation of test piece

The test specimen must be prepared following ISO 1795 and the relevant material standard for the rubber. The specimen should be taken from a compound prepared according to ISO 2393 and the relevant material standard for the rubber. Before testing, the specimen should be allowed to rest at standard laboratory temperature for at least 30 minutes. Testing should start no later than 24 hours after homogenization. The Mooney viscosity is influenced by how the rubber is prepared and stored. Therefore, it's essential to strictly adhere to the prescribed procedure outlined in methods for assessing a specific rubber. The test specimen consists of two rubber discs, each approximately 50 mm in diameter and 6 mm thick (20g), enough to fill the viscometer's die cavity completely. The rubber discs should be as air-free as possible to prevent air trapping against the rotor and die surfaces. A hole is made in the center of one disc to insert the rotor shaft.

***Figure III.12**: constant volume sample cutter for Mooney viscometers.*

***Figure III.13**: Mooney viscosity test samples.*

Temperature and duration of test

Conduct the test at a temperature of 100°C ± 0.5°C for 6 minutes (1minpreheat,4 min test and 1 min relaxation)

III.3.1.3. Procedure

Place the disc of the test piece in the center of the rotor and promptly close the dies. If necessary, a heat-stable film (e.g., polyester, 0.02 mm to 0.03 mm thick) can be placed between the rubber and die surfaces to aid in the removal of low-viscosity or sticky materials after testing.

Record the time when the dies are closed and allow the rubber to preheat for 1 minute. Start the rotor, with the running time specified. viscosity is continuously recorded.

Temperature gradients and heat transfer rates vary between viscometers, especially with different heating methods. Therefore, values obtained with different viscometers are expected to be more comparable after the rubber reaches the test temperature, usually within 10 minutes after closing the die cavity.

Figure III.14*: Mooney viscometer machine* ***[44].***

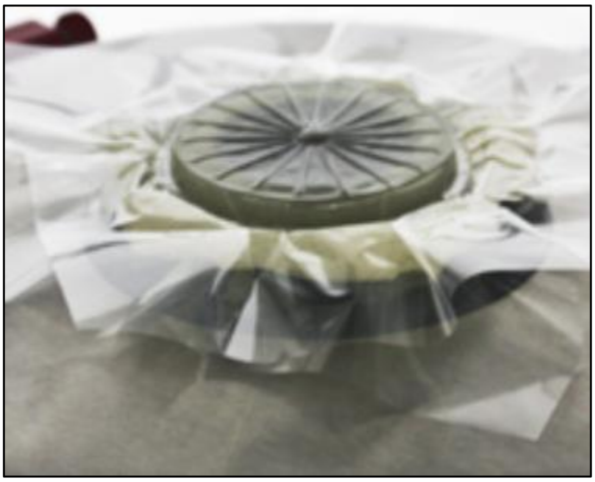


Figure III.15*: Rubber polymer sample after Mooney viscosity testing.*

III.3.2. Rheometer

III.3.2.1. Principle

The properties of a rubber compound undergo changes throughout the vulcanization process, which can be understood by monitoring properties over time and temperature. This is commonly done using instruments called curemeters, which apply cyclic stress or strain to a test piece while measuring the resulting strain or force. Typically, this test is conducted at a constant pre-set temperature ($170C^0$ /60min), with stiffness measurements continuously recorded over time.

Vulcanization characteristics can be gleaned from stiffness-time curves without adjustments, as depicted in Figure III.14.

Minimum force or torque	F_L or M_L
Force or torque at a specified time t	F_t or M_t
Scorch time (time to incipient cure= volcanic eruption)	T_{sx}
Time to a percentage y of full cure from minimum force or torque	Tc (y)
Plateau force or torque	F_{HF} or M_{HF}
Maximum force or torque (reverting cure)	F_{HR} or M_{HR}
Force or torque value attained after a specified time (marching-modulus cure)	F_H or M_H

The minimum force or torque F_L or M_L characterizes the stiffness of the unvulcanized compound at the curing temperature.

The scorch time (T_{sx}), representing the time to incipient cure, serves as an indicator of the processing safety of the compound.

The time (Tc) and the associated forces or torques (y) provide insights into the curing progression. Optimum cure is typically identified as Tc (90), denoting the time at which 90% of the curing is achieved.

Additionally, the peak force or torque signifies the stiffness of the vulcanized rubber at the curing temperature.

NOTE: The term F denotes force and the term M denotes torque.

The scorch time T_{sx} is the time required for the force or torque to increase by x units from F_L. It might be convenient to define the scorch as a given percentage, e.g. 2% or 5% of the total cure.

The time to a percentage of full cure from minimum force, t'c(y), is the time taken for the force (or torque) to reach:

-Tc (10) is a measure of the early stages of cure.

-Tc (90) is often used as an indicator of optimum press cure.

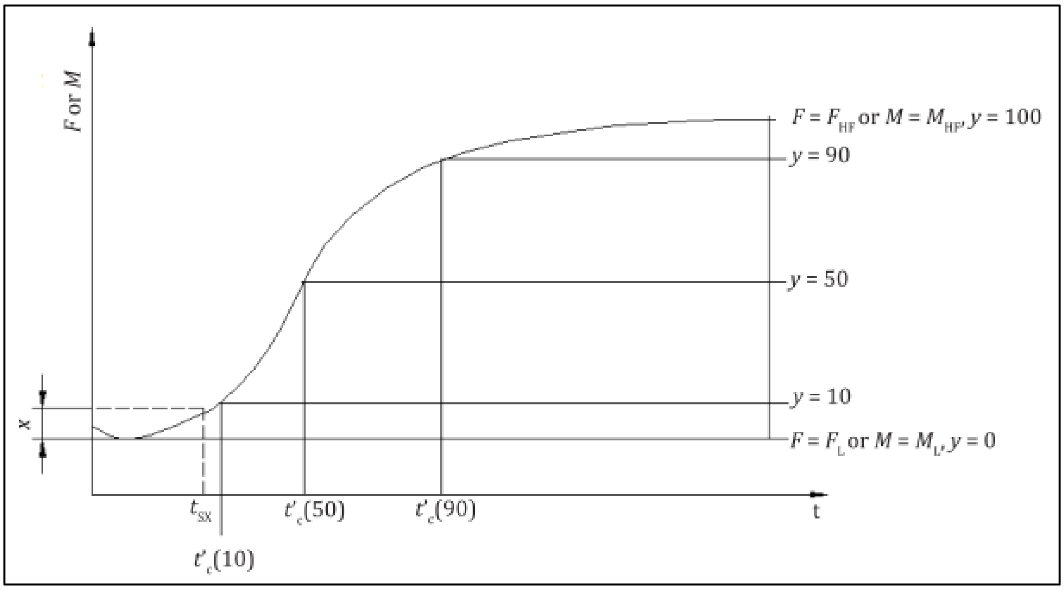


Figure III.16: Typical vulcanization curve and method of evaluation.

Three types of curemeters have found widespread use:

- oscillating-disc;
- reciprocating-paddle;
- rotorless.

Other geometries are possible, for example with a vibrating probe or needle.

Figure III.17**: Rheometer machine (oscillating-disc) **[45].

Figure III.18**: Test dies and die closing system **[45].

III.3.2.2. Procedure

A rubber sample (5g) is enclosed within a die cavity, and is kept at a heightened temperature. This cavity is created by two dies, one of which undergoes slight rotary movement (angle degree 0.50^0). This action produces a sinusoidal torsional strain in the sample and generates a sinusoidal shear torque, the magnitude of which is determined by the stiffness (shear modulus) of the rubber material.

As vulcanization progresses, the stiffness of the rubber sample gradually increases. The test concludes when the torque recorded reaches either a steady state or maximum value, or when a set period of time has passed (Figure III.17). A graph depicting the torque at maximum strain during one phase of the oscillation cycle is continuously plotted over time

Figure III.19: *Constant volume sample cutter for moving die rheometer.*

Figure III.20: *Rheometer test sample.*

III.3.3. Tensile

III.3.3.1. Principle

During tensile testing, standard specimens, such as the dumbbells, are gradually stretched using a constant traversal rate in the testing apparatus. Force and elongation measurements are recorded at intervals as the specimen undergoes continuous stretching until it fractures.

Figure III.21: *Traction machine* ***[46].***

III.3.3.2. Test pieces

Miniature test specimens often yield slightly different, typically higher, measurements for tensile strength and elongation at break compared to larger specimens. The available test options encompass five types, namely types 1, 2, 3, 4, and 1A (see Table III.3). Results obtained for a specific material are prone to variation based on the type of test specimen employed. Hence, comparisons between results for different materials should only be made when utilizing identical test specimens. Moreover, if the preparation of test specimens involves buffing or adjusting thickness, it could impact the results.

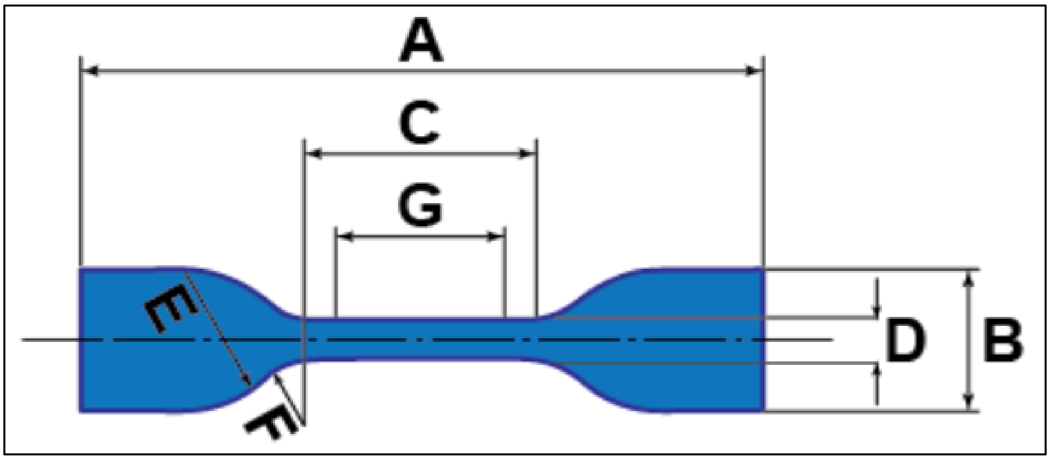


Figure III.22*: Dumb-bell test piece example.*

***Table III.3**: Dimensions of dies for dumb-bell test pieces.*

Dimension (mm)	Type 1	Type 1A	Type 2	Type 3	Type 4
A Overall length (minimum)	115	100	75	50	35
B Width of ends	25 ± 1	25 ± 1	12.5 ± 1	8.5 ± 0.5	6 ± 0.5
C Length of narrow portion	33 ± 2	21 ± 1	25 ± 1	16 ± 1	12 ± 0.5
D Width of narrow portion	6.2 ± 0.2	5 ± 0.1	4 ± 0.1	4 ± 0.1	2 ± 0.1
E Transition radius outside	14 ± 1	11 ± 1	8 ± 0.5	7.5 ± 0.5	3 ± 0.1
F Transition radius inside	25 ± 2	25 ± 2	12.5 ± 1	10 ± 0.5	3 ± 0.1
G Test “gauge” length	25	20	20	10	10

III.3.3.3. Specimen cutters

Die cutters can be sourced from various providers, but they must adhere to ISO 23529 standards, which specify the geometry and precision of the cutting head.

