

**THE EFFECT OF INCORPORATION SEQUENCE OF  
CURATIVE INGREDIENTS ON CURE  
CHARACTERISTICS OF SOLID TIRE MIDDLE  
COMPOUNDS AND PROPERTIES OF RESULTANT  
VULCANIZATES**

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Degree of Master of Science

Department of Chemical and Process Engineering

University of Moratuwa

Sri Lanka

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Thesis submitted in partial fulfillment of the requirements for the degree Master of  
Science in Polymer Technology

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February 2020

## **DECLARATION OF THE CANDIDATE & SUPERVISOR**

I declare that this is my own work and this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgment is made in the text.

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Date: 17/02/2020

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## ABSTRACT

The purpose of this research is to study the effect of modification of incorporation sequence of accelerator and activators on cure characteristics, physical properties, mechanical properties and dynamic properties of solid tire middle compound.

Accelerator-activator masterbatch (MB) was prepared by mixing activators & accelerator in a rubber phase. A series of masterbatches were prepared using different concentrations and maturation periods of accelerator-activator combination and pre-vulcanization inhibitor. They were subsequently used in 1<sup>st</sup> stage compound mixing of a solid tire middle compound. Cure characteristics and selected properties of these masterbatches incorporated solid tire middle compounds were studied. Economics analysis of the best system among the candidate systems was also carried out.

It was found that the cure rate index improved by 52% with the accelerator-activator MB compared to the conventional method of curatives usage when 58.5 pphr accelerator-activator MB is used. No significant effect of the maturation time of MB on the cure characteristics and other properties was found. With the incorporation of activators and accelerators in the MB form, scorch time of the compound showed a slight drop which was overcome by the addition of 0.3 pphr pre-vulcanization inhibitors at the 2<sup>nd</sup> stage mixing stage.

Mechanical properties, dynamic properties, and visco-elastic properties of vulcanizates prepared using accelerator-activator MB and conventional methods were compared. Tensile strength, elongation at the break, blow-out time and storage modulus showed an improvement when MB incorporated vulcanizate with a slight reduction in 300% modulus, heat build-up, crosslink density, and loss modulus.

It was found that cure rate index improvement achieved associated with the reduction of curing cycle and energy consumption by around 10% and 12% respectively while maintaining other properties studied within the standard range of the conventionally prepared ones.

Key Words: Vulcanization, Accelerator, Activator, Masterbatch, Cure rate index, Optimum cure time, curing cycle time, Solid tire middle compound

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## LIST OF ABBREVIATIONS

Abbreviation	Description
6PPD	N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
AAMB	Accelerator Activator Masterbatch
ALK	Alkanolamide
ASTM	American Society for Testing & Materials
BR	Butadiene Rubber
CB	Carbon black
COM	Cost Of Manufacturing
CRI	Cure Rate Index
CTP	N-(cyclohexyl-thio)phthalimide
CV system	Conventional curing system
DBP	Dibutyl Phthalate
DMA	Dynamic Mechanical Analyzer
DTB	1-phenyl- 2,4-dithiobiuret
EAB	Elongation at Break
EPDM	Ethylene Propylene Diene Monomer
Et al	And Others
EV system	Efficient curing system
FEA	Finite Element Analysis
FF	Fast-extruding Furnace
GDP	Gross Domestic Product
GPF	General Purpose Furnace
MB	Master Batch

MDR	Moving Die Rheometer
$M_H$	Maximum Torque
$M_L$	Minimum Torque
NR	Natural Rubber
ODR	Oscillating Disk Rheometer
PPHR	Parts Per Hundrands of Rubber
PRL	Plastic Retention Index
PVC	Poly Vinyle Chloride
RPA	Rubber Processing Analyzer
RSS	Ribbed Smoke Sheet
SBR	Styrene Butadiene Rubber
SG	Specific Gravity
SRF	Semi Reinforcing Furnace
$t_{90}$	Optimum Cure Time
TBBS	N-Tert-Butyl-2-Benzothiazole Sulfenamides
TMQ	Polymerized 2,2,4-Trimethyl-1,2-dihydroquinoline
TMTD	Tetramethylthiuram Disulfide
TMTM	Tetramethylthiuram Monosulfide
$t_{s2}$	Scorch Time
TSR	Technically Specified Rubber
ZnO	Zinc Oxide

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# **1. INTRODUCTION**

## **1.1 Background of Rubber Industry in Sri Lanka**

Rubber plantation was started in Sri Lanka in 1876 with planting 1,919 Brazilian rubber seedlings received from Kew Gardens in London. It was gradually expanded as commercial plantations and raw rubber produced was directly exported until the end of the 1930s. Value addition to the raw rubber which began in 1940 has been appreciably grown since early 1980 with the investments made by foreign and local investors by means of funds, technology, and management. At present, the Sri Lankan rubber industry manufactures a wide range of value-added globally competing rubber products such as tires, latex gloves, latex treads, clothing products, etc in significant quantities. Other than those, rubber carpets, hoses, rubber mats, bushes and sealing, footwear are some products that are also produced and exported. The entire sector contributes to 10% of Sri Lanka GDP [1].

Rubber industry can be categorized into two major sectors as dry rubber industry & latex industry. The dry rubber industry is the industry that uses rubber as a raw material in solid-state such as Ribbed Smoke Sheet (RSS), Crepe rubber and Technically Specified Rubber (TSR). The tire sector covers a major portion of the dry rubber industry in Sri Lanka which has approximately a 60% share of export turnover of rubber products exports in Sri Lanka. The tire industry in Sri Lanka consists of solid tires, pneumatic tires, bicycle tires, three-wheeler tires and different smaller tires as caster wheels. Solid and pneumatic tires contributed US\$ 549 Mn for exports in Sri Lanka in 2018. Currently, Sri Lanka is the leader of a solid tire exporter which full fills 25% of global demand [1].

## **1.2 Solid Tire**

Solid tire plays an important role in off-the road vehicle market due to its unique features. Solid tire is puncture resistance and therefore, it is a maintenance-free and economical product. Also stability, high load-bearing capacity in extreme conditions, less vibration, high wear resistance are some other features of solid tires which make them ideal for forklifts, airport vehicles, heavy-duty transport vehicles, platform

trucks, and other industrial vehicles. Solid tires can be categorized into three main subgroups as Resilient tires, Press-On tires, and Cured-on tires.

Resilient tires are strengthened by using beads. There are two-layer and three-layer resilient tires. Two-layer tires consist of heel compound and tread compound. The additional layer found in the three-layer resilient tire is the middle compound.



*Figure 1.1: Cross-section of the solid resilient tire*

Heel compound is the hardest compound layer in the resilient tire which has Shore A hardness 85. It helps to fit the tire on to the rim and bare high load during tire application. Therefore, the heel compound should be formulated to obtain a high compression load and better compression set properties. The tire should not slip on the rim during running and a better grip between rim & tire is provided by a combination of high hardness, high compression set and compression load in the heel compound.

Tread is the upper part of the resilient tire and it is the part which contacts with the floor. The tread compound should have better traction in both wet & dry surfaces. Other than traction, the tread compound is formulated to have better wear resistance, low heat build-up, chunking resistance, low rolling resistance. In many cases, a tread compound is formulated by using 100% of natural rubber, but in some cases, where wearing resistance is predominant, a blend of natural rubber with synthetic rubber-like SBR, BR is used.



The middle compound is an important segment in the three-layer resilient tire because it gives the cushioning effect for the resilient tire. Shore A hardness of the middle compound is around 60-65. To obtain low hardness, high particle size carbon blacks such as Fast-extruding furnace black (FF – N550), General-purpose furnace black (GPF-N660), Semi-reinforcing furnace black (SRF-N762) are used during compound designing of the middle compounds. Other than the cushioning effect, the middle compound should possess low hysteresis (low heat build), low rolling resistance, better thermal conductivity, and high rebound resilience to yield good performance of a resilient tire. The efficient curing system forms mono-sulfidic crosslinks which have more sulfur-carbon links. The conventional curing system forms poly-sulfidic crosslinks which have more sulfur-sulfur links. Bond energy is higher in sulfur-carbon links than sulfur-sulfur links. Consequently, mono sulfidic cross-links possess the highest thermal stability while poly-sulfidic networks possess the least thermal stability. During tire application heat is generated and accumulated in the middle. Therefore, thermal stability of the cross-links formed in the middle compound is an important requirement while assuring a higher fatigue life of the resilient tire. Generally, semi efficient curing systems are used for the middle compound in order to have a thermally stable cross-linking network and have better dynamic properties. The required curing system is generally achieved by adjusting the sulfur and accelerator ratio during the compounding mixing.

### **1.3 Compound mixing**

Irrespective of the above-mentioned vulcanization systems, all rubber compounds, should be undergone through the compound mixing process before building solid resilient tires. An internal mixer is used to mix all ingredients such as fillers (CB, silica), processing aids, activators, antioxidants, crosslinking agents, accelerators with the base polymer to have better-filled rubber compounds. However, rubber compound mixing is done in two steps in the preparation of solid tire middle compounds. In the first step, fillers and the other chemicals except curative agents and accelerators are mixed with rubber and it is called a 1<sup>st</sup> stage compound mixing. Normally activators (stearic acid, ZnO) are added to the compound at the 1<sup>st</sup> stage compound mixing. During 1<sup>st</sup> stage compound mixing, the temperature will be

increased to around 150-160 °C to have better filler incorporation, distribution, and dispersion.

Then 1<sup>st</sup> stage compounds are kept around 16 hours for maturation after which, second step mixing is performed using 1<sup>st</sup> stage compounds and curatives. Accelerators & sulfur is added to the compound at the 2<sup>nd</sup> stage compound mixing. During the 2<sup>nd</sup> stage mixing, the temperature should be maintained under 110 °C to prevent pre-curing. Accelerator-activator complexes are formed during the curing and hence it will take time to start the cross-link formation.

#### **1.4 Solid Tire Building and Vulcanization**

Tire building is commenced after the preparation of all the above three different compounds. Two roll mill is used to warm-up the compounds and build the green tire by rolling on the mill with the help of the collapsible core. As a first step heel compound is rolling on the inner heel which has steel beads. Then the middle compound is rolling on the heel and finally tread. During tire rolling, the compound temperature maintains at around 95-105 °C. At this stage, the rubber compound is at a plastic state. It does not have any technical use other than form any shape at the green tire stage. To convert this plastic rubber compound to an elastic rubber product, the vulcanization (or curing) process needs to be completed. Heat is provided under the compression load to vulcanize the three rubber compounds in the build green tire to form the final product (solid resilient tires). This step is one of the crucial steps determines the cost of manufacturing (COM) and product performance.

#### **1.5 The problem associated with the Solid Tire Vulcanization**

In the Sri Lankan solid tire industry, many companies are using 140-150 °C temperature to carry out the vulcanization or curing. To obtain this temperature electric heater (ovens) or steam are used. The major problem during solid tire manufacturing is the achievement of the complete and uniform vulcanization in the middle compound in a reasonable time scale. The thickness of the solid tire is very much higher than the other rubber products. Therefore, the inner compound (middle compound) should be totally cured before de-molding.

Figure 1.2 is illustrating that the heat flow of the solid tire during vulcanization. Heat is supplied to the outer mold and to the inner core. This heat is transfer to the middle compound through the tread and heel compounds while completing the vulcanization of these two compound layers first. Curing time of the whole tire should have good enough to vulcanize the center portion of the solid tire which is known as the critical point. If the middle compound has a lower cure rate, then vulcanization time will be increased.

Vulcanization time of solid resilient tire is varied 1.5 hours to 8 hours depending on the size of the tire. Table 1.1 shows some ideal curing cycles for the different solid tire sizes. These long curing cycles consume higher energy costs, labor costs, overhead costs, etc which is a huge problem for the solid tire industry. This will also impact productivity and finally, the cost of manufacturing (COM) will increase.