***Figure III.23**: cutter for tensile machine.*

***Figure III.24**: Tensile test sample.*

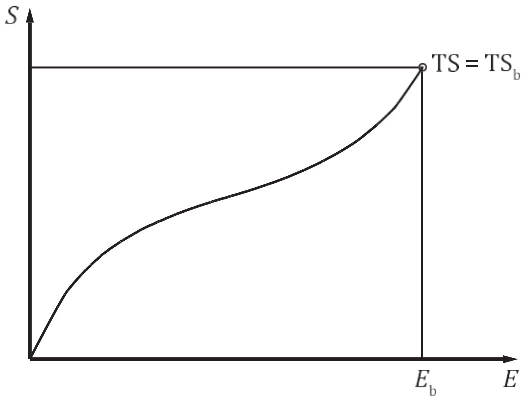
III.3.3.4. Procedure

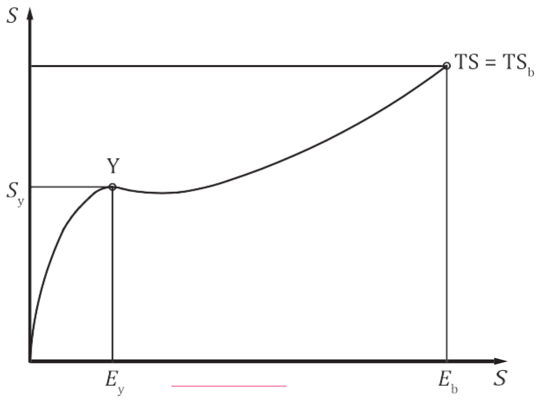
Determination of Tensile Stress, Tensile Strength and Yield Point

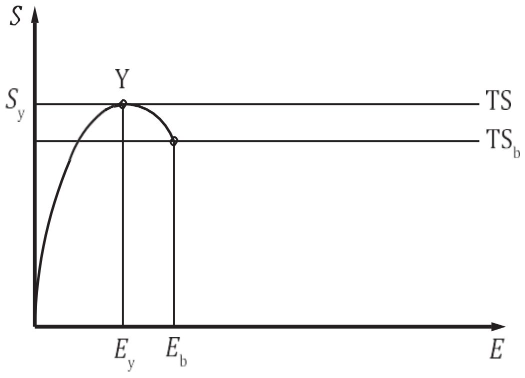
Place the dumbbell or straight specimen securely within the grips of the testing machine, ensuring careful adjustment for symmetrical alignment. This adjustment aims to evenly distribute tension across the cross-section of the specimen. This avoids complications that prevent the maximum strength of the material from being evaluated. The rate of grip separation shall be 500 ± 50 mm/min.

Commence operation of the machine and observe the distance between the benchmark points, being mindful to prevent any parallax errors. Record the force at the elongation specified for the test and at the time of rupture.

At rupture, measure and record the elongation to the nearest 10 %.







Key

E: elongation

Eb: elongation at break

Ey: elongation at yield

Sy: stress at yield

TS: tensile strength

TSb: tensile strength at break

Y: yield point

S: stress

Figure III.25: *Illustration of tensile terms.*

III.3.4. Durometer Hardness (Shore hardness)

III.3.4.1. Principle

Durometer Hardness is used to determine the relative hardness of soft materials, typically plastics or rubbers. This examination gauges the depth of penetration made by a designated indenter into the material, under specified conditions of force and time. The resultant hardness measurement commonly serves to delineate or specify a particular rigidity of elastomers.

Figure III.26: *Durometer machine* ***[47].***

TABLE. III.4**: Durometer Selection: Typical Uses* ***[48].

Type (scale)	Typical examples of Materials Tested	Durometer Hardness (Typical Uses)
A	Soft vulcanized rubber, natural rubber, flexible polyacrylics, nitriles, thermoplastic elastomers, and thermosets, wax, felt, and leathers.	20-90 A
B	Moderately hard rubber, , paper products, thermoplastic elastomers and fibrous materials	Above 90 A Below 20 D
C	Medium-hard rubber, thermoplastic elastomers, medium-hard plastics, and thermoplastics	Above 90 B Below 20 D
D	Hard rubber, thermoplastic elastomers, harder plastics, and rigid thermoplastics	Above 90 A
DO	Moderately hard rubber, thermoplastic elastomers, and very dense textile windings	Above 90 C Below 20 D
M	thin, irregularly shaped rubber, thermoplastic elastomer, and plastic specimens	20-85 A
O	Soft rubber, , very soft plastics and thermoplastic elastomers, thermoplastics, medium-density textile windings	Below 20 DO
OO	Extremely soft rubber, thermoplastic elastomers, extremely soft plastics and thermoplastics, sponge, foams, low-density textile windings, human and animal tissue	Below 20 O

The Durometer selection guide is intended to help choose the appropriate durometer type for different applications.

It is widely recognized that durometer hardness readings below 20 and above 90 may be unreliable. In such cases, it's advisable to use the next lower or higher durometer scale.

III.3.4.2. Procedure [48].

To operate the Type 3 Operating Stand required for Type M durometers, several steps should be followed:

- Minimize exposure of the instrument to adverse environmental conditions or factors that may affect test results.
- Adjust the presser foot to ensure table parallelism each time the support table is moved.
- Set the vertical distance from the presser foot to the test specimen contact surface to 25.4 ± 2.5 mm.
- Position the specimen on the support table.
- Actuate the release lever or electromechanical device to apply the presser foot to the specimen in a controlled manner, ensuring parallel contact without shock and with sufficient force.
- Use an operating stand that applies mass at a controlled descent rate without shock for Type M durometers.
- Record the maximum indicated reading once the presser foot makes contact with the specimen, following standard time intervals or as agreed upon.
- Record and report the indicated reading accordingly.
- Make five hardness determinations at different specimen positions, at least 6.0 mm apart (0.80 mm) apart for Type M), and calculate the arithmetic mean or median. Reporting should adhere to specified protocols.

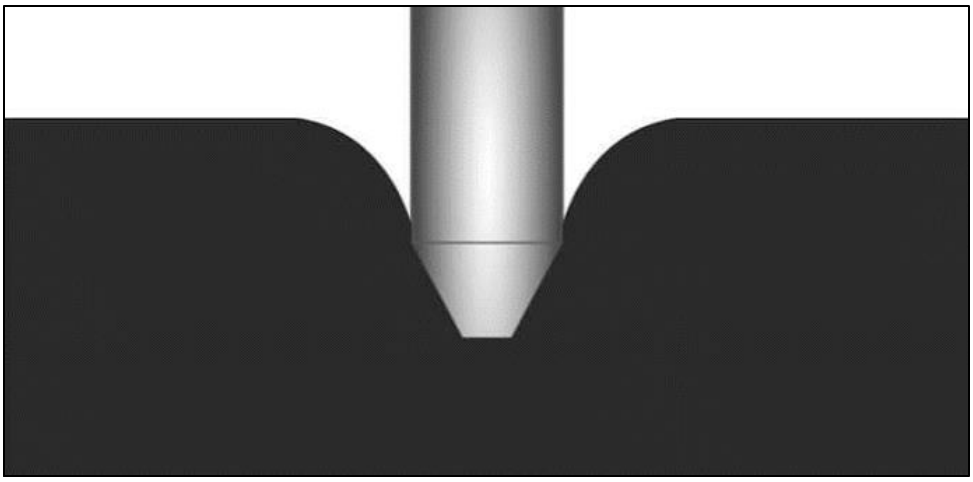


Figure III.27: *Hardness test application.*

III.3.5. Density

III.3.5.1. Principle

The weight of the sample and the weight of water equivalent to its volume are measured using a balance with a pan straddle. When the sample is submerged in water, its apparent weight decreases by the weight of the water it displaces, which is equal to its own volume.

Figure III.28*: density meter.*

III.3.5.2. Test piece

The test specimen must be made of rubber with smooth, crack-free surfaces, and devoid of any dust, weighing at least 2.5 grams. The specimen should be shaped to allow for cutting into appropriate pieces.

A minimum of two test pieces shall be made.

For all testing purposes a minimum time lapse of 16 hours between the formation of the specimen and its testing is required.

Samples and test pieces must be shielded from direct sunlight from the moment of vulcanization until testing.

The test should typically be conducted at a standard laboratory temperature, either 23°C ± 2°C or 27°C ± 2°C, with consistency in temperature maintained throughout a single test or a series of tests to ensure comparability.

III.3.5.3. Procedure

Hang the test piece from the hook on the balance, ensuring that the bottom of the test piece is approximately 25 mm above the straddle.

Measure the test piece's weight to the closest milligram while it's in the air. Conduct another weighing with the test piece submerged in freshly boiled and then cooled distilled or deionized water, ensuring the water is at a standard laboratory temperature (either 23 °C ± 2 °C or 27 °C ± 2 °C). Place the beaker containing the water and the test piece on the straddle. Eliminate any air bubbles clinging to the test piece and record its weight to the nearest milligram. Observe for a few moments to confirm that the reading remains stable and isn't influenced by convection currents causing gradual drift.

If this procedure is applied to rubber with a density lower than 1 Mg/m^3, a sinker becomes essential; an additional weighing of the sinker alone submerged in water becomes necessary. Alternatively, a liquid with a density different from water, which doesn't interact with the rubber, can replace the water. In this scenario, Formula (1) need modification, replacing the density of water with the density of the substituted liquid.

The density, ρ, expressed in megagrams per cubic metre, is given by Formula (1):

$$\rho = \rho_w \frac{m_1}{m_1 - m_2} \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where

ρ_w : is the density of water;

m_1 : is the mass of the rubber, determined by weighing in air;

m_2 : is the mass of the rubber less the mass of an equal volume of water, determined by weighing in water, both at standard laboratory temperature.

The main potential sources of error include:

a) Air bubbles clinging to the surfaces of the test piece while weighing in water.
b) Surface tension impacts.
c) Convection currents within the water where the test piece is suspended. To mitigate these, ensure that the water and air temperature within the balance case are equalized.

To reduce the likelihood of air bubbles sticking to the test piece, you can either introduce a small amount (approximately 1 part in 10,000) of a surface-active substance like detergent to the distilled water, or briefly immerse the test piece in a compatible liquid, such as methyl alcohol or denatured spirit, that mixes well with water and has minimal impact on rubber (such as swelling or leaching). If opting for the latter approach, take care to minimize any alcohol carry-over.

CHAPTER IV: Results and discussion

IV.1.1. Mooney Viscosity

Mooney viscosity, is an important measure in the rubber industry because it provides an indication of the viscosity and processability of the rubber compound. The viscosity of different formulations (versions) is summarized in table IV.1 and presented in Figure IV.1. In master batch, for all versions, it is observed that the Mooney viscosity is constant, the values are around 77 MU. However, in final batch the data indicated that the viscosity of samples depends on the nature of accelerators.

Table IV.1: Mooney viscosity measurements for the five different versions.

versions	**Version 01 (CBS)**	**Version 02 (TBBS)**	**Version 03 (DCBS)**	**Version 04 (DPG)**	**Version 05 (ZBEC)**
Mooney Viscosity (Master batch) (MU)	77.76				
Mooney Viscosity (Final batch) (MU)	55.95	53.95	56.01	55.27	54.79

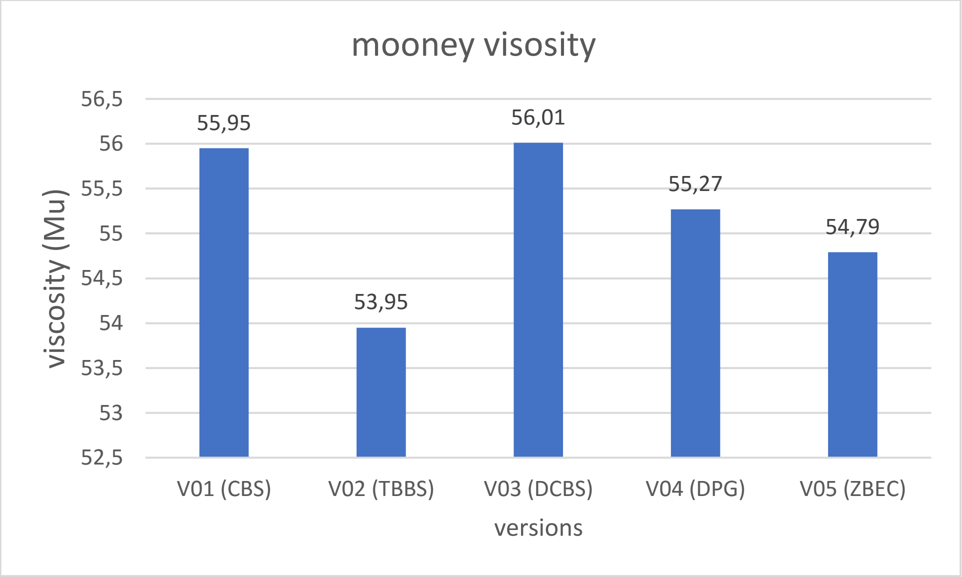


Figure IV.1: *Mooney viscosity comparison between different versions.*

This figure illustrates the Mooney viscosity for both the Master Batch and Final Batch across different versions. The Master Batch viscosity remains constant at around 77 MU, indicating uniform viscosity before the addition of accelerators. In the Final Batch, the viscosity varies: TBBS (53.95 MU) shows the lowest final viscosity, indicating the best processability, followed by ZBEC (54.79 MU), DPG (55.27 MU), CBS (55.95 MU), and DCBS (56.01 MU).