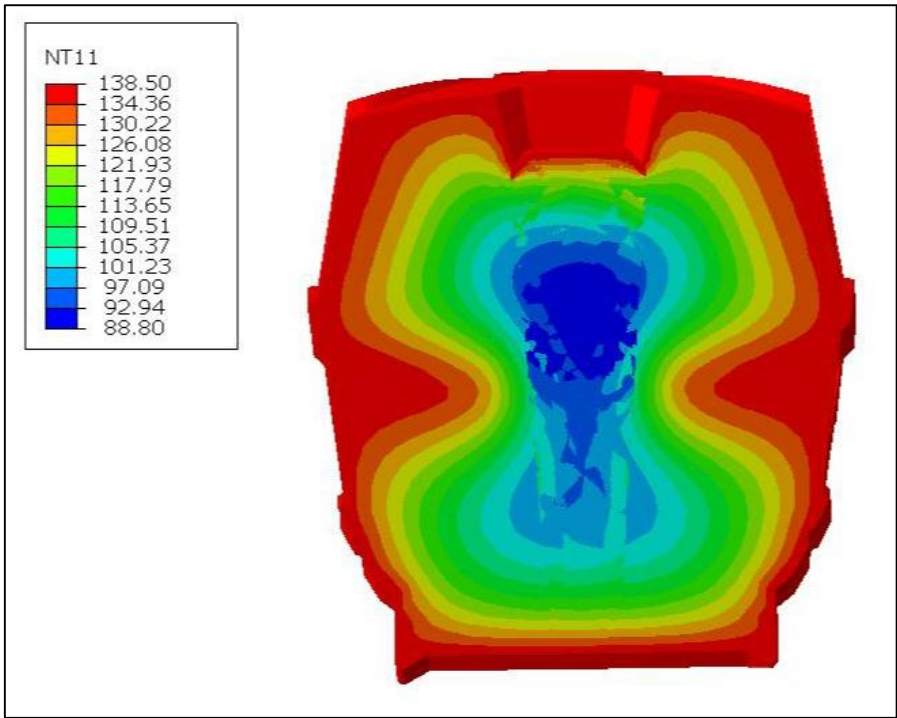


Figure 1.2: FEA middle of temperature profile during vulcanization of solid tire

Table 1.1: Summary of curing cycles for resilient tires

<b>Tire size</b>	<b>Curing cycle time (Hrs: min)</b>	<b>Energy (MJ)</b>
18x7-8	1:40	52.9
7.00-12	2:00	118.4
23x9-10	2:30	120.9
3.00-15	2:45	277.2
12.00-20	3:40	554.4
14.00-24	8:00	705.6

To overcome this issue, the solid tire industry has given high priority to improve the cure rate of the middle compound and reduce the curing time of the solid tires because a small amount of cure rate improvement of the middle compound is largely affected for the solid tires due the thickness of the product. This will increase productivity and save energy ie reduction in the COM in order to improve competitive advantage.

### **1.6 Research Objectives**

The objectives of the study are;

- To develop a new vulcanization process to shorten the vulcanization time by improving the cure rate of solid tire middle compounds
- To compare the curing characteristics of rubber compounds prepared with the new process and conventional process
- To compare the physical, mechanical and dynamic properties of rubber vulcanizates prepared with the new process and conventional process

## **2. LITERATURE REVIEW**

### **2.1 Rubber vulcanization**

#### **2.1.1 Introduction of Rubber Vulcanization**

Vulcanization or curing process of natural rubber (heating natural rubber with sulfur) was invented by Charles Goodyear in Springfield, Massachusetts in 1839 [2]. Except few rubber products such as shoe soles and rubber-based adhesives, rubber compounds of all most all the rubber products such as tires, hoses, gloves, gaskets, seals, etc are vulcanized to obtain required product properties and performance since un-vulcanized rubber is generally a weak material which has no capability to maintain its shape after a great deformation and resist the thermal oxidation to avoid being sticky under heated environment [3].

An elastomer is a high molecular weight material with low elasticity. Un-stressed state these molecules are entangled and they can readily disentangle upon stressing leading to viscous flow. During vulcanization these long chains are chemically linked together to form a network, thereby transforming the material from a viscous liquid to tough elastic solid. In other words, vulcanization increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force. Thus vulcanization increases elasticity while it decreases plasticity [4]. A model for network formation through sulfur vulcanization of elastomeric material is presented in Figure 2.1. According to the theory of rubber elasticity, resistance to the deformation of rubber articles under the force is proportional to the number of crosslink points per unit volume of the material elastomer [3].

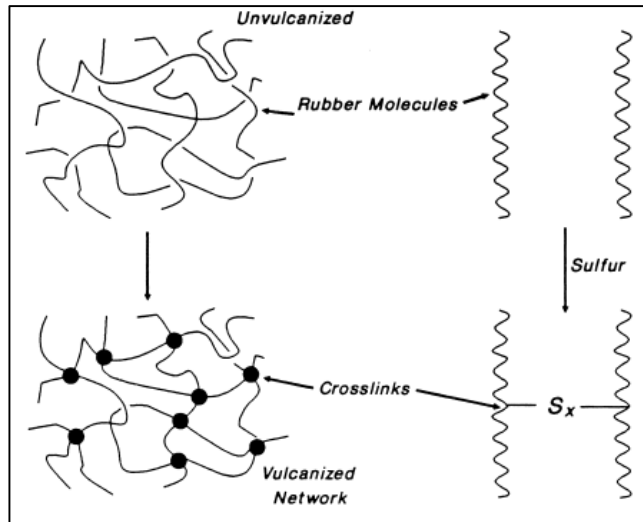


Figure 2.1: Network formation during Sulfur vulcanization

Source: [3]

The vulcanization process of elastomers changes material properties depending on the degree of cross-linking. Major property changes due to vulcanization are illustrated in Figure 2.2. As it is shown in Figure 2.2, hysteresis, which is the ratio of viscous part to the elastic part of deformation resistance is reduced with increasing crosslink density [3]. In other words, it is the energy that is lost during deformation without storing. It is a positive effect when the performance such as rolling resistance, heat build-up of the solid tires are considered. Breaking energy of vulcanized (cured) rubber articles can be described by tear strength, fatigue life, and toughness. These properties increase with a small amount of crosslinking, but they are reduced by further crosslink formation. Tensile strength is increased up to some extent of the crosslinking and after that it reduced. Elastic recovery and the stiffness gradual increases with the cross-link density [3].

However, it should be noted that these properties are not a function of only cross-link density, as they are also influenced by other factors such as type of polymer, type of the filler, it's loading, etc [3].

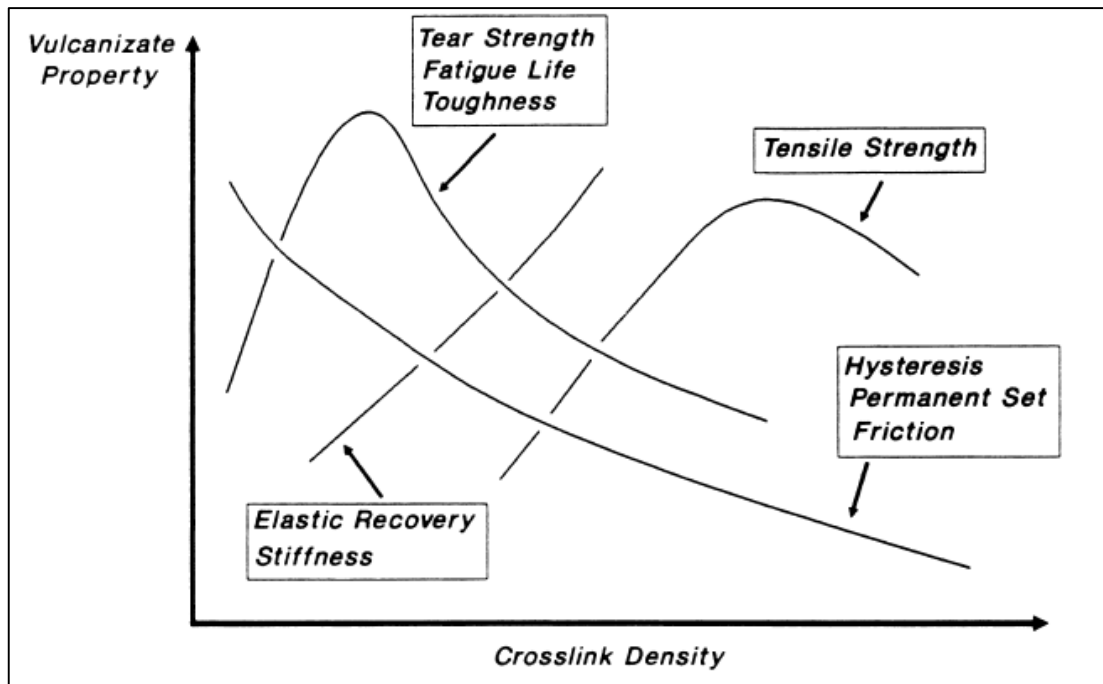


Figure 2.2: Vulcanizate properties as a function of the extent of vulcanization  
Source: [3]

### 2.1.2 Vulcanizing agents

There should be a cross-linking agent to form cross-links between elastomer chains. Sulfur is the most common material which is used as a cross-linking agent for general purpose rubbers like NR, SBR, BR. Other than that, the following materials are also used as cross-linking agents for rubbers depending on the rubber molecular structure and the application of the product [4].

- Organic Peroxide
- Metallic Oxide
- Organic Amines
- Phenolic Resins

Table 2.1 gives a general account of the use of the above types of crosslinking agents in different rubbers.

Table 2.1: Types of vulcanizing agents & their usage

Type	Common Uses
Sulfur or Sulphur bearing materials.	Natural Rubber, Isoprene, SBR, Butyl, Poly Butadiene, EPDM, Nitrile, Norsorex.
Organic Peroxides	Urethane, Silicone, Chlorinated Polyethylene, Crosslinked Polyethylene, Vamac, Vynathene, PVC/Nitrile.
Metallic Oxide	Polychloroprene, Chlorosulphonated Polyethylene, Polysulphide
Organic Amines	Acrylic, Fluorocarbon, Epichlorohydrin, Vamac.

Only having a crosslinking agent (specially Sulphur) around 8 pphr in the vulcanization system, it may take 5-6 hours to form crosslinks in the polymer matrix. To accelerate the vulcanization process, accelerators and activators are used along with the sulfur in the vulcanization system in the rubber industry. It will significantly reduce crosslinking formation time to 30-45 minutes [2]. Stearic acid and zinc oxide are used as activators and Sulfenamides, Thiurams, Thiazoles are some of the common accelerators used in the tire industry [2]. Table 2.2 shows the development of the sulfur vulcanization system through the introduction of activators and accelerators to achieve shorter vulcanization cycles. It clearly shows the influence of accelerators in shortening the optimum vulcanization period [2].

Table 2.2: Reduction of vulcanization time obtained over 70 years

Year	1850	1880	1905	1920
<b>Natural Rubber</b>	100	100	100	100
<b>Sulfur</b>	8	8	6	3
<b>Zinc Oxide</b>	-	5	5	3
<b>Aniline</b>	-	-	2	-
<b>Stearic Acid</b>	-	-	-	1
<b>2-Mercaptobenzothiozole</b>	-	-	-	1
<b>Optimal Vul. Time at 142 °C, min</b>	360	300	180	30

Source: [2]



### 2.1.3 Structure of a Sulfur Vulcanizate

Elemental Sulfur or Sulfur donors are used to vulcanized rubber and sulfur is combined with the vulcanization network in different ways. It is depended on the Sulfur dosage, accelerator type, accelerator: sulfur ratio and the cure time [5]. Sulfur can be present as mono-sulfide (only one sulfur atom between two rubber chains), di-sulfide (two sulfur atoms between two rubber chains) or poly-sulfide (more than two sulfur atoms between two rubber chains) and mainly it will depend on the accelerator/sulfur ratio It is shown in Figure 2.3 (a). Other than these three methods, Sulfur can be attached to the rubber chains as pendant sulfides terminated by moiety X, derived from the accelerator, or cyclic monosulfides or disulfides [4]. These crosslinking types are shown in Figure 2.3 (b) & (c) respectively [4].

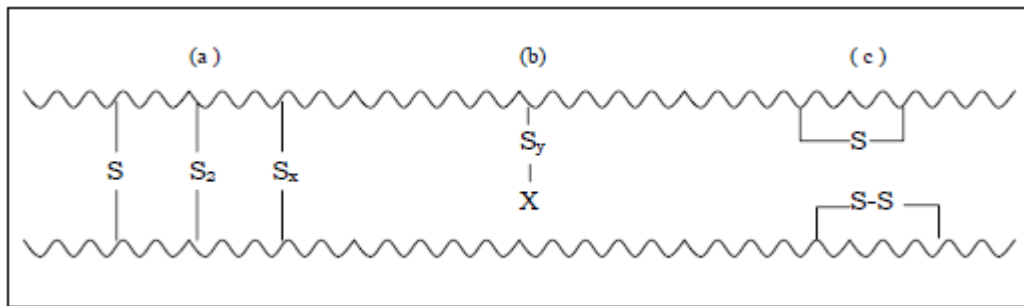


Figure 2.3: (a) Mono, di, polysulfide links, (b) Pendant sulfide, (c) Cyclic sulfide  
Source: [4]

Vulcanization along with the Sulfur (un-accelerated vulcanization) is a very slow process & chemistry behind this is controversial. Some researches proposed mechanisms involving free radicals is given in Figure 2.4 [4].

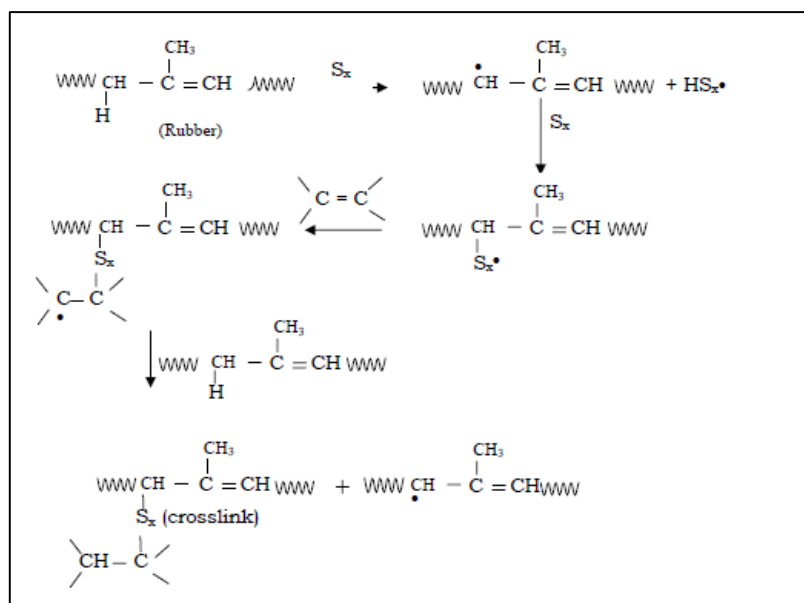


Figure 2.4: Un-accelerated vulcanization by sulfur, free radical mechanism  
Source: [4]

#### 2.1.4 Accelerators for Sulfur Vulcanization

Sulfur vulcanization with an accelerator (around 1pphr of an accelerator to 2-3 pphr of Sulfur) shortened the cure cycle while improving the vulcanizate properties. At the beginning of the acceleration of sulfur vulcanization, aniline was discovered by Oenslager in 1906 as an effective accelerator for sulfur vulcanization. Then further studies were continued and as a result, a series of accelerators such as guanidine, thiurams, and dithiocarbamates were found in 1919 [4]. These accelerators are activated the crosslinking quickly and hence these are known as very fast accelerators. Scorch time is very low. Therefore, these accelerators are not suitable for thick article vulcanization and therefore, they are mainly limited to the latex product industry where generally thinner rubber products are manufactured [4].

To have better vulcanization particularly for thick rubber articles together with scorch time, delayed action accelerators were invented in 1925. Some of the examples for such accelerators are thiazoles (MBT, MBTS) [4]. Further scorch time and fast vulcanization were needed to produce much thicker rubber products and as a solution, sulfenamide (CBS, TBBS) was invented in 1937 [4]. At present,

sulfenamide is the most common accelerator that is used in the solid tire industry to have better scorch time and fast cure.

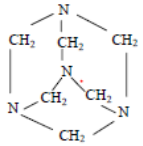
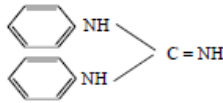
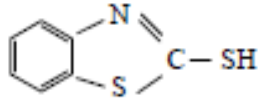
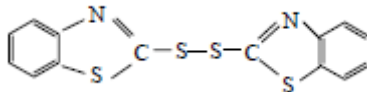
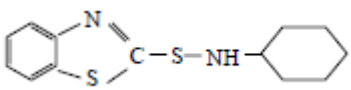
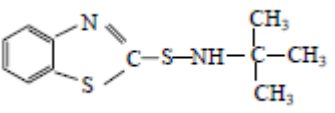
In general, there are some common practices that have been introduced in the rubber industry to achieve a shorter cure time with adequate scorch time as briefed below [4].

- Use a single accelerator system (primary accelerator) – sufficient cure within the specified time
- Combination of two or more accelerators (high amount of primary accelerator & low amount of secondary accelerator) – to have better vulcanizate properties
- Delayed action accelerators – to have safe scorch time as well as the fast cure rate

Numerous accelerator groups have been developed and are being developed in the rubber industry to meet different objectives ie. adjust scorch time, adjust cure rates, health safety, and their combinations. Table 2.3 lists some of the principal accelerators in each of the main types together with examples and remarks on their properties. Figure 2.5 shows the different accelerator families and their influence on the vulcanization process [3].

Summary of the effect of different accelerators on scorch time, cure rate, and crosslink density can be visualized as Figure 2.6.

Table 2.3: Accelerators for sulfur vulcanization

Type	Example & Structure	Remarks
Aldehyde amines	Hexamethylene Tetramine (HMT) 	<ul style="list-style-type: none"> <li>- Moderately fast</li> <li>- Primary accelerator for NR and synthetic rubbers</li> <li>- Occasionally used as a secondary plasticizer</li> <li>- Used in self-curing adhesive</li> </ul>
Guanidine	1,3 Diphenyl Guanidine (DPG) 	<ul style="list-style-type: none"> <li>- Moderately fast</li> <li>- Secondary accelerator for thiazoles, sulfenamides, and thiurams</li> </ul>
Benzothiazole	Mercaptobenzothiazole (MBT)  Dibenzothiazyl disulfide (MBTS) 	<ul style="list-style-type: none"> <li>- Fast accelerator</li> <li>- Tend to be scorch</li> <li>- General-purpose</li> <li>- Primary accelerators for NR &amp; synthetic rubber</li> <li>- Delayed action</li> <li>- Safe processing</li> <li>- Moderate cure rate</li> <li>- Primary accelerator for NR</li> </ul>
Sulfenamides	N-cyclohexyl benzo thiazyl sulfenamide (CBS)  N-t-butyl -2- benzothiazole sulfenamide(TBBS) 	<ul style="list-style-type: none"> <li>- Delayed action, semi ultra-Safe processing</li> <li>- Moderate cure</li> <li>- For NR and synthetic rubbers</li> <li>- Delayed action</li> <li>- primary accelerator for NR and synthetic rubbers</li> </ul>

Dithiocarbamates	<p>Zinc diethyldithiocarbamate (ZDC)</p> $\left\{ \begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right\} \text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{S} \Bigg\}_2 \text{Zn}^{++}$ <p>Sodium diethyldithiocarbamate (SDC)</p> $\begin{array}{c} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{S} \cdot \text{Na}^+$	<ul style="list-style-type: none"> <li>- Delayed action</li> <li>- Safe processing</li> <li>- Primary accelerator for NR &amp; synthetic rubbers</li> <li>- Ultra accelerator</li> <li>- Low-temperature use</li>   <li>- Water-soluble ultra accelerator used for latex</li> </ul>
Thiurams	<p>Tetramethylthiuram disulfide (TMTD)</p> $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{S} - \text{S} - \overset{\text{S}}{\parallel} \text{C} - \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{N}$ <p>Tetramethyl thiuram monosulfide (TMTM)</p> $\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{N} - \overset{\text{S}}{\parallel} \text{C} - \text{S} - \overset{\text{S}}{\parallel} \text{C} - \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{N}$	<ul style="list-style-type: none"> <li>- Ultra-fast accelerator</li> <li>- Safe, especially good for IIR &amp; CR</li> <li>- Excellent for fast press cure</li>   <li>- Ultra-fast accelerator</li> <li>- Booster for thiazoles especially for nitrile rubber</li> </ul>

Source: [4]

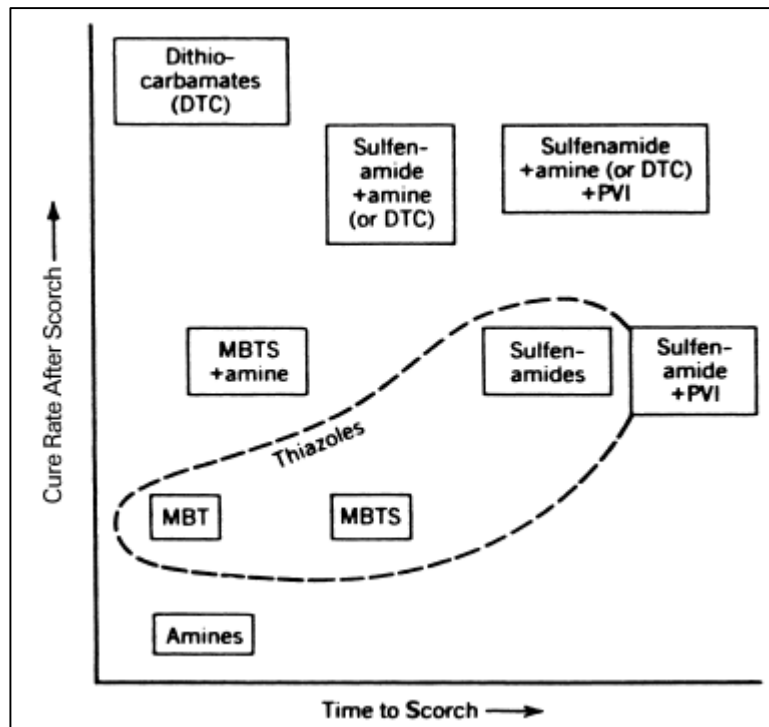


Figure 2.5: Vulcanization characteristics given by various accelerators

Source: [3]

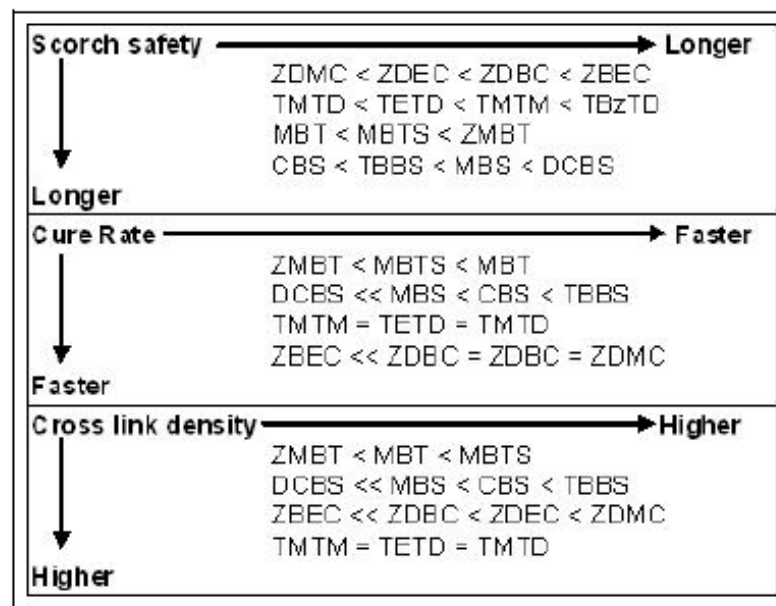
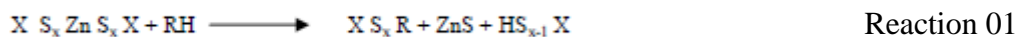


Figure 2.6: Summary of the effect of different accelerators

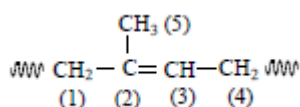
Source: [5]

### 2.1.5 The Chemistry of Accelerated-Sulfur Vulcanization

As an initial step of the vulcanization sulfur react with the zinc salt of the accelerator by forming perthio-salt,  $XS_x Zn S_x X$ , where X is a group derived from the accelerator. This salt reacts with rubber hydrocarbon as reaction 01 [4].