Interpretation of Mooney Viscosity Values:

- **Version 01 (CBS)**

Mooney Viscosity = 55.95 MU

This value indicates that the compound is relatively easy to work with and mold. A Mooney viscosity around this value is typically desired to achieve a good balance between processability and mechanical performance of the rubber.

- **Version 02 (TBBS)**

Mooney Viscosity = 53.95 MU

A slightly lower viscosity than the version with CBS, suggesting that this compound is a bit easier to process. The decrease in viscosity can lead to better dispersion of ingredients and more efficient processing in some manufacturing procedures.

- **Version 03 (DCBS)**

Mooney Viscosity= 56.01MU

Slightly higher than the version with CBS, indicating that this compound might be a bit more challenging to handle. This can affect the ease of mixing and molding, but it may also result in slightly different mechanical properties.

- **Version 04 (DPG)**

Mooney Viscosity=55.27MU

This value is very close to that of the CBS version, indicating similar processability. DPG as an accelerator does not have a major effect on viscosity compared to the other accelerators tested.

- **Version 05 (ZBEC)**

Mooney Viscosity= 54.79MU

A slightly lower viscosity than the CBS version, suggesting that this compound is slightly easier to work with. ZBEC seems to provide a good balance between processability and final properties.

NOTE:

- **Processability:** Lower Mooney viscosity values generally indicate better processability of the rubber compound, facilitating mixing, molding, and extrusion.
- **Mechanical Properties:** Variations in viscosity can also influence the mechanical properties of the final product. For example, higher viscosity can sometimes correlate with better resistance to deformation under load.
- **Choice of Accelerator:** The choice of accelerator (CBS, TBBS, DCBS, DPG, ZBEC) affects not only the vulcanization speed and final properties of the rubber but also its Mooney viscosity. The measured values indicate that all the accelerators used provide viscosity within a reasonable range for tire applications.

IV.1.2. Moving die rheometer

a) Maximum torque (S’ Max)

The Moving Die Rheometer (MDR) test measures the curing characteristics of rubber compounds, providing important information about the maximum torque (S' Max) during vulcanization. This torque value (measured in deci Newton-meters, dN.m) reflects the stiffness and crosslink density of the cured rubber. Higher torque values generally indicate higher stiffness and crosslink density, which can correlate with better mechanical properties like strength and durability.

Moving Die Rheometer (MDR) characteristics provide crucial insights into the curing behavior of rubber compounds, including parameters such as maximum torque (S' Max), scorch time (Ts2), and curing time (Tc90). These properties are summarized in Table IV.2 and presented in Figures IV.2, IV.3 and IV.4. In the MDR tests, it is observed that the maximum torque varies significantly across different versions, indicating differences in mechanical strength and cross-link density. The scorch time and curing time also vary, reflecting the impact of different accelerators on the processing safety margin and the time required for complete curing. These variations underscore the importance of choosing the right accelerator to optimize both processing and final product properties.

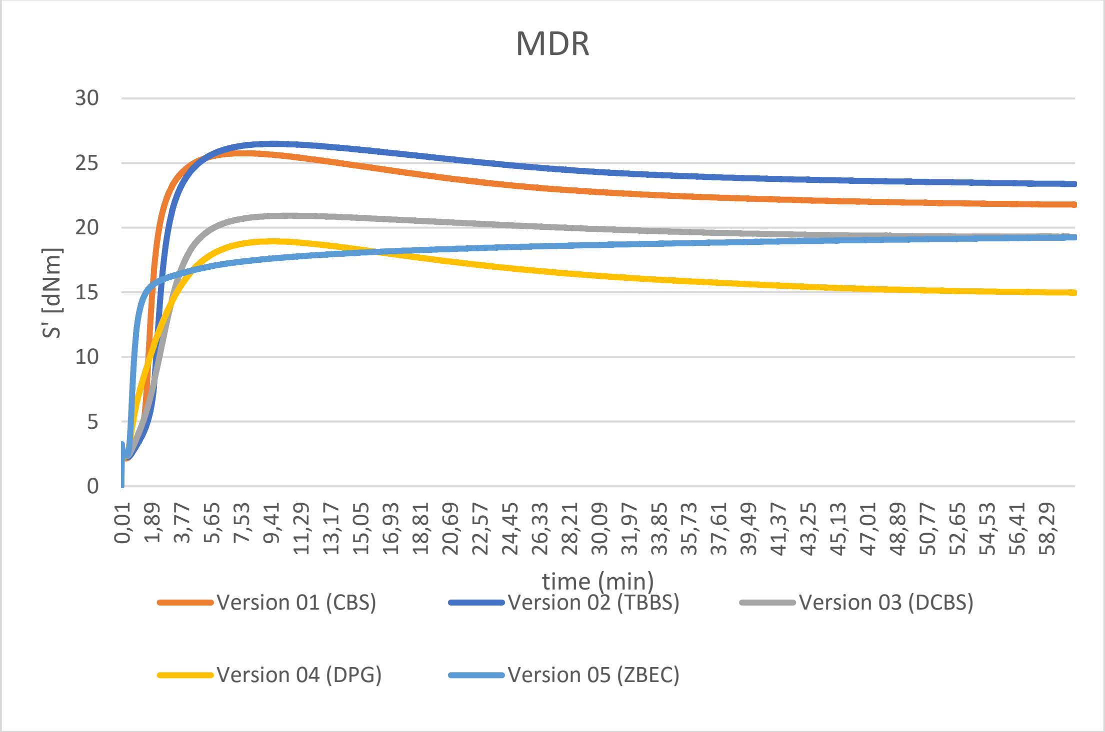


Figure IV.2: *Moving die rheometer (MDR) curve of s' for different versions.*

Table IV.2: *Moving Die Rheometer (MDR) Characteristics for Different Versions.*

Versions	**Version 01 (CBS)**	**Version02 (TBBS)**	**Version 03 (DCBS)**	**Version 04 (DPG)**	**Version 05 (ZBEC)**
S' Max (dN.m)	25.76	26.48	20.92	18.94	19.24
Ts 2 (min)	1.26	1.42	1.17	0.64	0.57
Tc 10 (min)	0.87	0.88	0.67	0.44	0.42
Tc 90 (min)	3.27	4.17	4.84	4.95	8.94

Here is the interpretation of the S' Max values for each version of the rubber recipe used in tire manufacturing:

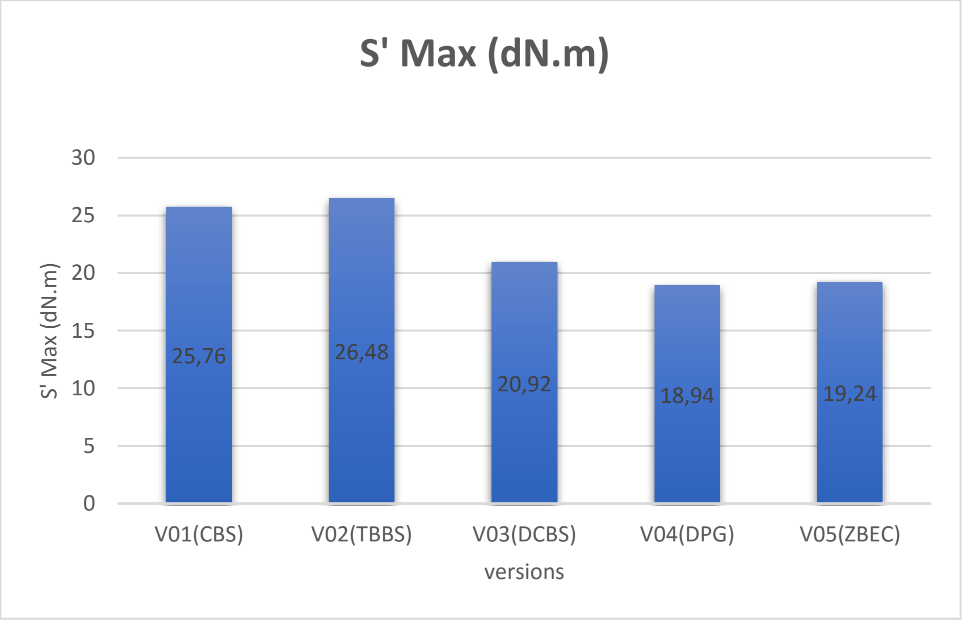


Figure IV.3: *Maximum torque (s' max) from MDR testing for different versions.*

This figure presents the maximum torque (S' Max) obtained from MDR testing for each version. TBBS has the highest S' Max (26.48 dN·m), indicating the greatest mechanical strength and cross-link density. CBS follows closely (25.76 dN·m), then ZBEC (19.24 dN·m), DCBS (20.92 dN·m), and DPG has the lowest (18.94 dN·m), suggesting increased flexibility.

- ***Version 01 (CBS)***

S' Max=25.76 dN·m

This value indicates that the compound has a relatively high stiffness and cross-link density upon vulcanization. It suggests good mechanical strength and resistance to deformation, which are desirable properties in tire manufacturing.

- **Version 02 (TBBS)**

S' Max= 26.48 dN·m

A slightly higher S' Max value compared to CBS, indicating an even higher stiffness and cross-link density. This suggests the compound will have very good mechanical strength and durability, potentially enhancing the tire's performance under load.

- **Version 03 (DCBS)**

S' Max: 20.92 dN·m

A lower S' Max value compared to CBS and TBBS, indicating a lower stiffness and cross-link density. While this might result in a less stiff compound, it can also provide better flexibility and impact resistance, which might be beneficial in certain tire applications.

- **Version 04 (DPG)**

S' Max=18.94 dN·m

This value is significantly lower than those of the other versions, indicating a much lower stiffness and cross-link density. This suggests that the compound will be more flexible but may lack the mechanical strength required for certain high-stress applications in tire manufacturing.

- **Version 05 (ZBEC)**

S' Max= 19.24 dN·m

Similar to DPG, this value indicates a lower stiffness and cross-link density compared to CBS and TBBS. The compound will likely have good flexibility and impact resistance, but it might not be as strong or durable as those with higher S' Max values.

NOTE:

- **Stiffness and Cross-Link Density**: Higher S' Max values indicate greater stiffness and cross-link density, which typically correlate with better mechanical strength and durability. This is crucial for tire components that need to withstand high loads and stresses.
- **Flexibility and Impact Resistance:** Lower S' Max values suggest a more flexible compound, which can be beneficial for parts of the tire that require good impact resistance and flexibility.
- **Application-Specific Requirements:** The choice of rubber compound should consider the specific requirements of the tire application. For example, treads might benefit from higher S' Max values for durability, while sidewalls might benefit from lower values for flexibility.

In conclusion, each version of the rubber compound presents different characteristics based on the S' Max values, indicating varying degrees of stiffness and cross-link density. The final choice of the compound will depend on the specific performance requirements of the tire being manufactured.

b) Scorch time

Scorch time (Ts2), measured using a Moving Die Rheometer (MDR), indicates the time it takes for the rubber compound to begin vulcanizing. It is defined as the time at which the torque rises to 2 dN·m above the minimum torque value. Scorch time is an important parameter because it reflects the safety margin during processing, indicating how long the compound can be processed before it starts to cure.

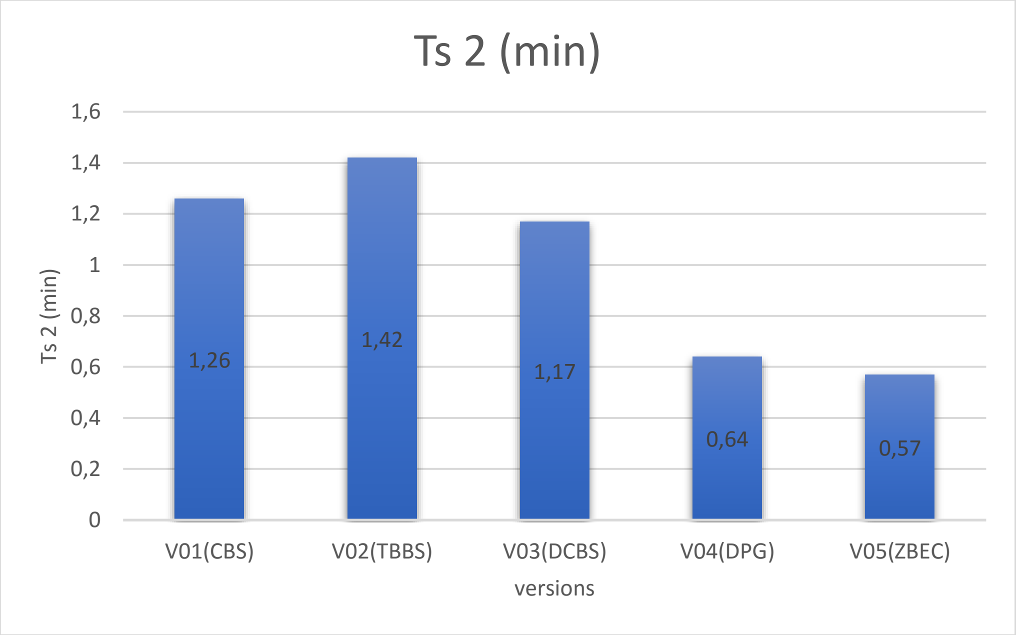


Figure IV.4: *Scorch Time (Ts2) from MDR Testing for Different Versions*

The scorch time (Ts2) for each version is depicted in this figure. TBBS has the longest scorch time (1.42 minutes), offering the largest safety margin. CBS (1.26 minutes) follows, then DCBS (1.17 minutes), DPG (0.64 minutes), and ZBEC has the shortest (0.57 minutes), indicating a need for more precise processing control to avoid premature curing.

here is the interpretation of the scorch time (Ts2) values for each version of the rubber recipe:

- **Version 01 (CBS)**

Ts2=1.26 minutes

This scorch time indicates a moderate onset of vulcanization. It provides a reasonable processing window, allowing adequate time for handling and shaping the compound before it starts curing.

- **Version 02 (TBBS)**

Ts2=1.42 minutes

This version has the longest scorch time among all versions, suggesting the best processability. The longer scorch time provides a larger safety margin during processing, reducing the risk of premature vulcanization.

- **Version 03 (DCBS)**

Ts2= 1.17 minutes

A slightly shorter scorch time compared to the CBS version, indicating that this compound will start to cure somewhat faster. This requires careful monitoring during processing to avoid premature vulcanization.

- **Versions 04 (DPG) and 05 (ZBEC)**

with very short scorch times (0.64 and 0.57 minutes, respectively), indicate rapid onset of vulcanization, requiring very fast and precise processing to avoid premature curing.

NOTE:

- **Processing Window:** Longer scorch times provide a greater processing window, making the compound easier to handle and shape before vulcanization starts. Shorter scorch times reduce this window, increasing the risk of premature curing during processing.
- **Safety Margin:** A longer scorch time allows more flexibility and reduces the risk of scorching (premature vulcanization), which can spoil the material during mixing, extrusion, or molding operations.

- **Vulcanization Control:** Short scorch times require more precise control over processing conditions to avoid premature curing, which can lead to defects in the final product.

c) Curing time

The curing time (Tc90), represents the time required for the rubber compound to reach 90% of its maximum torque during vulcanization. This value is crucial because it indicates the cure time, which affects the overall production efficiency and the properties of the final product.

The evolution of Tc 90 for the different versions are presented in **figure IV.5**

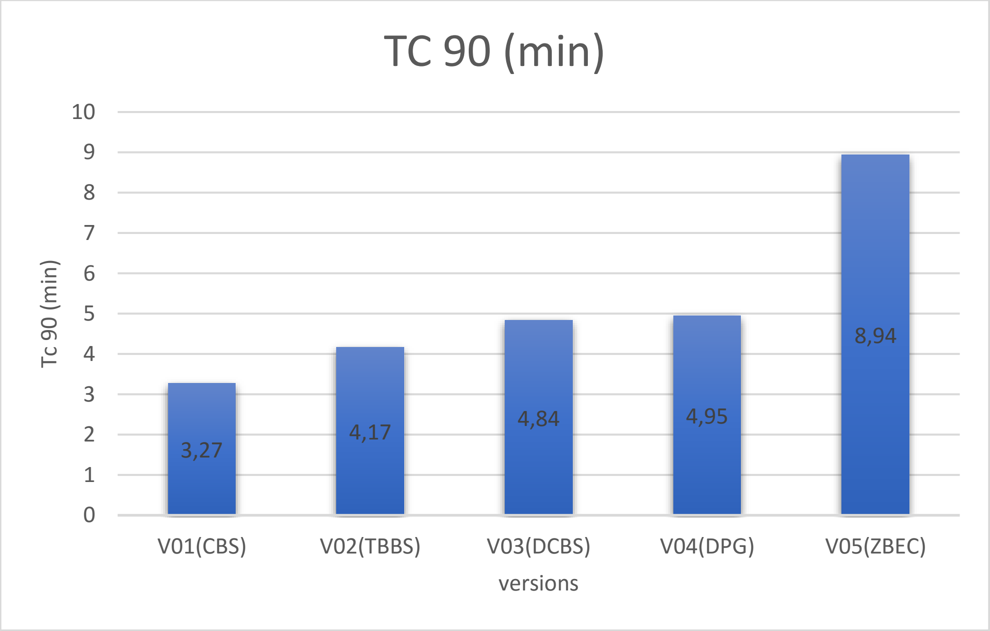


Figure IV.5: *Curing time (tc90) from MDR testing for different versions.*

This figure shows the curing time (Tc90) for the different versions. TBBS has a moderate curing time (4.17 minutes), balancing production speed and handling time. DCBS (4.84 minutes) and DPG (4.95 minutes) have longer curing times, allowing more handling time. CBS has a shorter curing time (3.27 minutes), and ZBEC has the longest (8.94 minutes), indicating slower curing.

Here is the interpretation of the Tc90 values for each version of the rubber recipe:

- **Version 01 (CBS)**

Tc90=3.27 minutes

This version has the shortest cure time, indicating rapid vulcanization. This can increase production efficiency as the compound cures quickly. However, it requires precise control over the process to avoid over-curing, which could affect the properties of the final product.

- **Version 02 (TBBS)**

Tc90=4.17 minutes

This cure time is longer than the CBS version, suggesting a slower vulcanization process. This provides a better window for handling and molding the compound before it fully cures, potentially leading to better final properties due to more controlled vulcanization.

- **Version 03 (DCBS)**

Tc90= 4.84 minutes

An even longer cure time compared to TBBS, indicating a slower vulcanization process. This further extends the processing window, allowing more time for shaping and molding, which can be beneficial for complex tire designs.

- **Version 04 (DPG)**

Tc90=4.95 minutes

Similar to DCBS, this version also has a longer cure time, indicating that the vulcanization process is slower. This extended cure time can enhance the handling and processing of the compound, ensuring better dispersion and homogeneity.

- **Version 05 (ZBEC),**

The longest Tc90 (8.94 minutes), indicates a very slow vulcanization process, which might be less efficient for mass production but beneficial for applications requiring high precision and superior mechanical properties.

NOTE:

- **Production Efficiency:** Shorter Tc90 times (like those with CBS) can increase production throughput, making the process faster. However, they require careful control to avoid defects.
- **Handling and Molding:** Longer Tc90 times (like those with ZBEC) provide more time for handling, shaping, and ensuring uniform dispersion of ingredients, which can be crucial for achieving high-quality final products.
- **Final Properties:** The vulcanization process affects the final properties of the rubber. Slower curing (longer Tc90) can sometimes result in better mechanical properties and more consistent product quality.

The optimal recipe choice will depend on the specific needs of the tire manufacturing process, including the required production speed, the complexity of the tire design, and the desired balance between processability and the mechanical properties of the final product

IV.1.3. Hardness

Hardness, measured in Shore A (ShA), is a key property of rubber compounds used in tire manufacturing. It indicates the material's resistance to indentation, which relates to its stiffness and durability.

hardness measurements, as summarized in Table IV.3 and presented in Figure IV.5, provide an indication of the material's resistance to indentation and overall stiffness. The hardness values vary across different versions, influenced by the type of accelerator used. Hardness aging, detailed in Table IV.3 and presented in Figure IV.6, shows how the hardness of the rubber compounds changes over time at elevated temperatures, highlighting the thermal stability and aging resistance of each formulation.

Table IV.3: *Hardness measurements for different versions*

versions	**Version01 (CBS)**	**Version02 (TBBS)**	**Version 03 (DCBS)**	**Version 04 (DPG)**	**Version 05 (ZBEC)**
Hardness (ShA)	73.3	73.2	70.4	66	68.8

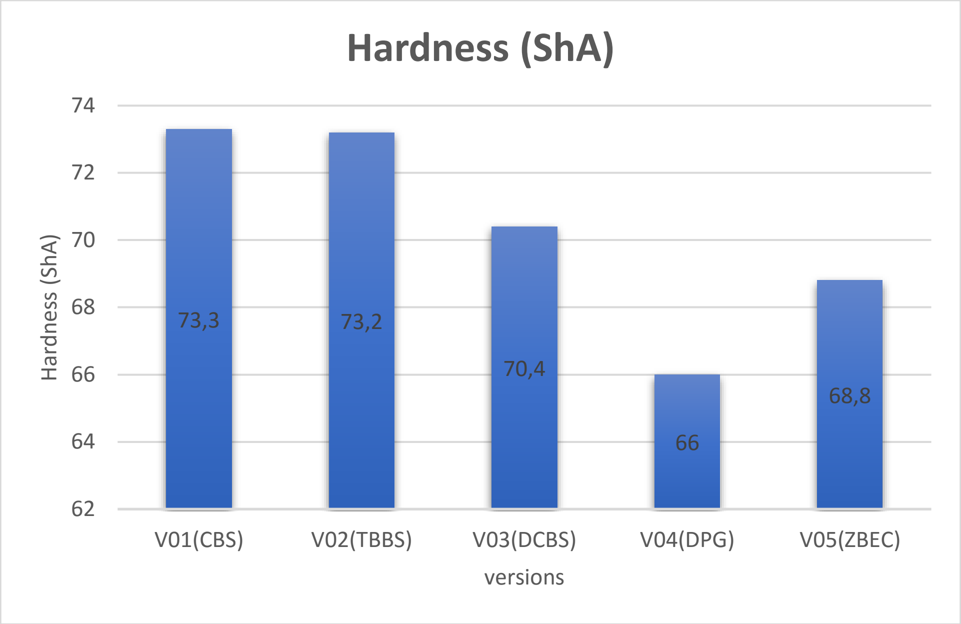


Figure IV.6: *Hardness measurements for different versions.*

The hardness measurements for each version are illustrated in this figure. TBBS (73.2 ShA) and CBS (73.3 ShA) have the highest hardness, indicating better durability and load-bearing capacity. DCBS (70.4 ShA) and ZBEC (68.8 ShA) are in the middle, while DPG (66 ShA) has the lowest hardness, suggesting better flexibility.

Here is the interpretation of the hardness values for each version of the rubber recipe:

- **Version 01 (CBS)**

The highest hardness (73.3 ShA), is best suited for applications requiring high stiffness, durability, and wear resistance.

- **Version 02 (TBBS)**

Very close to the CBS version, this hardness value (73.2 ShA) also indicates a stiff and durable compound. The slight difference in hardness is negligible, suggesting that TBBS provides similar mechanical properties in terms of hardness and stiffness.

- **Version 03 (DCBS)**

Hardness of (70.4 ShA), offers a balance between stiffness and flexibility, suitable for applications needing moderate durability and improved grip.

- **Version 04 (DPG)**

The lowest hardness (66 ShA), is ideal for applications where comfort and flexibility are prioritized over durability and stiffness.

- **Version 05 (ZBEC)**

This value (68.8 ShA)is higher than DPG but still lower than CBS and TBBS, indicating a moderately soft compound. It strikes a balance between flexibility and stiffness, offering good grip and comfort while maintaining reasonable durability.