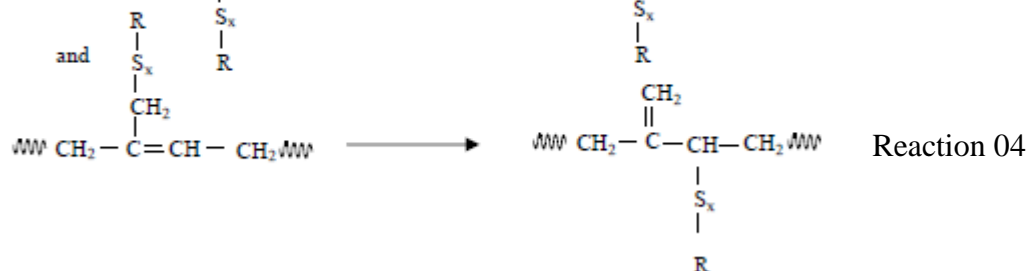
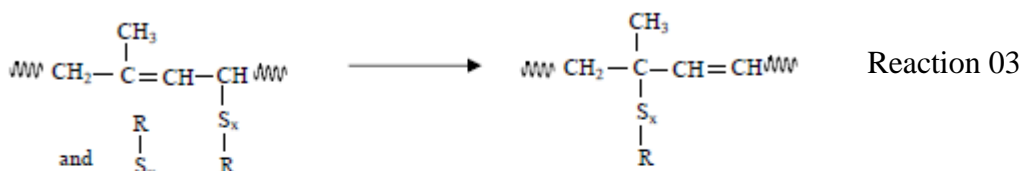
A removed hydrogen atom is attached to the natural rubber. The most likely position would be a methylene group in the  $\alpha$ - position to the double bond. The hydrogen atoms at positions 4 and 5 are the most labile in this type of reaction [4].



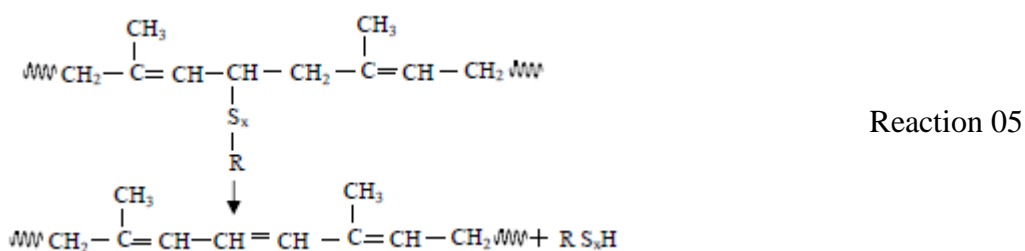
On the other hand, intermediate  $XS_x R$  reacts with the rubber hydrocarbon molecule RH by forming a crosslink and also regenerating more accelerators.



Degree of polysulfides crosslinks decreases due to prolonged heating and crosslinks which are at the position 4 & 5 undergo an allylic shift by forming new molecule configurations [4].



Conjugated trienes are forming by the disappearing of disulfide and polysulfide crosslinks.



### **2.1.6 Activators for Sulfur Vulcanization**

Only by using accelerators are not effective in terms of cure rate, because it should be activated to perform the crosslinking formation. Therefore, activators are used to activate the accelerators to increase the vulcanization rate. Activators can be grouped as follows.

- a. Inorganic compounds (metal oxides): Zinc oxide is the common activator that is used in the tire industry. A fatty acid is used together with zinc oxide to form a rubber soluble soap in the rubber matrix. The normal use level of zinc oxide is 2 to 5 pphr. Other than zinc oxide hydrated lime, litharge, red lead, white lead, magnesium oxide also used as an activator [4].
- b. Organic acids: Stearic acid is the most common fatty acid used in the tire industry together with zinc oxide. Organic acids are generally monobasic fatty acids or mixtures of the types, stearic, oleic, lauric, palmitic and myristic acids, and hydrogenated oils from palm, castor, fish, and linseed oils [4]. The normal use level of zinc oxide is 1 to 3 pphr.

Fatty acids together with zinc oxide (or metal oxide) make a salt which can be formed intermediate complex reacting with accelerators. Sulfur is activated by these complex and hence increases the cure rate by forming crosslinking effectively [4].

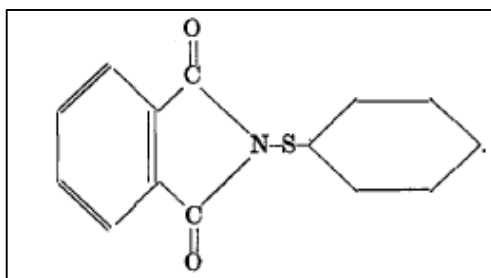
### **2.1.7 Pre-vulcanization Inhibitors and Retarders**

The curing system is activated by heat & heat is generated during the processing like mixing, milling, extrusion, calendaring, etc. In the rubber industry, faster processing is desirable for economic reasons. There is a conflict between the processing and curing stages. The balance of these two is required to have the best economical product with having rapid curing after it is processed [6]. There are some accelerators (especially Sulfenamides) which provide scorch delay time during processing (initial part of the heating) without crosslinking, then after rapid crosslinking formation. Therefore, only thing is needed to adjust process conditions to provide enough heat history to eliminate most of the scorch delay so that the cure time will be minimized. But in some times uncontrollable changes may happen in factory equipment like



internal mixers, warming mills, extruders, calendars, and operating parameters. This will be a cause for un-processable (scorched) compounds [6].

This issue could be overcome by adding some additive which increases only the scorch delay time with minimal effect on other cure parameters and vulcanizate properties [6]. Such materials are called as pre-vulcanization inhibitors or retarders. The most common inhibitor used in industry is N-(cyclohexyl-thio)phthalimide (CTP). Its structure is shown in Figure 2.7.



*Figure 2.7: Structure of CTP*  
Source: [6]

Normally, scorch time linearly increases with the incremental addition of CTP in different sulfur base curing systems. This effect is shown in Figure 2.8 for an NR-BR blend with three Sulfenamides accelerators [6]. CTP increases scorch delay with little or no significant effect on cure rate and vulcanizate physical properties. CTP can also be used together with secondary accelerators like TMTM, TMTD to obtain a faster cure rate with good scorch delay [6]. CTP also can be used to prevent the reworking or scrap compounds which have marginal processing safety but not yet cross-linked. Fully compounded rubber compounds (green stock) need to be stored for some days before it takes to the production. During this period scorch delay time is gradually reduced due to slow reactions of the curing system at ambient temperatures. This problem also can be controlled by the presence of CTP [6].

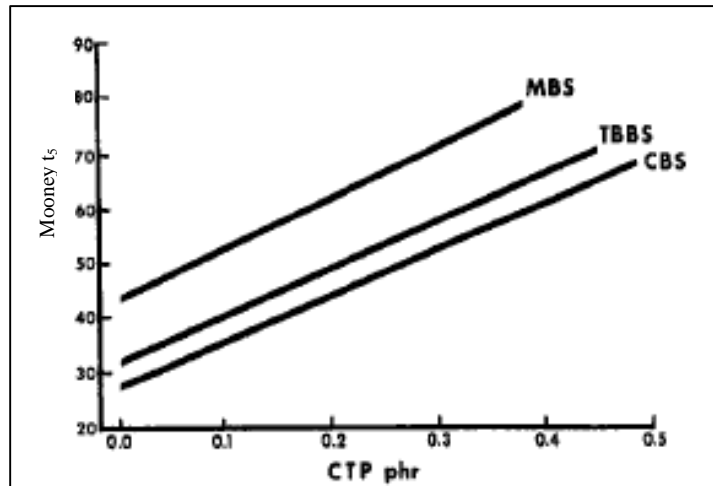


Figure 2.8: Effect of CTP level on scorch delay

Source: [6]

Reactions that happens when CTP is used together with MBT is illustrated in Figure 2.9. CTP molecules can react rapidly with MBT. As a result, there is depletion of the accelerator and thereby stopping the vulcanization process. Further, reactive species generated from CTP can quench the crosslinking precursor thiyl radicals. Hence CTP is effective in preventing premature vulcanization [7].

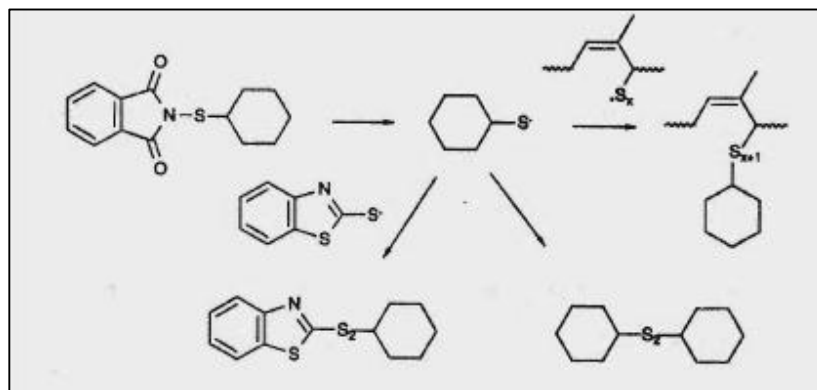


Figure 2.9: Reactions of CTP & MBT

Source: [7]

## 2.2 Factors Affected to the Vulcanization & Vulcanizate Properties

As discussed earlier, vulcanization is a chemical process that linear rubber molecules transformed into a three-dimensional network by forming crosslinks due to reactions between vulcanizing agents and accelerators under certain temperature & pressure

conditions. Vulcanization and its properties are depended on several factors. Therefore, controlling such factors is very important to undergo effective vulcanization.

### 2.2.1 Vulcanization temperature & time

Vulcanization temperature & time has a significant effect on the crosslinking structure. The lowest possible temperature gives the optimum properties for the cured product and the cure characteristics behaviors with the change of temperature are shown in Figure 2.10. But to improve productivity, high temperature is used in the rubber industry, especially solid tire industry [5]. Like all chemical reactions, vulcanization reactions also accelerated with the temperature. As a result, at a high temperature, it is easy to form more low sulfur crosslinks. Formed poly-sulfidic crosslinks are converted to shorter crosslinks ie. mono-sulfidic, di-sulfidic or shorter crosslinks due to the longer cure time with sacrificing high tensile strength, tear strength & flex-fatigue resistance. Therefore, optimum vulcanization time is necessary to have better performance as well as increase productivity [5].