NOTE:

Durability and Load-Bearing Capacity: Higher hardness values generally indicate better durability and load-bearing capacity, which are important for high-performance and long-lasting tires.

Flexibility and Comfort: Lower hardness values suggest a softer compound, which can enhance ride comfort and provide better traction, especially in certain road conditions.

Application Suitability: The choice of compound hardness should align with the specific requirements of the tire application. For example, racing tires might prioritize higher hardness for durability, while passenger car tires might prioritize lower hardness for comfort and grip.

IV.1.4. Tensile

The tensile test results provide important information about the mechanical properties of the rubber compounds. These results include the modulus, the elongation at break, and the force at break.

Tensile properties, including modulus. elongation at break, and force at break, are summarized in Table IV.5 and presented in Figures IV.7 to IV.9. These properties offer insights into the flexibility, ductility, and mechanical strength of the rubber compounds.

The tensile tests reveal significant differences between versions, reflecting the impact of different accelerators on the material's performance under stress.

Table IV.4: *Tensile Properties for Different Versions.*

	Version 01 (CBS)	Version02 (TBBS)	Version 03 (DCBS)	Version 04 (DPG)	Version 05 (ZBEC)
Modulus (MPa)	4,4567	4,6444	3,5733	2,56	3,4611
Elongation. at break (%)	314.0333	287.9333	369.2889	448.2778	271.8444
Force at break (MPa)	20.5333	18.9444	20.7667	19.4556	13.2

This table summarizes the tensile properties, including modulus, elongation at break, and force at break, for different rubber formulations.

IV.1.4.1. Modulus

The modulus values indicate the stiffness of the material under stress. TBBS shows the highest modulus values, reflecting its high stiffness and mechanical strength. CBS and DCBS also exhibit relatively high modulus values, while ZBEC and DPG have lower modulus values, indicating greater flexibility.

IV.1.4.2. Elongation at Break

The elongation at break measures the material's ability to stretch before failure. DPG and DCBS have the highest elongation at break values, suggesting superior flexibility and ductility. CBS and TBBS are moderate in this respect, while ZBEC has the lowest elongation at break, indicating the least flexibility but the highest durability.

IV.1.4.3. Force at Break

The force at break reflects the maximum load the material can withstand before breaking. DCBS has the highest force at break, indicating the greatest mechanical strength. CBS follows, then DPG, with TBBS and ZBEC showing the lowest values, suggesting they are less strong but more flexible.

Here's the interpretation of these values for each version of the rubber recipe:

- **Version 01 (CBS)**

This version exhibits high modulus values at all elongations, indicating it is quite stiff and resistant to deformation. It also has high elongation at break and force at break, suggesting it is both strong and reasonably flexible.

- **Version 02 (TBBS)**

This version has the highest modulus values, indicating it is the stiffest and most resistant to deformation. It has slightly lower elongation at break compared to CBS, suggesting it is less flexible. The force at break is slightly lower, indicating slightly less strength than CBS.

- **Version 03 (DCBS)**

This version has moderate modulus values, indicating a balance between flexibility and stiffness. It has the lowest elongation at break, suggesting it is the least flexible. The force at break is also the lowest, indicating it is the weakest mechanically.

- **Version 04 (DPG)**

This version has the lowest modulus values, indicating it is the most flexible and least resistant to deformation. It has the highest elongation at break, indicating excellent flexibility and ductility. The force at break is high, suggesting good mechanical strength despite its flexibility.

- **Version 05 (ZBEC)**

This version has lower modulus values compared to CBS and TBBS, indicating it is more flexible. It has the highest elongation at break, suggesting excellent flexibility and ductility. The force at break is the highest, indicating strong mechanical strength.

NOTE:

- **Stiffness and Flexibility:** Higher modulus values indicate stiffer materials, while lower values indicate more flexible materials.
- **Strength and Durability:** Higher force at break values indicate stronger materials. Elongation at break indicates how much a material can stretch before breaking, which is important for flexibility and durability.

- **Application Suitability:** The optimal choice of rubber compound depends on the specific application requirements, balancing stiffness, flexibility, and mechanical strength.

The choice of the optimal recipe will depend on the specific performance requirements of the tire, including desired balance between stiffness, flexibility, and mechanical strength.

IV.1.5. Density

Density is a measure of mass per unit volume, indicating how compact the material is In the context of rubber compounds, density can influence the weight and performance characteristics of the final product. Here's what the results imply:

Tabe IV.5: *Density measurements for different versions*

versions	**Version 01 (CBS)**	**Version02 (TBBS)**	**Version 03 (DCBS)**	**Version 04 (DPG)**	**Version 05 (ZBEC)**
Density (g/cm3)	1.117	1.111	1.115	1.112	1.112

The densities of all five versions are very close, ranging from 1.111 to 1.117 g/cm³. This suggests that the overall composition of the rubber compounds is similar, with only slight variations attributable to the different accelerators used (CBS, TBBS, DCBS, DPG, ZBEC).

IV.2. Ageing tests

The ageing tests provide critical insights into the long-term performance and durability of rubber compounds when exposed to elevated temperatures over extended periods. These tests are designed to simulate the conditions that rubber materials may encounter during their service life, helping to predict their behavior and structural integrity over time.

In this section, we will focus on the results of various ageing tests, including hardness ageing and tensile ageing measurements. These tests assess how different rubber formulations, each containing distinct accelerators, respond to prolonged heat exposure. By examining changes in properties such as hardness, tensile strength, elongation at break, and modulus, we can evaluate the stability and resilience of each formulation.

IV.2.1. Hardness ageing

Hardness measurements over time at elevated temperatures (95°C) give insight into how the rubber compounds age. An increase in hardness and potential brittleness, which can affect the material's performance, durability, and flexibility.

Table IV.6: *Hardness aging measurements over time for different versions*

versions	V01 (CBS)	V02 (TBBS)	V03 (DCBS)	V04 (DPG)	V05 (ZBEC)
Hardness (ShA) 1DAY	75.8	76.1	73.7	68	69.3
Hardness (ShA) 3DAYS	77.9	78.5	75	69	71.3
Hardness (ShA) 7DAYS	79.3	80	76.4	69.6	71.7

This table presents the hardness values of different rubber compound versions measured over time at elevated temperature, providing insights into their aging behavior.

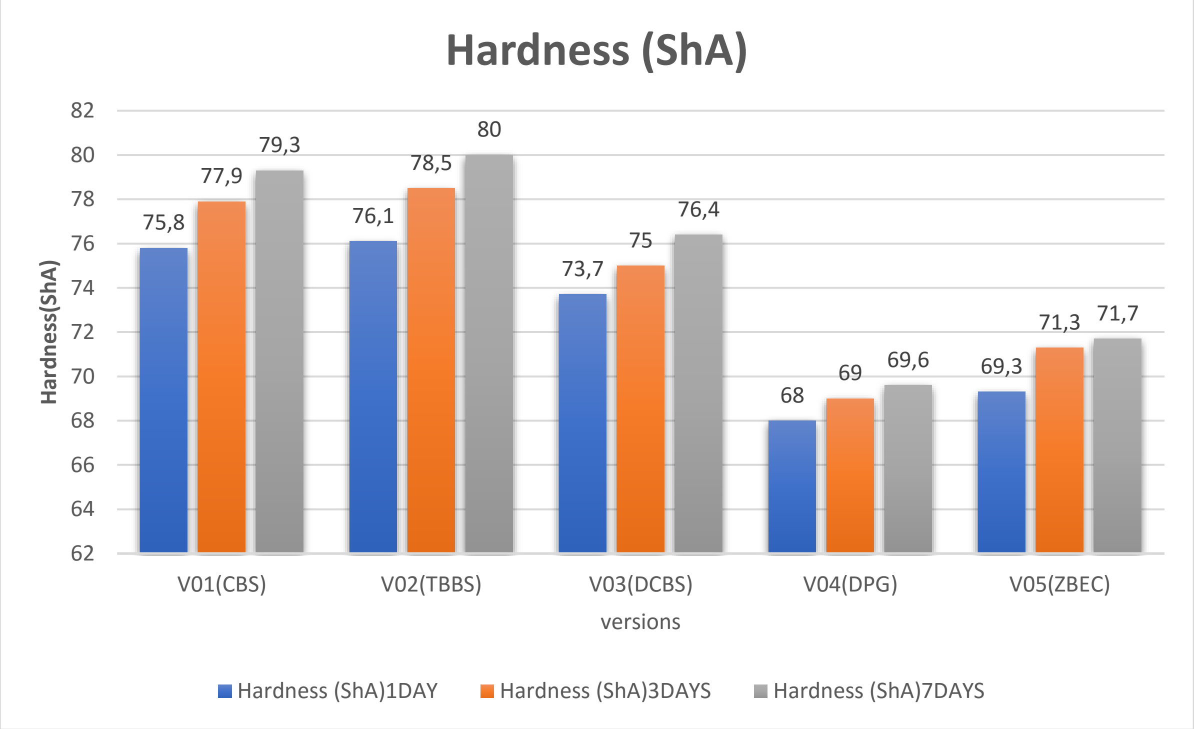


Figure IV.7: *Hardness Increase Over Time at Elevated Temperature.*

This figure displays the increase in hardness over time when subjected to elevated temperatures, providing insights into the aging behavior of the rubber compounds. A lower increase in hardness suggests better resistance to thermal aging, maintaining flexibility and preventing brittleness over time.

Over time, all versions show an increase in hardness when exposed to heat, indicating a loss of flexibility and an increase in brittleness. Version 01 (CBS) and Version 02 (TBBS) exhibit the greatest increases in hardness, suggesting they become the stiffest and most brittle over time. Version 04 (DPG) and Version 05 (ZBEC) show smaller increases, indicating better retention of flexibility and resistance to becoming brittle. Version 03 (DCBS) maintains a moderate increase in hardness, balancing between flexibility and rigidity.

NOTE:

- **Thermal Aging Resistance:** Versions with lower increases in hardness (DPG and ZBEC) are more resistant to thermal aging and retain their flexibility longer.
- **Durability vs. Flexibility:** Versions with higher increases in hardness (CBS and TBBS) become stiffer, which may enhance durability but could reduce flexibility and increase brittleness.
- **Application Suitability:** The specific needs of the tire application should guide the choice. For example, racing tires may prioritize initial stiffness (CBS, TBBS), while passenger tires might prioritize long-term flexibility and comfort (DPG, ZBEC).

IV.2.2. Tensile ageing

The tensile aging test measures how the mechanical properties of rubber compounds change over time when exposed to elevated temperatures (95°C).

Table IV.7: *tensile Aging Measurements Over Time for Different Versions*

		Version 01 (CBS)	**Version02 (TBBS)**	**Version 03 (DCBS)**	**Version 04 (DPG)**	**Version 05 (ZBEC)**
1Day	Modulus (MPa)	5,74	5,8067	4,92	3,1633	3,9933
	Elongation. at break (%)	204.8333	184.3667	239.8333	232.8333	176.5667
	Force at break (MPa)	15.2333	14	15.9667	9.5367	8.64
3Days	Modulus (MPa)	6,89	7,4433	5,7133	3,5	4,4767
	Elongation. at break (%)	159.7333	142.6667	188.4333	175.8667	144.7333
	Force at break (MPa)	13.1333	12	13.2	6.8533	6.86
7Days	Modulus (MPa)	7,1333	8,31	6,9667	4,34	4,547
	Elongation. at break (%)	127.3333	110.9333	125.4	121.9	122.6
	Force at break (MPa)	10.1033	9.5967	9.3133	5.2767	3.9767

This table summarizes the tensile aging properties of different rubber formulations, including changes in modulus, elongation at break, and force at break after aging.

a) Modulus Changes

Aging typically increases the modulus of rubber compounds, indicating increased stiffness. In this table, TBBS shows a significant increase in modulus after aging, suggesting reduced flexibility but enhanced stiffness and mechanical strength. CBS and ZBEC also show considerable increases in modulus, whereas DCBS and DPG show moderate increases, indicating they retain more flexibility after aging.

b) Elongation at Break Changes

The elongation at break generally decreases after ageing, indicating reduced ductility. TBBS has a substantial reduction in elongation at break, reflecting its higher stiffness post-ageing. CBS and ZBEC show moderate reductions, while DCBS and DPG have the smallest reductions, indicating they maintain better ductility and flexibility after aging.

c) Force at Break Changes

Aging tends to reduce the force at break, indicating decreased maximum load capacity. TBBS shows a significant decrease in force at break after ageing, yet it retains the highest value among the versions, indicating it remains the strongest. CBS and ZBEC also show notable reductions, while DCBS and DPG exhibit smaller reductions, indicating they maintain better mechanical properties after aging.