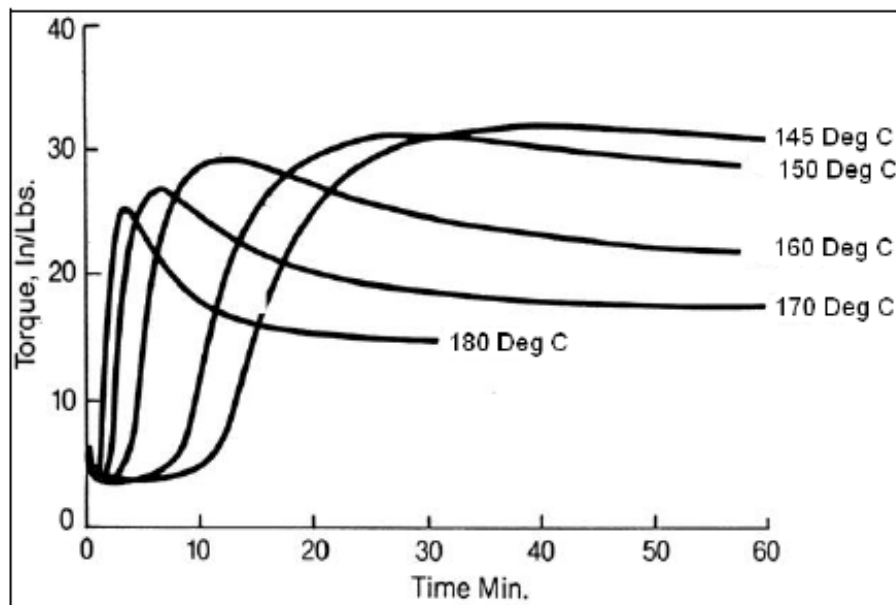


Figure 2.10: Cure curves behavior with temperature

### **2.2.2 Type of the Accelerator**

Different types of accelerators have their own characteristics and selection of the appropriate accelerator type or combination is very important. The following points need to be considered during the selection of the accelerator type [5].

- High solubility in rubber to avoid blooming and improve dispersion in the rubber matrix
- Required scorch time depending on the processing conditions
- Required cure rate & maximum vulcanization temperature available
- Desired crosslinking pattern and the properties
- No negative effect on other properties like aging, adhesion, etc
- Safety, regulations and the product application (food contact/ surgical use)

### **2.2.3 Accelerator: sulfur ratio**

The amount of accelerator and the sulfur is decided based on the accelerator: sulfur ratio depending on the required properties of the rubber product. There are three types of sulfur-based curing systems used in the rubber industry [5].

1. Conventional system (CV) – Accelerator: Sulfur ratio 0.1-0.6
2. Efficient system (EV) – Accelerator: Sulfur ratio 2.5-12.0
3. Semi Efficient system (Semi EV) - Accelerator: Sulfur ratio 0.7-2.4

Tensile strength, tear strength, flex-fatigue resistance is better in the CV system due to the presence of poly-sulfidic crosslinks. Heat aging properties and compression set properties are better in the EV system due to the presence of mono-sulfidic crosslinks. Semi EV system has balance properties which are most suitable for the solid tire middle compound.

## 2.3 Characterization of Vulcanization

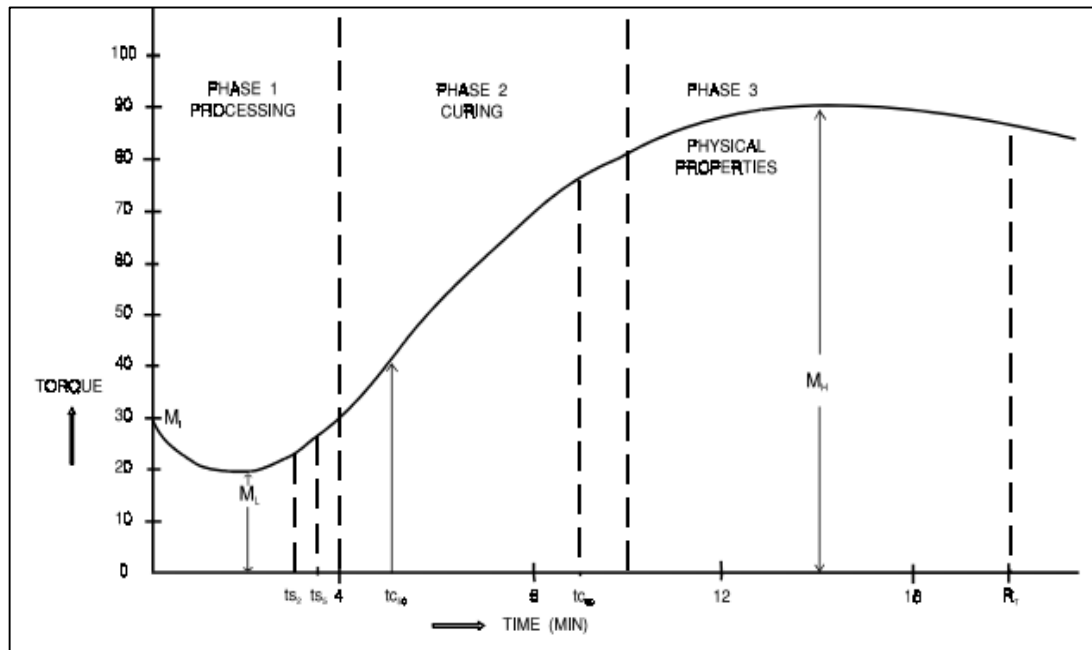


Figure 2.11: Rheometer cure curve and different phases of the cure curve

There are three major phases in the cure curve which shown in Figure 2.11. They are the processing safety phase, vulcanizing (curing) phase and physical property phase [8]. At the processing safety phase, the compound behaves as viscous (plastic) material. Therefore, it gives processability and the ability to withstand the heat history of the compound. Then in the vulcanizing phase, the compound is started crosslinking formation. The slope of this region gives the speed of cross-linking formation or in other words cure rate. Therefore, the shape and the slope of the cure curve are important to design the curing cycle of a solid tire. The aim of this project is to increase this slop of the curve and increase the cure rate. The latter part of the curve gives some indication about physical properties and maximum torque gives some indication on crosslink density. If formed crosslinks are distorted due to thermal energy, then reversion will be there at the end [8]. The followings are the important measurements that can get from the MDR cure curve.

- $M_L$  (Minimum torque): The lowest value of the torque of the cure curve is known as  $M_L$ . Due to the heat and pressure, the viscosity of the compound decreases and torque falls. It is a measure of the viscosity of the unvulcanized compound.
- $M_H$  (Maximum torque): The maximum value of the torque of the cure curve is known as  $M_H$ . Due to the crosslink formation, stiffness of the compound increases and torque also increases accordingly.
- $t_{s2}$  (Scorch time): It is the time to reach a two-unit increase in torque above the  $M_L$ . It gives processing safety time of the compound which can be used before starting the vulcanization.
- $t_{90}$  (Optimum cure time): It is the time to reach a 90% cure has taken place. Curing cycles are designed based on this result.

Other than the above direct readings, the cure rate index can be calculated by using the above values. After the scorching point, cross-linking formation is started and the rate of cross-linking formation is known as cure rate index. It is indicated by the slope of a linear part of the rising curve [8]. The calculation method of the Cure Rate Index is as equation 01.

$$\text{Cure Rate Index} = 100 / (t_{90} - t_{s2})$$

Equation 01: Cure rate index calculation

Irrespective of the cure system, attempts are being carried out continuously to improve the cure rate while maintaining adequate scorch time, reduce the amount used in formulations and replace certain accelerators that are identified as risk chemicals. Some approaches that could be found in the literature for the improvement of the cure rate are discussed in the next section.

## 2.4 Cure Rate Improvement and Related Researches

Numerous studies have been carried out on the cure rate behavior of sulfur-based rubber compounds. Use of different curing ingredients, modification of curing ingredient incorporation and mixing sequences, a combination of curatives by

reacting them before incorporation are some of the areas studied to understand the effect of these changes on the cure rate of the sulfur vulcanization process.

Surya et al. incorporated alkanolamide (ALK) to unfilled NR based compounds and studied cure rate improvement. It was found that the compound which had used ALK have a higher cure rate than ALK free compound. According to his explanation, ALK was functioned as an additional accelerator which increased the number of reactive sites on the rubber molecules used for the crosslinking reactions. Up to 0.6 pphr of ALK crosslink density, tensile strength and modulus increased and exceeding this level, these properties are decreased. According to their explanation, a decrease in properties beyond 0.6 pphr loading of ALK may due to the “excessive amount of ALK which dissolved a part of the elemental sulfur and as a consequent, a less sulfur was attached to the NR chains” [9].

The influence of a binary accelerator system based on 1-phenyl-2,4-dithiobiuret (DTB) and sulfenamide accelerators on the cure rate and the other properties (curing characteristics/mechanical properties) are studied by Abi Santhosh Aprem et al. [10]. They have observed that the cure rate index increased with the DTB dosage. It was proposed that this was due to the reduction of the activation energy to start vulcanization reactions by secondary accelerator DTB. This was confirmed from the kinetic studies conducted by the research team.

Abu Hasan et al. conducted research to observe the effect of vulcanization temperature and ingredients mixing sequence on the vulcanization rate [11]. Results showed that higher vulcanizing temperature increases the vulcanization reactions and reaction rate constant. Different mixing sequences were studied like reducing mastication time, subsequent ingredient mixing (accelerators, CB, activators, antioxidants) rather than simultaneous ingredient mixing, etc. They have reported that both the reduction of mastication time and subsequent ingredient mixing increased vulcanization rate compared to the simultaneous mixing.

Upul Wijayantha et al. has reported the possibility of the use of combined curing ingredients to minimize the use of ZnO, stearic acid and TBBS contents in the recipe since these materials have safety issues on humans and the environment. In their

study, these materials are mixed in ethyl acetate solvent to functionalized ZnO with TBBS to obtain a single material that can be used as an additive [12]. Results have shown that the  $t_{90}$  reduced and cure rate index improved with the addition of combined curatives to the compound. This outcome is an additional advantage of their study because their aim was to reduce curatives. But this technique is not industrially viable in the solid tire industry because the formation of these kinds of single material yields several practical issues as well as economic barriers connected with the additional curative ingredient mixing process, disposal of solvent, etc.

The science behind cure rate improvement of the above-mentioned study was the possible formation of accelerator-activator precursor before those ingredients are incorporated into the rubber matrix. Instead of using a solvent, the rubber phase could be used as the reaction medium for the formation of the activator-accelerator complex eliminating the above-mentioned drawbacks found when a solvent is used. Therefore, accelerator-activator masterbatch (MB) could be prepared by the early incorporation of activators and accelerators found in a recipe in the rubber phase using an internal mixer. Then appropriate amounts of MB could be added during 1<sup>st</sup> stage mixing. Activator-accelerator complexes should have been formed at the MB and therefore, curing time is expected to be reduced since the complexes are already formed when the vulcanization starts as observed in the work carried out by Upul Wijayantha et al.

Studies focus on this approach are not reported in the literature. Various factors, such as curing ingredients concentration, reaction time allowed ect could have an effect on the cure rate. In our study, therefore, curing ingredient MB in the rubber phase was prepared to study the effect of ingredient concentration (stearic acid, ZnO, TBBS) in the accelerator-activator MB. To overcome any possible unsafe scorch time reduction, it is suggested to use pre vulcanized inhibitors at the final batch mixing stage and study the curing and vulcanizate performance.



### 3. MATERIALS AND METHODOLOGY

#### 3.1 Research plan

The main goal of this study was to increase the cure rate of solid tire middle compounds to reduce the vulcanization period without affecting the other compound properties and product performance. In this work, accelerator-activator MB was mixed before the 1<sup>st</sup> stage compound mixing and this MB was used for 1<sup>st</sup> stage compound mixing together with other materials. Experiments were planned under 04 different stages to identify the most promising recipe and mixing set-up to have the best results.

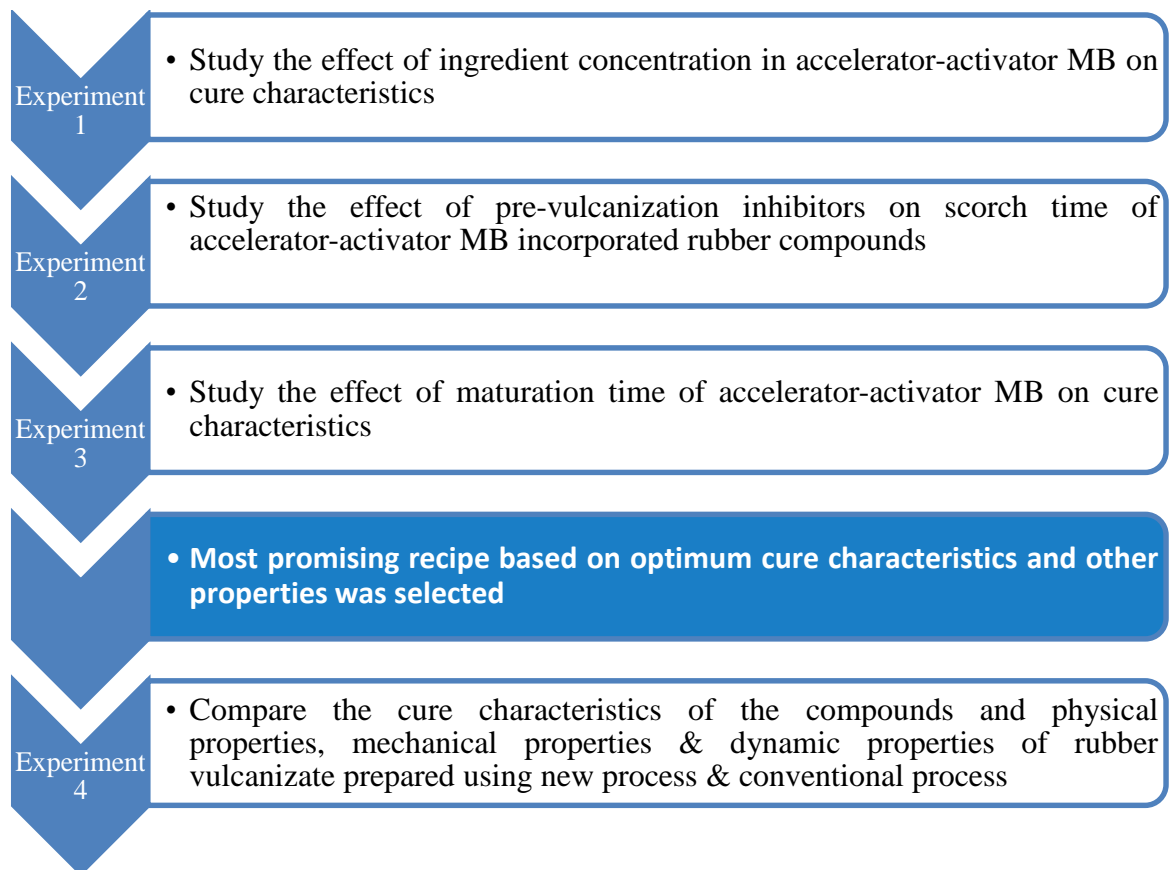


Figure 3.1: Research plan of the study

### 3.2 Materials

A typical solid resilient tire middle compound recipe was selected as a base formulation for this study. The base formulation and origin of the materials are given in Table 3.1.

Table 3.1: Base formulation and origin of materials

<b>Name of the Material</b>	<b>Origin/Manufacture</b>	<b>Quantity (pphr)</b>
<b>Polymer</b> (Natural rubber-TSR 20)	Thai Hua Rubber Public Co. Ltd, Thailand	100.0
<b>Semi-Reinforcing Filler</b> (Carbon black - N550)	SKI Carbon Black (Pvt) Ltd, India	45.0
<b>Organic Activator</b> (Stearic Acid)	IOI PAN Century Oleo Chemical SDN BH, Malaysia	2.0
<b>Inorganic Activator</b> (Zinc Oxide 99.5% purity)	Agromet Asia (Pvt) Ltd, Sri Lanka	4.5
<b>Protecting Agent-1</b> (N-[1,3-Dimethylbutyl]-N'-phenyl-p-phenylenediamine – 6PPD)	Shandong Sun Sine Chemical Co. Ltd, China	1.5
<b>Protecting Agent-2</b> (Polymerized 2,2,4-Trimethyl-1,2-dihydroquinoline – TMQ)	Shandong Sun Sine Chemical Co. Ltd, China	1.0
<b>Vulcanizing Agent</b> (Sulfur)	Miwon Commercial, Korea	1.6
<b>Accelerator</b> (N-tert-butyl-2-benzothiazole sulfenamide - TBBS)	Shandong Sun Sine Chemical Co. Ltd, China	2.0

In addition, N-(cyclohexyl-thio)phthalimide (CTP) supplied from Shandong Derec New Materials Co Ltd, China was used as a pre-vulcanization inhibitor and p-xylene (specific gravity-0.87 g/ml) was used as the solvent for the swelling test.

### **3.2.1 Quality consistency in raw Materials**

As explained in the research plan, four experiment stages were carried out during this study. Therefore, throughout all experiments, the same raw material source was maintained to minimize the material property variations. This action ensures the minimum influence of material quality variations on final results. However, raw materials from the different batches from the same source were used for different series of experiments. All the ingredients were of industrial grade and were used without further purification.

### **3.3 Compound preparation**

A Farrel BR1600 laboratory-scale Banbury mixer was used to perform all mixing processes of this experiment such as accelerator-activator MB mixing, 1<sup>st</sup> stage compound mixing & 2<sup>nd</sup> stage compound mixing. It is a variable speed mixer, but 80-100 rpm was maintained in all mixing stages. Compound ingredients (Table 3.2) were added based on the time of the mixing cycle presented in Table 3.3, but temperature also was taken into account to discharge the compound. Temperature behavior throughout the mixing cycle was taken. Rotors generate the friction ratio of 1:1.16 in this mixer. Four different experiments were conducted throughout the study and mixing sequences used for each one are illustrated in section 3.4.

200 mm x 400 mm size laboratory mill was used to sheet out the compound lump coming from the internal mixer. 1: 1.2 friction ratio was used throughout the experiments to maintain consistency.

Laboratory hydraulic ram press which was operated from electrical heaters was used for sample curing. Specific pressure on samples was maintained at 4.5 bar.  $150 \pm 2$  °C was used as setting temperature and optimum cure time was used to cure the samples.

### 3.4 Methodology

#### 3.4.1 Study the effect of ingredient concentration in accelerator-activator MB on cure characteristics

In the first step, the effect of accelerator & activator concentration in MB on the cure characteristics as well as physical & mechanical properties were studied. Rubber (TSR 20), stearic acid, ZnO and TBBS were mixed together during MB mixing keeping the activator-accelerator quantity constant and varying the rubber quantity. Table 3.2 shows the different TSR 20 & other ingredients quantities used in the preparation of MB.

Table 3.2: Design of experiment (different TSR 20 pphr in MB)

Mixing Stage	Material	Test Number & pphr					
		Control	R10	R25	R50	R75	R100
Master Batch Mixing	TSR 20	0.0	10	25	50	75	100
	Stearic acid	0.0	2.0	2.0	2.0	2.0	2.0
	Zinc Oxide	0.0	4.5	4.5	4.5	4.5	4.5
	TBBS	0.0	2.0	2.0	2.0	2.0	2.0
1 <sup>st</sup> Stage Mixing	TSR 20	100	90	75	50	25	0
	N 550 CB	45	45	45	45	45	45
	Stearic acid	2.0	0.0	0.0	0.0	0.0	0.0
	Zinc Oxide	4.5	0.0	0.0	0.0	0.0	0.0
	6PPD	1.5	1.5	1.5	1.5	1.5	1.5
	TMQ	1.0	1.0	1.0	1.0	1.0	1.0
2 <sup>nd</sup> Stage Mixing	Sulfur	1.6	1.6	1.6	1.6	1.6	1.6
	TBBS	2.0	0.0	0.0	0.0	0.0	0.0

*\*Ingredients are incorporated to the recipe in the form of a masterbatch which contains the activators and accelerators as per the base formulation presented in Table 3.1*

All mixing steps were conducted in the laboratory internal mixer and selected fill factors for MB, 1<sup>st</sup> stage & 2<sup>nd</sup> stage mixing are 0.63, 0.74 & 0.68 respectively. Different fill factors were selected because of different heat generations and temperature controls were needed to have better mixing. Mixing sequences are in Table 3.3.

Table 3.3: Mixing sequences of different mixing stages

Mixing Stage	Mixing sequence	Time (Sec)	Temperature (°C)	Rotor speed (rpm)	Ramp Pressure (bar)
<b>Master Batch Mixing</b>	TSR 20	0	NA	80	3.4
	SA+ZnO+TBBS	+ 50	NA	80	3.4
	Ramp clean	+ 40	NA	80	3.4
	Dump	+ 60	NA	98	3.4
<b>1<sup>st</sup> Stage Mixing</b>	TSR 20 + MB	0	NA	80	3.4
	N 550 + Other chemicals	+50	NA	80	3.4
	Ramp clean	+60	NA	80	3.4
	Dump	+100	150	98	3.4
<b>2<sup>nd</sup> Stage Mixing</b>	1 <sup>st</sup> stage compound	0	NA	75	3.2
	Curatives	+30	NA	75	3.2
	Dump	+60	100	75	3.2

### 3.4.2 Study the effect of pre-vulcanization inhibitors on scorch time of accelerator-activator MB incorporated rubber compounds

Scorch time of the solid tire middle compound in the MDR test at 150 °C should be more than 3 minutes to have safer processing conditions during mixing, milling & tire building. Therefore, to improve scorch time without changing the cure rate index, a selected recipe from the results yielded from experiment 01 was used in experiment 02 where the different amounts of pre-vulcanization inhibitors (CTP) were introduced. These amounts of CTP used were presented in Table 3.4. Curing, physical & mechanical properties of the relevant systems were studied to find to

optimum CTP level. The same mixing sequences and mixing operational procedures used in experiment 1 were used in this experiment too. CTP was added to the compound at the 2<sup>nd</sup> stage compound mixing together with Sulfur (crosslinking-agent).

For easy identification, the last digit of the recipe name indicates the amount of CTP without decimal places. As an example, 0.2 pphr of CTP recipe is nominated as RX/I2 where X is the optimum level of rubber content in selected MB.

Table 3.4: Design of experiment (different CTP pphr at 2<sup>nd</sup> stage mixing)

Mixing Stage	Material	Control	RX/I0	RX/I1	RX/I2	RX/I3	RX/I4
<b>Master Batch Mixing</b>	TSR 20	0.0	50	50	50	50	50
	Stearic acid	0.0	2.0	2.0	2.0	2.0	2.0
	Zinc Oxide	0.0	4.5	4.5	4.5	4.5	4.5
	TBBS	0.0	2.0	2.0	2.0	2.0	2.0
<b>1<sup>st</sup> Stage Mixing</b>	TSR 20	100	50	50	50	50	50
	N 550 CB	45	45	45	45	45	45
	Stearic acid	2.0	0.0	0.0	0.0	0.0	0.0
	Zinc Oxide	4.5	0.0	0.0	0.0	0.0	0.0
	6PPD	1.5	1.5	1.5	1.5	1.5	1.5
	TMQ	1.0	1.0	1.0	1.0	1.0	1.0
<b>2<sup>nd</sup> Stage Mixing</b>	Sulfur	1.6	1.6	1.6	1.6	1.6	1.6
	TBBS	2.0	0.0	0.0	0.0	0.0	0.0
	CTP	0.0	0.0	0.1	0.2	0.3	0.4

### 3.4.3 Study the effect of maturation time of accelerator-activator MB on cure characteristics

In this study, all compounds were kept for different time intervals after incorporation of the accelerator activator system in the rubber phase of MB prior to 1<sup>st</sup> stage mixing. This time interval is referred to as maturation time and studied maturation

times are given below. However, for this study, the selected compound from previous studies was used.

- 1 hour           RX-1h
- 24 hours        RX-24h
- 48 hours        RX-48h
- 72 hours        RX-72h

Curing, physical and mechanical properties were used to evaluate the results in experiment 3 and select the best maturation time for the next step. Where X in the RX is the optimum level of rubber content in selected MB.

#### **3.4.4 Compare the cure characteristics of the compounds and physical properties, mechanical properties & dynamic properties of rubber vulcanizate prepared using new process & conventional process**

During step four, cure characteristics and other properties of the selected compound and the subsequent vulcanizate and control (rubber compound with the unmodified recipe and mixing processes) related to the solid tire middle compound were compared. The modified compound recipe was selected based on the results of the previous experiments.