In conclusion, all rubber compound versions exhibit an increase in stiffness (modulus) over time when exposed to heat, with Versions 01 (CBS) and 02 (TBBS) showing the highest increase, indicating they become the stiffest. Versions 04 (DPG) and 05 (ZBEC) retain more flexibility initially but still lose it over time, while Version 03 (DCBS) maintains a balance between stiffness and flexibility. Despite the overall loss of strength over time across all versions, Version 03 retains the most strength, whereas Version 05 experiences the greatest reduction in strength.

Overall, TBBS demonstrates the greatest increase in stiffness and reduction in ductility after aging, making it suitable for applications where high stiffness and mechanical strength are critical, even after aging. DCBS and DPG retain better flexibility and ductility, making them suitable for applications where these properties are essential post-aging. CBS and ZBEC provide a balance, offering moderate changes in properties after aging.

IV.3. Conclusion

Based on the detailed analysis of the rubber compound properties, Version 02, which uses TBBS (N-tert-Butyl-2-benzothiazolesulfenamide), appears to be the most effective accelerator overall. The Mooney viscosity for Version 02 (TBBS) is one of the lowest (53.95 MU) among the final batches, indicating excellent processability. In terms of MDR characteristics, Version 02 exhibits a high maximum torque (S' Max) value of 26.48 dN·m, suggesting good mechanical strength and durability. The scorch time (Ts2) is relatively long at 1.42 minutes, providing a safer margin during processing. Although its curing time (Tc90) is longer at 4.17 minutes, it allows more handling and shaping time, which improves overall product quality. Additionally, Version 02 maintains a high hardness value of 73.2 ShA, indicating good durability and load-bearing capacity. The tensile properties of Version 02 show high modulus values, indicating stiffness and mechanical strength, which are desirable for many rubber applications.

Overall, TBBS offers a balanced combination of good processability, mechanical strength, durability, and a safer processing margin, making it the most effective accelerator among the tested formulations.

The final choice of recipe will depend on specific processability requirements and the desired mechanical properties of the finished tire.

General conclusion

General conclusion

This master thesis provides an in-depth analysis of rubber compounds for automotive tires, focusing on the experimental evaluation of different accelerators and their impact on the material properties.

It offers an in-depth analysis of the properties of various rubber compounds, focusing on the impact of different accelerators used. The accelerators studied include CBS, TBBS, DCBS, DPG and ZBEC. Each accelerator was evaluated based on several properties, such as Mooney viscosity, Moving Die Rheometer (MDR) characteristics, hardness, tensile properties, and aging behavior.

The Mooney viscosity tests reveal that the final batch viscosity varies with the type of accelerator used, highlighting TBBS as the most effective in enhancing processability. MDR tests demonstrate that TBBS imparts the highest mechanical strength and optimal curing times while maintaining a suitable safety margin with its longer scorch time.

Hardness measurements indicate that TBBS and CBS provide the highest initial hardness, making them ideal for applications requiring robust load-bearing capacity. In contrast, DPG and ZBEC offer better initial flexibility. The tensile tests confirm TBBS's superior mechanical strength, though it sacrifices some flexibility compared to other formulations like DCBS and DPG.

Aging tests, including hardness and tensile aging measurements, show that all rubber compounds stiffen over time when exposed to heat. TBBS and CBS become the stiffest, while DCBS retains the most flexibility, demonstrating better aging resistance. ZBEC and DPG maintain a balance between stiffness and flexibility, proving versatile for various applications.

The detailed experimental approach and comprehensive analysis not only validate the effectiveness of TBBS but also provide a valuable reference for future research aimed at further optimizing rubber compound formulations.

This thesis underscores the importance of selecting the right accelerator for rubber compounds in tire manufacturing. The careful balance between processability, mechanical strength, and durability is crucial for producing high-quality tires.

Future research should continue to explore the interactions between different compound formulations and processing variables to further enhance tire performance and manufacturing efficiency. The findings from this thesis provide a solid foundation for such endeavors, contributing to the advancement of rubber compound technology in the automotive industry.

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Appendices

Appendices

Appendix1. Per hundred rubber (PHr)

"PHr" stands for "parts per hundred rubber." It's a measure used in rubber compounding to denote the quantity of an additive in relation to the amount of rubber. For example, if you have 100 parts of rubber and you add 5 parts of an additive, then the PHR of that additive is 5.

- For converting PHr to the mass in (grams)

we have:

$$\text{PHr} = \frac{\text{mass in grams}}{\text{Kf}} \text{ ……… } (1)$$

$$Kf = \frac{Vm.dt.FF}{PHr(Tot)} \quad \text{………. } (2)$$

And:

V =1.78 L

FF = 60-65%

PHr =170.4

$$\text{dt}= \frac{Mt}{Vt} \rightarrow \text{dt}=\frac{PHr(TOt)}{Vt} \text{ ……… } (3)$$

$$\text{Vt} =\sum\text{Vi}=\sum\text{Vcn+Vzno+… …. } (4)$$

$$Vi = \frac{Mi}{di} \rightarrow Vt = \frac{PHri}{di}$$

-replace (Vi) values in equation (4), we find Vt

-replace the value of (Vt) in equation (3), we find (dt)

-replace the value of (dt) in equation (2), we find (Kf)

then, we find the mass in grams:

$$\boxed{\text{mass in grams =PHr.Kf …(gr)}}$$

Kf: K factor

Vm: mixer volume

FF: fill factor

Vt: total volume

Vi: additive volume

Mi: the mass of additive

d: density

Appendix2. Rheometer

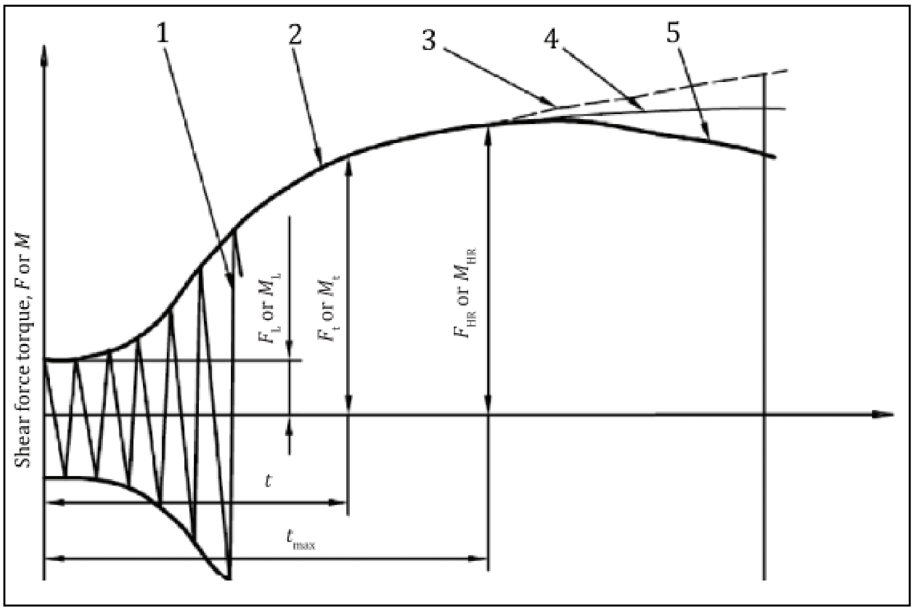


Figure 1:*Vulcanization curve F or M = f(t).*

Key :

1 sinusoidal curve

2 envelope curve

3 vulcanization curve with steady increase to FH or MH at time tc at end of test (marching-modulus cure)

4 vulcanization curve with plateau at FHF or MHF (plateau cure)

5 vulcanization curve with maximum FHR or MHR at time tmax (reverting cure)

Appendix3. Durometer Hardness (Shore hardness)

➢ Choice of Durometer

When employing durometers, select the scale according to the following guidelines:

- For readings under 20 using a type D durometer: utilize for type A.
- If readings are under 20 with a type A durometer: utilize type AO.
- If values exceed 90 with a type A durometer: utilize type D.
- For thin test pieces, specifically those less than 6 mm thick: utilize type AM.