### **3.5 Evaluation of the performance of compounds and vulcanizates**

#### **3.5.1 Moving die rheometer**

Around 5 mg of 2<sup>nd</sup> stage compound sample is placed on the Montech MDR 3000 Professional machine which sets up the temperature of the cavity to 150 °C. Die is oscillating at 0.5° arc and 100 rpm speed at 30 minutes (ASTM D 5289). The following measurements were taken from the MDR cure curve.

- $M_L$  = Minimum torque
- $M_H$  = Maximum torque

- $t_{s2}$  = Scorch time (Time to reach 2 unit increase in torque above the minimum)
- $t_{90}$  = Cure time (at 90% cure has taken place)

The cure rate index was calculated by the equation 01.

$$\text{Cure Rate Index} = 100 / (t_{90} - t_{s2})$$

Equation 01: Cure rate index calculation

### 3.5.2 Specific gravity

Alfa Mirage MD 300S Electronic Densimeter was used to measure the specific gravity of all the vulcanizate during this experiment. It gives direct measurement based on Archimedes' principle according to the ASTM D 297.

### 3.5.3 Hardness

BAREISS (Germany) durometer rubber hardness tester was used to measure the hardness which tells the stiffness of the cured rubber compound. ASTM D 2240 test procedure was used for this test and Shore A was the unit of the measurement.

### 3.5.4 Tensile properties

GOTECH tensile machine (GT-7010-AE) and ASTM D412-A were used for the experiment. 2 mm thickness rubber sheet was cured by laboratory press and dumb-bell shaped vulcanizates (Die C) were cut by standard die cutters. Vulcanizates were kept 24 hours for the conditioning at room temperature and the test was performed at room temperature. The strain rate followed for the test was  $500 \pm 50$  mm/min. The following parameters were calculated to evaluate the physical properties of the tested samples.

- Tensile strength =  $F/A$
- Modulus at 300% elongation (300% modulus) =  $F'/3A$
- Elongation at break % =  $(L-L_0)/L_0$



Where;

F - Breaking force

A - Initial cross-sectional area

F' - The force at 300% elongation

L<sub>0</sub> – Initial length

L – Length at break

### **3.5.5 Rebound resilience**

FRANK Prufgerate GmbH rebound testing machine was used to measure the resilience of the vulcanizates which indirectly indicates the hysteresis of the compound. It was a Schob Type pendulum rebound device that expresses resilience as a percentage and the circular shape vulcanizate (70 mm diameter x 10 mm thickness) was used for the test. ASTM D7121 standard was followed and direct measurements were taken.

### **3.5.6 Heat Build-up**

GABOMETER 2000 flexometer was used to measure the heat build-up of the vulcanizates. According to the ASTM D-623-93, test specimens were conditioned at 100 °C for 30 minutes and the test was conducted for 30 minutes in an oven operated at 100 °C under sinusoidal compression load. The temperature rise of the vulcanizate was taken as the measure of heat build-up.

### **3.5.7 Blow-out time**

BF Goodrich Flexometer was used to measure the blow-out time of the vulcanizate. The same operating conditions stated in Section 3.5.6 was maintained. Time taken to blow the vulcanizate due to heat generation was taken as blow-out time.

### **3.5.8 Viscoelastic properties**

DMA<sup>+</sup>100 – Metra ViB machine was used to measure the viscoelastic properties and the temperature sweep (30 °C to 100 °C) test was conducted under compression mode at 1 Hz cyclic load. Viscoelastic properties such as G' (storage modulus or

elastic modulus),  $G''$  (loss modulus or viscous modulus),  $\tan \delta$  (ratio of loss modulus to storage modulus:  $G''/G'$ ) was plotted against the temperature to study the effect of cure rate on these properties.

### 3.5.9 Estimation of molecular weight and crosslink density

Rubber Processing Analyzer (RPA 2000 ALPHA) is the rotor-less rotational shear rheometer which is used to characterize rubber compounds and processing conditions. Molecular weight estimation was carried out at 100 °C temperature and 10% strain, under a frequency range of 0.5 to 10 Hz.  $G''$  at 1 Hz frequency was taken as the indirect indicator for the molecular weight. Crosslink density estimation was carried out at 100 °C temperature and 2 Hz frequency, under a strain range of 1 to 140 %. Before the strain sweep, the compound sample was cured at 170 °C for 10 minutes.  $G'$  behavior was taken as the indirect indicator for the crosslink density of the vulcanizate.

### 3.5.10 Crosslink Density

Swelling measurements can be used to evaluate the crosslink density of rubber vulcanizates. The solvent is embedded into the rubber molecules and swelling occurred. The degree of swelling is dependent on the crosslink density of the polymer network and the degree of swelling is inversely proportional to the crosslink density. The equation 02 was used to calculate percentage swelling by volume [13].

$$\% \text{ Swelling by volume} = \frac{\text{Gain in weight of solvent}}{\text{Specific gravity of solvent}} \times \frac{\text{Specific gravity of specimen}}{\text{Original weight of specimen}} \times 100$$

Equation 02: Percentage swelling by volume calculation

The vulcanizates having dimensions 20 mm x 10 mm x 2 mm were weighed and were immersed in p-xylene for 72 hours at room temperature. After the immersion, samples were rapidly blotted with a tissue and weighed.

### **3.6 New curing cycle design based on improved optimum cure time**

The in-house method was used to design the curing cycles based on the  $t_{90}$  observed from the selected accelerator-activator MB system. New curing cycles were proposed for the following resilient solid tire sizes.

- 18x7-8
- 7.00-12
- 23x9-10
- 3.00-15
- 12.00-20
- 14.00-24

Energy-related to the tire curing was also calculated for the new curing cycles and it was compared with the energy-related to the current curing cycles which were tabulated in Table 1.1.

## 4. RESULTS AND DISCUSSION

This chapter presents the cure characteristics and physical, mechanical & dynamic properties of the compounds/vulcanizates studied as explained in Chapter 3. Firstly the effect of ingredient concentration of accelerator-activator MB is presented. The effect of pre-vulcanization inhibitors on scorch time of accelerator-activator MB incorporated rubber compounds are then discussed. The effects of MB maturation time on the curing characteristics and the properties of the vulcanizates are also presented. Finally, a comparison of the performance of compounds prepared using the new process & conventional process is presented.

### 4.1 Effect of ingredient concentration in accelerator-activator MB on cure characteristics

The concentration of accelerator, activator in MB varied as presented in Table 3.2. Cure characteristics of the compounds prepared using different concentrations of accelerator-activator MB are tabulated in Table 4.1.

Table 4.1: Effect of ingredient concentration in MB on cure characteristics

<b>Rheological Parameter</b>	<b>Units of Measurement</b>	<b>Control</b>	<b>R10</b>	<b>R25</b>	<b>R50</b>	<b>R75</b>	<b>R100</b>
$M_L$	dNm	2.14	2.02	1.99	1.97	1.92	1.93
$M_H$	dNm	20.62	20.38	19.93	19.85	20.02	19.51
$t_{s2}$	Min: Sec	3:39	2:28	2:19	2:18	2:07	1:57
$t_{90}$	Min: Sec	9:42	6:29	6:05	5:59	5:48	5:16
<b>Cure Rate Index</b>	No units	16.5	24.9	26.5	27.1	26.4	30.2

$M_L$  is an indirect measure of the viscosity of a un-vulcanized compound. The chain length of rubber in the compound is proportional to the viscosity of the compound [8]. During compound mixing in an internal mixer (especially during mastication), rubber chains are broken down due to the mechanical shear exerted between rotor

tips and rotor & sidewall and thermal oxidation. If the rubber is undergone for more mixing steps, in other words, subjected to higher shear, then the molecular break down will be higher due to mechanical shear. Consequently, lower the viscosity of the compounds yields lower  $M_L$ . This effect is in agreement with the work reported by E. A. Oluwatobi et al [14].

Figure 4.1 shows the  $M_L$  behavior of the compounds. According to these results, Control which does not use accelerator: activator MB has the highest  $M_L$  while other compounds show lower  $M_L$ . Rubber in Control was subjected to the molecular breakdown only in the 1<sup>st</sup> mixing stage. In other compounds, a portion of rubber was subjected to additional mixing stages and a higher degree of the molecular breakdown has occurred in MB preparation. This justifies the lower  $M_L$  values of these samples [8]. When compounds with rubber content from 10 to 100 pphr are considered, there is a gradual increase in rubber content used for MB preparation. Therefore, molecular breakdown becomes higher as the higher rubber quantity is mixed in a mixing chamber with a constant volume. Consequently, the viscosity of the final compound reduces gradually as explained by E. A. Oluwatobi et al reported on their study [14]. However, the viscosity of the solid tire middle compound ( $M_L$ ) does not influence product performance significantly. Therefore, these values lie in the acceptable range as the recommended range of 1.50-2.50 dNm.

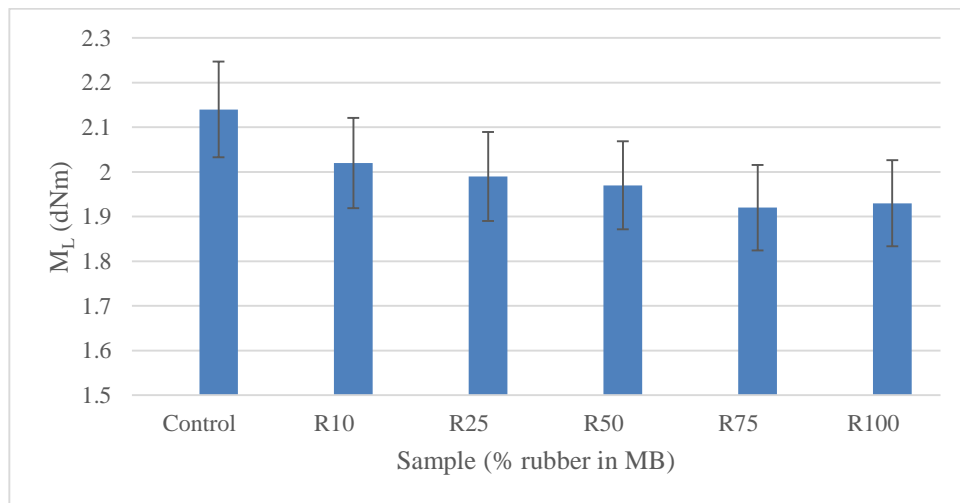
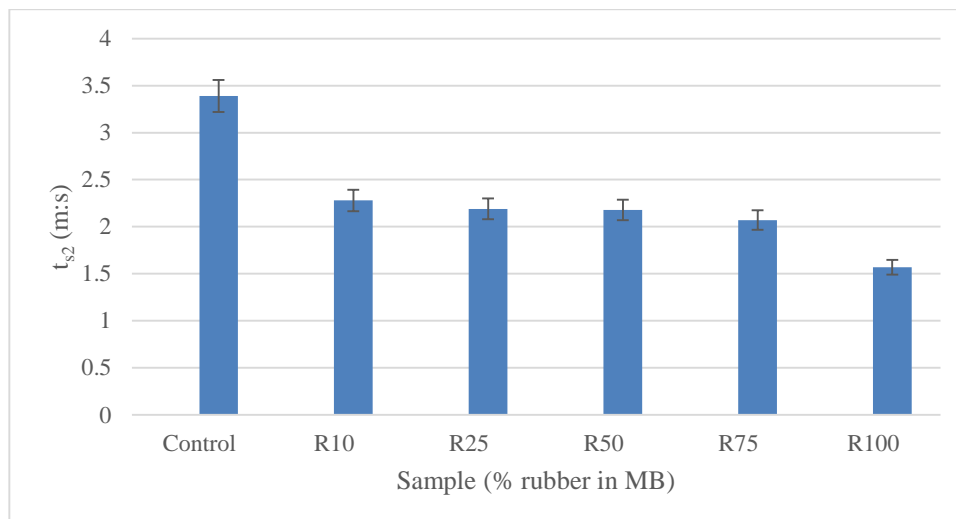
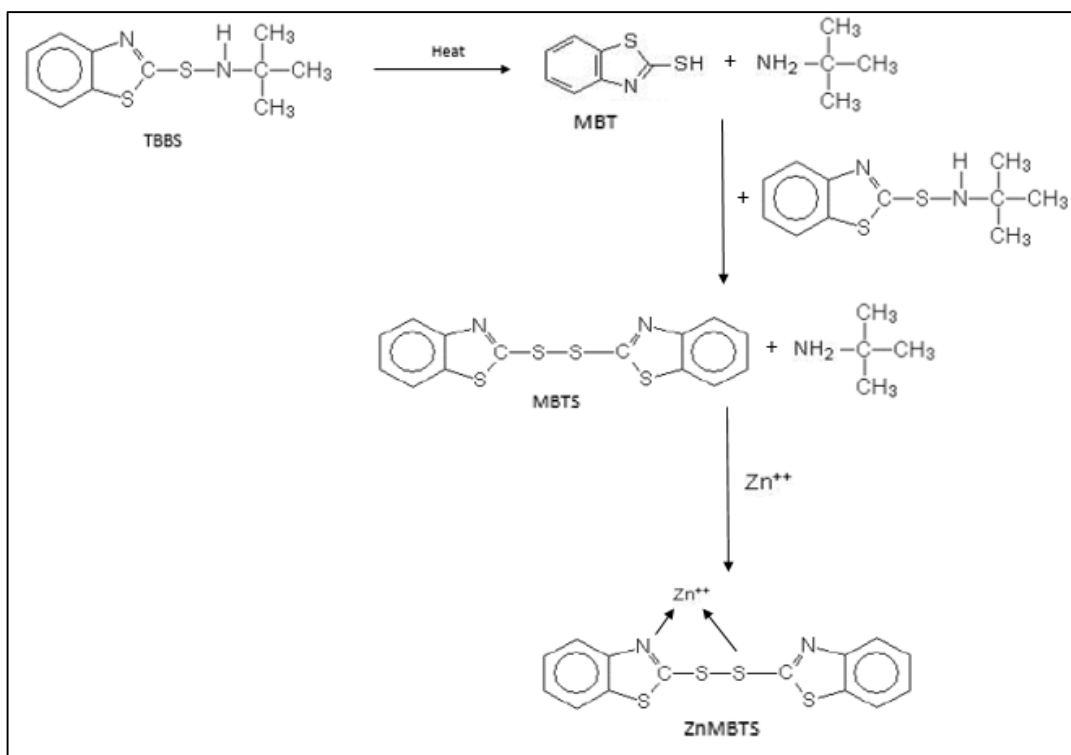