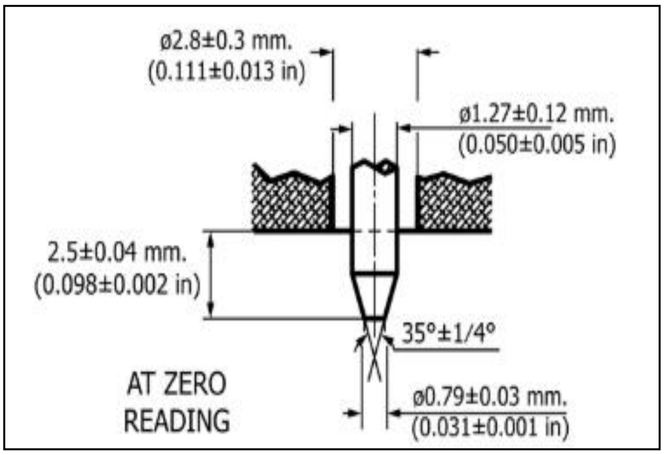


***Figure 2: (a)** Type A and C Indentor.*

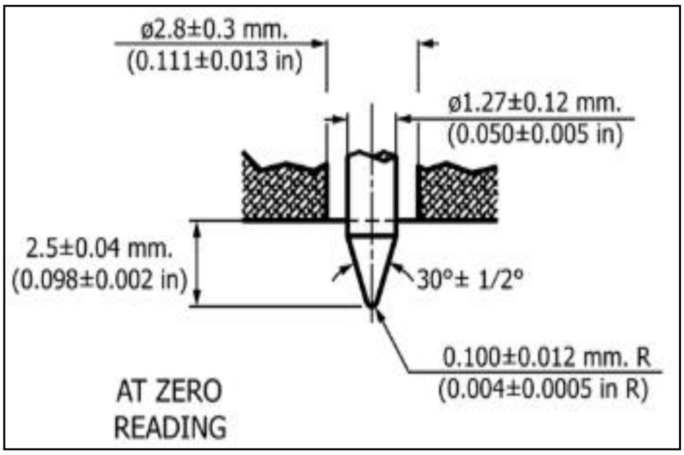


***Figure 3: (b)** Type B and D Indentor.*

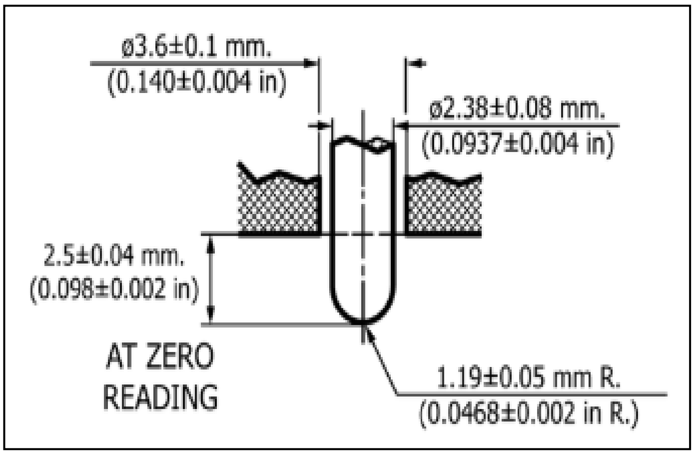


***Figure 4: (c)** Type O, DO, and OO Indentor.*

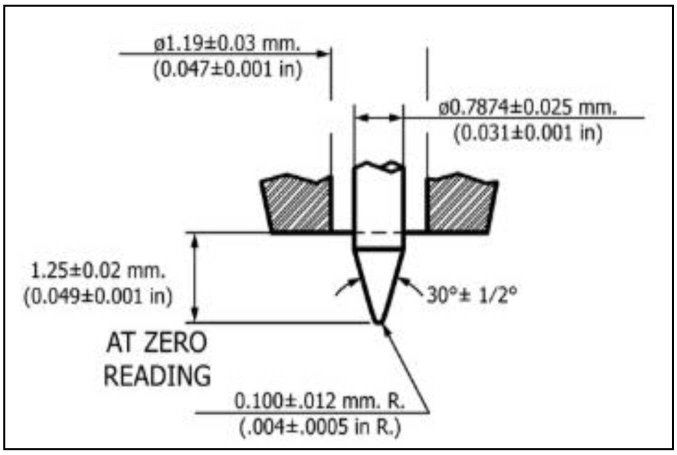


***Figure 5: (d)** Type M Indentor.*

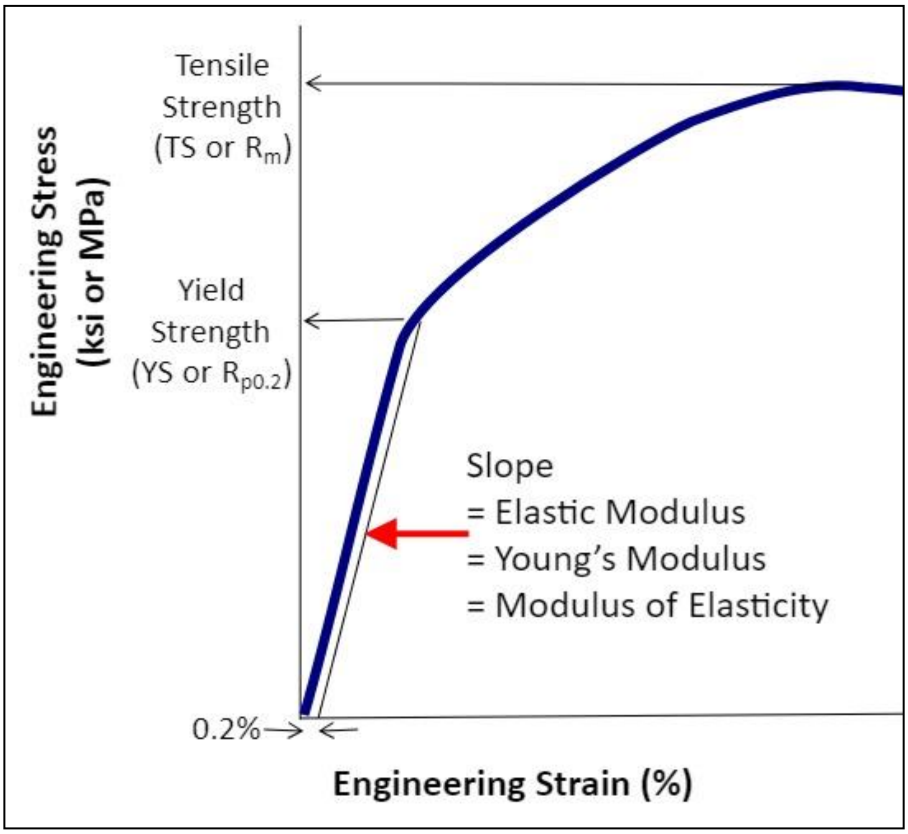


Figure 6: *Modulus.*

where:

$$\boxed{\text{Mod}= \frac{stress}{\text{strain}}}$$

Appendix4.Classification of accelerators

A. Thiazole Class Accelerators

- **MBT**

MBT'(2-mercaptobenzothiazole), is indeed a versatile accelerator used in rubber vulcanization processes. Its longer plateau of vulcanizing period helps enhance the physical and mechanical properties of vulcanizates. Additionally, it serves as an anti-scorching agent for rubber compounds without sulfur. Alkaline accelerators like aldehyde-amines, guanidines, thiurams, and dithiocarbamates can activate MBT, further aiding in the vulcanization process.

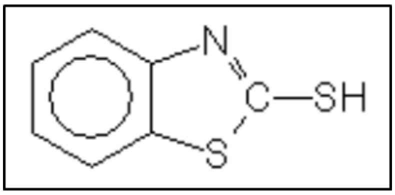


Figure 7: *synthesis of 2-mercaptobenzothiazole.*

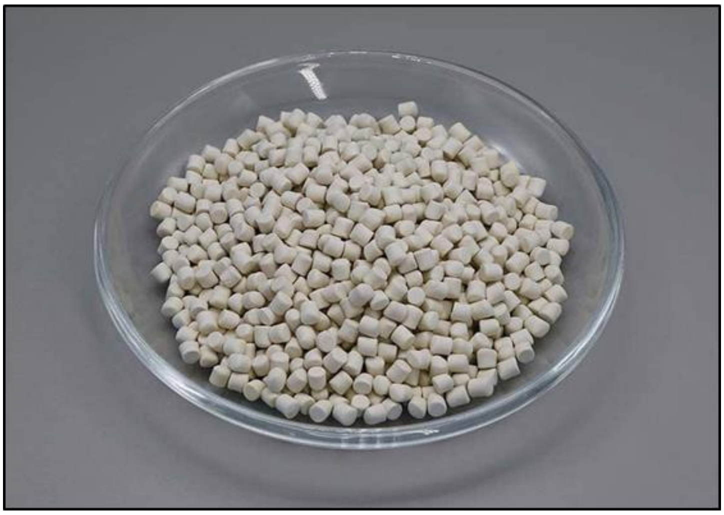


Figure 8: *2-mercaptobenzothiazole.*

- **ZMBT**

ZMBT (Zinc-2-mercaptobenzothiazole), It is utilized in the vulcanization of natural rubber (NR), isoprene rubber (IR), styrene-butadiene rubber (SBR), nitrile rubber (NBR), ethylene-propylene-diene monomer (EPDM), and latex. Often employed as a secondary accelerator alongside PZ and EZ, it demonstrates comparable performance to MBT at curing temperatures in dry rubber applications, boasting lower scorch and improved processing safety. Ideal for mold curing, it typically requires zinc oxide and stearic acid as activators in various rubber batches.

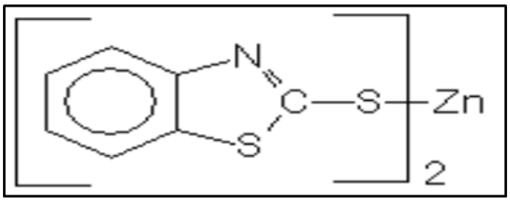


Figure 9: *synthesis of Zinc-2-mercaptobenzothiazole.*

Exhibiting easy dispersion within rubber compounds, it yields non-staining and non-discoloring products, primarily serving in the manufacturing of latex products, foam rubber, latex coating gloves, and similar applications.

Figure 10: *synthesis of Zinc-2-mercaptobenzothiazole.*

B. Sulfenamide Class Accelerators:

- **DCBS**

Accelerator DCBS (N, N'-dicyclohexyl-2-benzothiazole sulfenamide) functions as a delayed action sulfenamide accelerator suitable for both natural and synthetic rubbers. It is ideal for applications demanding prolonged flow times, particularly in rubber goods exposed to high dynamic stresses. Acting as a primary accelerator, it can be applied independently or in conjunction with various secondary accelerators. Notably, DCBS provides superior scorch resistance compared to other commonly used sulfenamide accelerators.

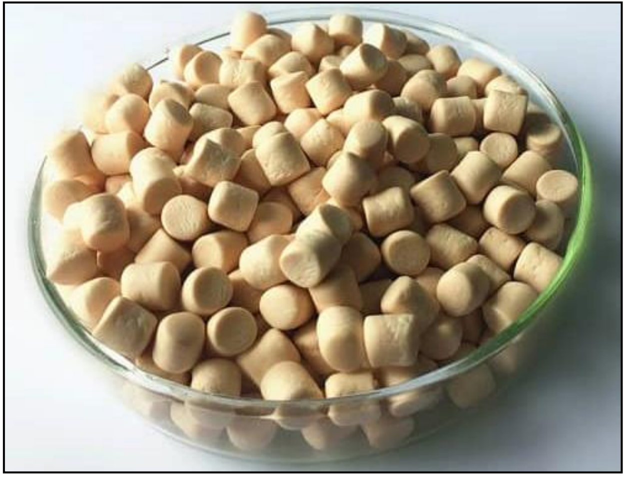


Figure 11: *N, N'-dicyclohexyl-2-benzothiazole sulfenamide.*

DCBS demonstrates remarkable efficacy in thick cross-section molded articles, particularly in scenarios with high processing temperatures or when delayed cures are essential for optimal adhesion. Although total curing times may be lengthier compared to other sulfenamides, the flow time/curing time ratio remains advantageous. Its applications extend to conveyor belts, driving belts, shock absorbers, mountings, and intricately shaped molded goods that necessitate prolonged flow periods during the molding process. The incorporation of zinc oxide is essential, and stearic acid should be included in compounds aiming for high modulus values.

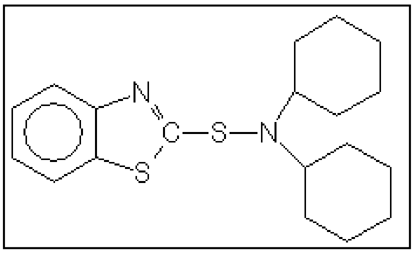


Figure 12: *synthesis of N, N'-dicyclohexyl-2-benzothiazole sulfenamide.*

- **TBBS**

TBBS (N-tert-butyl-2-benzothiazole sulfenamide) Accelerator is a commonly employed delayed-action accelerator utilized in both natural and synthetic rubbers. It boasts outstanding scorch safety alongside rapid cure rates. Activation of TBBS occurs through acidic substances like stearic acid.

Figure 13: *N-tert-butyl-2-benzothiazole sulfenamide.*

TBBS can be utilized either independently or in conjunction with numerous secondary accelerators. It offers a similar modulus at lower concentrations (approximately 10% less) compared to standard loadings of other sulfenamides. However, TBBS offers slightly less processing safety compared to CBTS or OBTS.

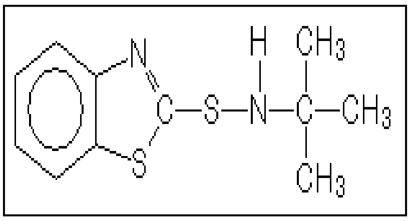


Figure 14: *synthesis of N-tert-butyl-2-benzothiazole sulfenamide.*

- **CBS**

The rubber accelerator CBS (N-Cyclohexyl-2-benzothiazole sulfenamide) is a highly active delayed-action accelerator renowned for its excellent resistance to scorching.

Figure 15: *N-Cyclohexyl-2-benzothiazole sulfenamide***.**

It ensures a safe and rapid vulcanization process. At temperatures exceeding 138°C, its promoting effect becomes notably robust. It's frequently paired with TMTD or other alkaline accelerators to formulate a secondary accelerator. Alkaline promoters like thiuram and disulfide carbamate can further enhance its activity. Primarily employed in the production of tires, rubber pipes, rubber shoes, cables, and various other industrial rubber goods.

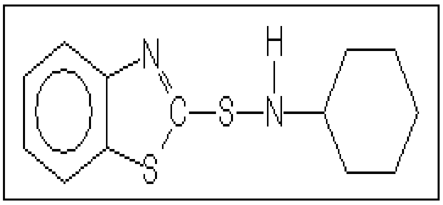


Figure 16: *synthesis of N-Cyclohexyl-2-benzothiazole sulfenamide.*

C. Guanidines

- **DPG**

Accelerator DPG (Diphenyl Guanidine) serves as a valuable accelerator/activator for natural rubber, SBR, and NBR (Nitrile rubber), activating accelerators like MBT, MBTS, and sulfenamides. It exhibits strong secondary properties for CBTS, BBTS, OBTS, MBT, and MBTS. To enhance its effectiveness, zinc oxide and fatty acids are necessary.

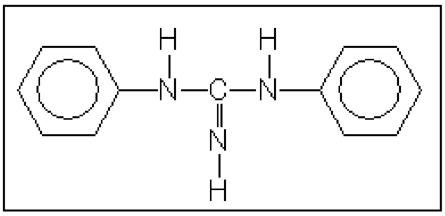


Figure 17: *synthesis of Diphenyl Guanidine.*

Although DPG offers satisfactory processing safety and storage stability to rubber compounds, it may cause brown discoloration in light-colored products and impart a bitter taste in food-contact compounds. For optimal aging results, an antioxidant is recommended. The suggested dosages of DPG, in combination with zinc oxide, stearic acid, and sulfur, vary according to the type of rubber:

Natural Rubber.................................. 0.10- 0.50 phr with sulfenamides or MBTS
SBR .... 0.20 - 0.75 phr with sulfenamides, MBTS or MBT
NBR .... 0.20 - 0.50 phrwith CBTS, MBTS

Figure 12: *Diphenyl Guanidine.*

- **DOTG**

DOTG, or N, N’-Diorthotolyl Guanidine, is suitable for a range of rubber types including natural rubber (NR), styrene-butadiene rubber (SBR), isobutylene-isoprene rubber (IIR), isoprene rubber (IR), nitrile rubber (NBR), styrene-butadiene copolymer (SNR), and chloroprene rubber (CR).

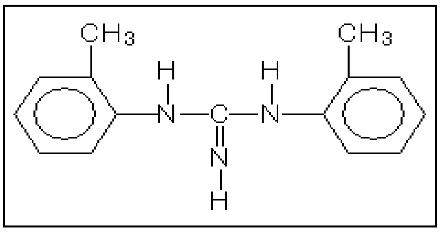


Figure 13: *synthesis of N, N'-Diorthotolyl Guanidine.*

It is typically used in combination with thiazoles, thiurams, dithiocarbamates, and sulphenamides to enhance its activity, rather than being employed alone. With a critical temperature of 141°C, DOTG functions as a plastic decomposing agent in CR. However, it is not recommended for use in food-related or medical products.

Figure 4: *N, N'-Diorthotolyl Guanidine.*

D. Dithiocarbamates

- **ZDBC**

ZDBC (Zinc dibutyldithiocarbamate) serves primarily as an ultra-fast primary accelerator or a booster accelerator in NR, synthetic rubber, latex compounds and dry rubber compounds to produce transparent or brightly colored rubber products. In NR latex compounds, ZDBC demonstrates high activity above 70°C, surpassing the speed of ZDMC or ZDEC. However, in dry rubber compounds, ZDBC acts as a slower accelerator compared to ZDMC or ZDEC due to its higher molecular weight.

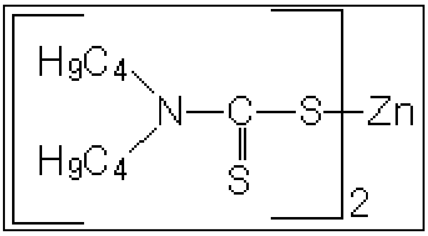


Figure 5: *synthesis of Zinc dibenzyldithlocarbamate.*

When combined with thiazoles, ZDBC shows a tendency for scorching, faster curing, and higher crosslink density, resulting in bloom-free vulcanizates with excellent aging resistance when antioxidants are present. ZDBC also enhances transparency in finished products in NR latex-based compounds by eliminating the need for zinc oxide. It disperses easily in both latex and dry rubber compounds and remains stable in the absence of sulfur. Additionally, ZDBC serves as an effective antioxidant in the production of hot melt adhesives, thermoplastic elastomers, unvulcanized rubber cements, and adhesives.

Figure 6: *Zinc dibenzyldithlocarbamate.*

- **ZDMC**

ZDMC (Zinc dimethyldithiocarbamate) functions as a secondary ultra accelerator within thiazole and sulfenamide cure systems for a range of general-purpose polymers, including NR, SBR, IIR, and EPDM.

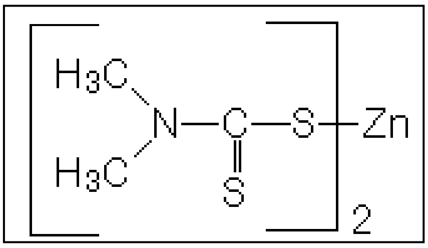


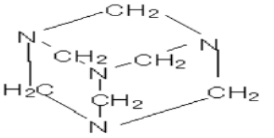
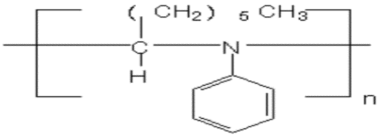
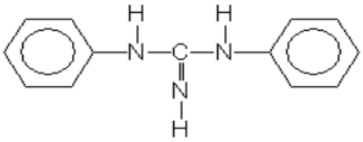
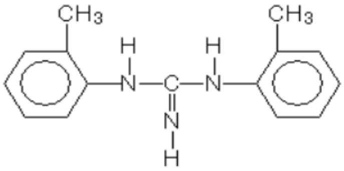
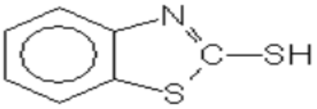
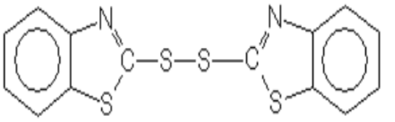
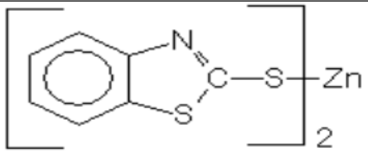
Figure 7: *synthesis of Zinc dimethyidithlocarbamate.*

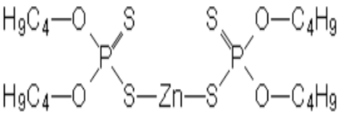
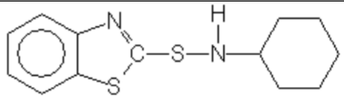
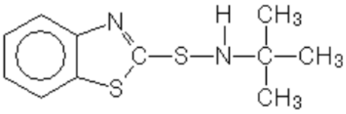
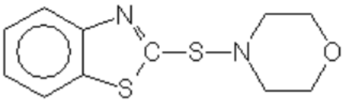
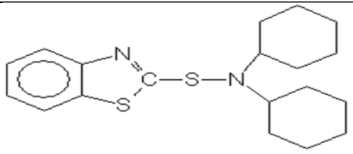
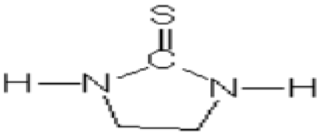
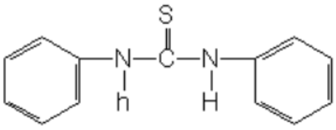
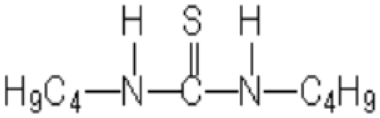
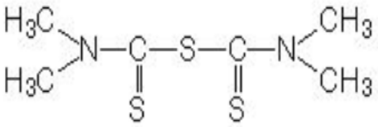
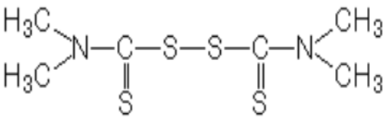
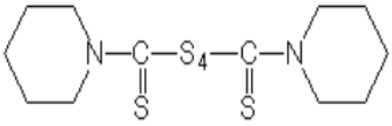
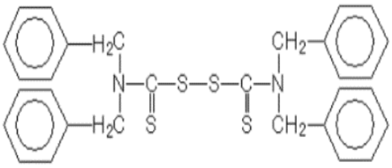
It can also act as a primary accelerator in specific continuous cure scenarios. Its versatility extends to both natural and synthetic lattices. Moreover, lack of pollution, and resistance to discoloration make it suitable for use in rubber products intended for tape, food, and pharmaceutical applications. Notably, ZDMC has obtained approval from the FDA in the United States.

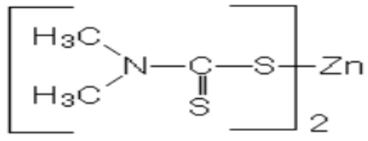
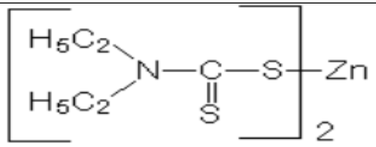
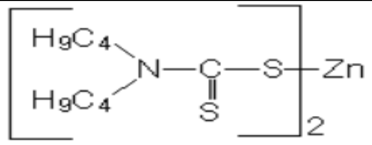
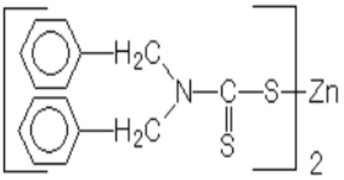
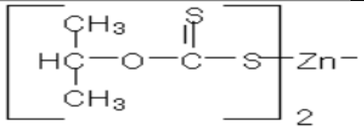
Figure 8: *Zinc dimethyidithlocarbamate.*

Appendix5. Commonly used Accelerators.

Table II.2: Commonly used Accelerators.

Accelerator	**Chemical structure**	**Remarks**
Hexamethylene Tetramine (HMT)		Group: Amines. Speed: Scorchy & Slow cure rate. Use: As a secondary accelerator
Heptaldehyde-Aniline condensation Product (BA)		Group: Aldehyde-Amines. Speed: Scorchy & Slow cure rate. Use: As a Primary accelerator.
Diphenyl Guanidine(DPG)		Group: Guanidines. Speed: Scorchy & Slow cure rate. Use: As a Primary & Secondary accelerator
N, N'-Diorthotolyl Guanidine (DOTG)		Group: Guanidines. Speed: Scorchy & Slow cure rate. Use: As a Primary & Secondary accelerator
2- Mercaptobenzothiazole (MBT)		Group: Thiazoles. Speed: Scorchy Ultra-fast. Use: As a Primary accelerator
2-2'- Dithiobis (benzothiazole) (MBTS)		Group: Thiazoles. Speed: Less scorchy than MBT. Ultrafast. Use: As a Primary accelerator
Zinc-2mercaptobenzothiazole (ZMBT)		Group: Thiazoles. Speed: Scorchy. Ultra-fast. Use: As a Primary accelerator

Zinc-O,O-di-N-phosphorodithioate (ZBDP)		Group: Thiophosphate. Speed: Scorchy. Ultra fast. Use: As a Primary accelerator
N-Cyclohexyl-2 benzothiazole sulfenamide (CBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator
N-tert-butyl-2-benzothiazole sulfenamide (TBBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator
2-(4-Morpholinothio)-benzothiazole (MBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator
N.N'-dicyclohexyl-2-benzothiazole sulfenamide (DCBS)		Group: Sulfenamides Speed: Delayed Action. Ultra fast. Use: As a Primary accelerator
Ethylene Thlourea (ETU)		Group: Thloureas Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Di-pentamethyleneThlourea (DPTU)		Group: Thloureas Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Dibutyl Thlourea (DBTU)		Group: Thloureas Speed: Ultra fast. Use: As a Primary / Secondary accelerator
TetramethyithluramMono sulfide (TMTM)		Group: Thlurams Speed: Ultra fast. Use: As a Primary / Secondary accelerator. Not a sulfur donor
Tetramethytthluram Disulfide (TMTD)		Group: Thlurams Speed: Ultra fast. Use: As a Primary / Secondary accelerator, Sulfur donor
Dipentamethylenethluramtetrasulfide (DPTT)		Group: Thlurams Speed: Ultra fast. Non-nitrosamine Use: As a Primary / Secondary accelerator; Sulfur donor.
Tetrabenzyithluram Disulfide (TBzTD)		Group: Thlurams Speed: Ultra fast. Use: As a Primary/ Secondaryaccelerator, Non-nitrosamine, Sulfur donor,

Zinc dimethyidithlocarbamate (ZDMC)		Group: Dithlocarbamates Speed: Ultra fast. Use: As a Primary Secondary accelerator.
Zinc diethyldithlocarbamate (ZDEC)		Group: Dithlocarbamates Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Zinc dibutyidithlocarbamate (ZDBC)		Group: Dithlocarbamates Speed: Ultra fast. Use: As a Primary / Secondary accelerator
Zinc dibenzyldithlocarbamate (ZDBC)		Group: Dithlocarbamates Speed: Ultra fast. Use: As a Primary/ Secondaryaccelerator, Non-nitrosamine.
Zinc-Isopropyl Xanthate(ZIX)		Group: Xanthates Speed: Super fast. Use: As a Primary accelerator.