Figure 4.1: Behavior of  $M_L$  with the concentration of ingredients in the accelerator-activator MB



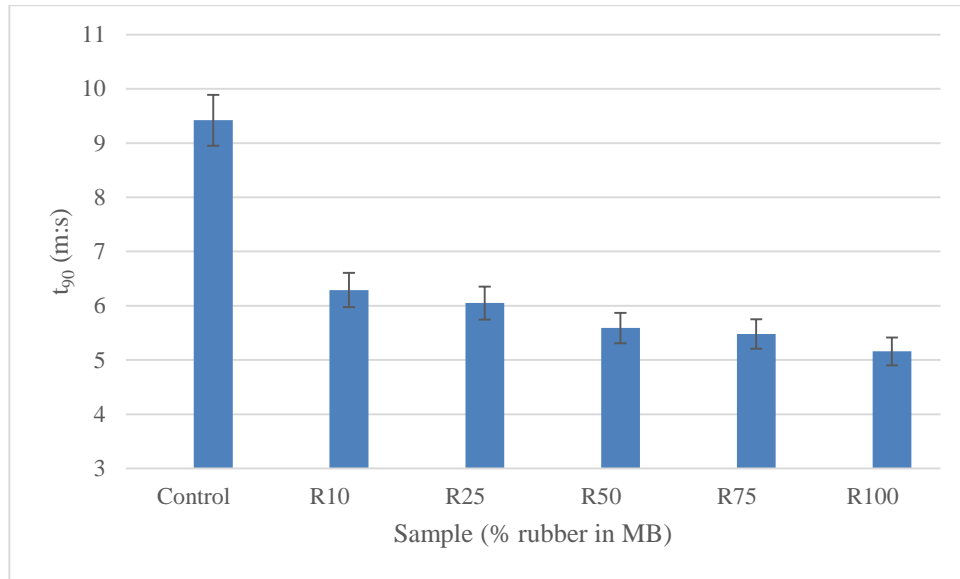
*Figure 4.2:* Behavior of  $t_{s2}$  with the concentration of ingredients in the accelerator-activator MB

The  $t_{s2}$  is the measurement of scorch time of the rubber compounds for the processing. Generally, scorch time for the solid tire middle compound should be more than 3 minutes. According to the results, the Control compound has more than the required safety time. When the accelerator-activator MB is used, scorch time is reduced in all other compounds ( Figure 4.2). It could be inferred that when ZnO, Stearic acid & TBBS mixed in the rubber phase, there could be a tendency to react to these materials and to form accelerator-activator complexes [12]. Figure 4.3 shows that the proposed reaction scheme of accelerator-activator complex formation in the MB. These complexes which are already formed could react with sulfur to form crosslinks earlier than Control ie conventional mixing where accelerators and activators are incorporated separately. This is the reason for shorter scorch time in MB compounds (R10 to R100).

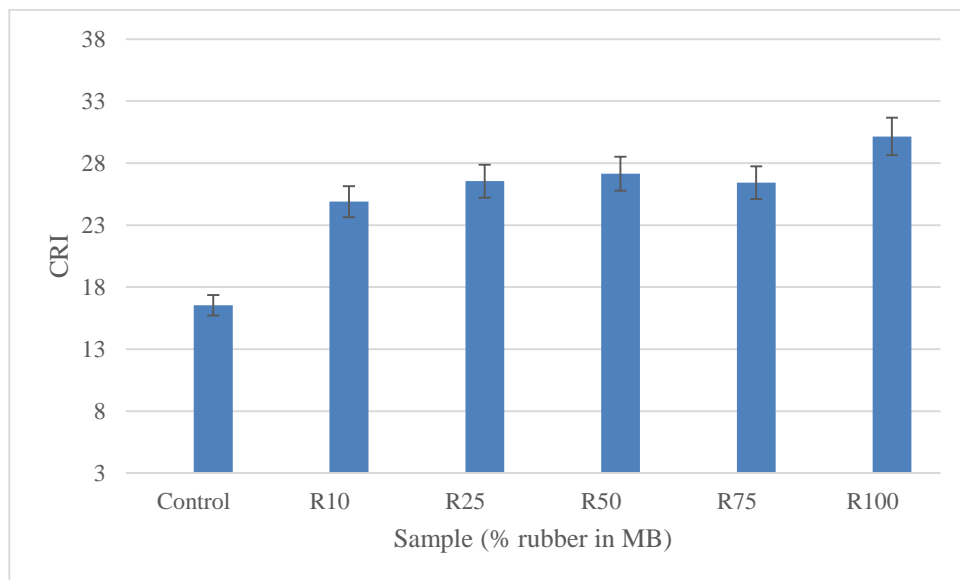


*Figure 4.3:* Proposed reaction scheme of accelerator-activator complex formation at MB mixing

The  $t_{90}$  is the measurement of the time taken to achieve 90% of crosslink formation in the compound and it is used to set the cure time of the compound during vulcanization to obtain the final product [8]. For the solid tire middle compound, shorter  $t_{90}$  is better to reduce the total curing time of a solid tire, as the main objective of this study was to reduce  $t_{90}$  by incorporating accelerator together with the activator in the form of accelerator-activator MB. As expected the compounds, where accelerator-activator MB is used to exhibit a reduction in  $t_{90}$  and increase the cure rate index as shown in Figure 4.4 & Figure 4.5 respectively.



*Figure 4.4:* Behavior of  $t_{90}$  with a concentration of ingredients in the accelerator-activator MB



*Figure 4.5:* Behavior of cure rate index with a concentration of ingredients in the accelerator-activator MB

When the TBBS accelerator was added at the 2<sup>nd</sup> stage mixing following conventional mixing process, accelerator & activator reaction is initiated only during the curing cycle. TBBS is activated at 140 °C [15] and therefore, a certain time is required to form the activator-accelerator complexes at the curing temperature (150 °C). This leads to an increase in  $t_{s2}$  and  $t_{90}$  were in the Control. However, when



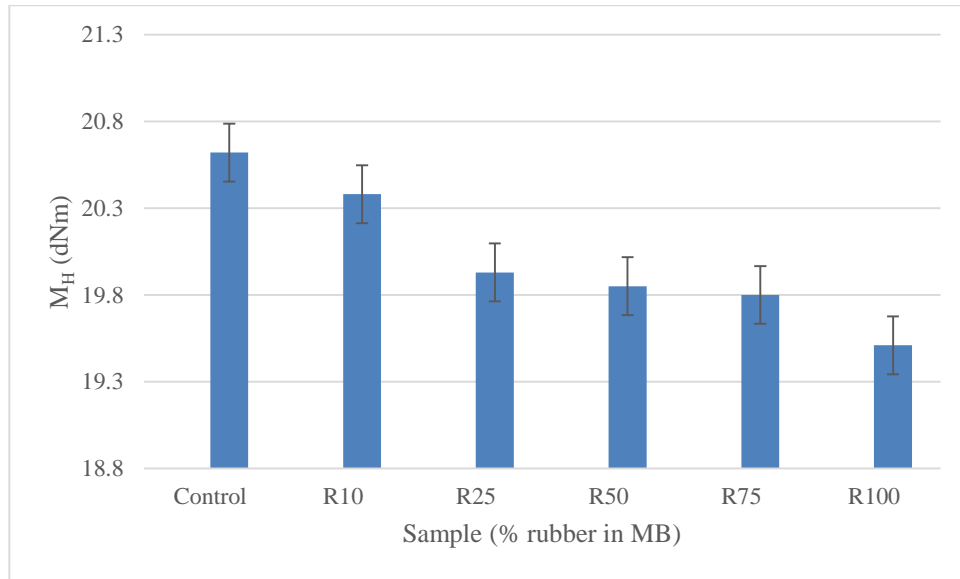
accelerator and activator are mixed in prior to 1<sup>st</sup> stage mixing, activator-accelerator complexes could be formed in MB as explained earlier. When the sulfur (crosslinking agent) introduces to this system during the 2<sup>nd</sup> stage mixing, crosslinking formation by sulfur is become faster due to the availability of the already formed activator-accelerator complexes. Therefore, the time taken to reach the state of cure is reduced. Consequently, the cure rate index is increased and subsequently,  $t_{90}$  is reduced when accelerator- activator MB is used. Upul Wijayantha et al. also observed that reduction of  $t_{90}$  and improvement of cure rate index in their study [12].

It has been shown that as the accelerator-activator concentration higher in the MB,  $t_{s2}$  and  $t_{90}$  has become longer. However, Figure 4.2 & Figure 4.4 show that  $t_{s2}$  and  $t_{90}$  are reduced gradually with the increasing content of rubber in the accelerator-activator MB. This can be explained by analyzing the dumping temperature of MB as shown in Table 4.2. Appendix A shows the mixing parameter chart in accelerator-activator MB mixing (R50) which was used to get batch temperatures.

Table 4.2: Dumping temperatures of MB for different concentrations

<b>Compound Version</b>	<b>Dumping Temperature (°C)</b>
R10	90
R25	92
R50	105
R75	109
R100	118

According to Table 4.2, the dumping temperature of the accelerator-activator MB was increased with the increasing rubber content in MB. When the rubber content is higher in the MB, the temperature of the batch increases due to the high shear and therefore, a higher amount of accelerator-activator complexes may form. Consequently,  $t_{s2}$  and  $t_{90}$  of the rubber compounds are decreased gradually with the increasing rubber content in the accelerator-activator MB.



*Figure 4.6:* Behavior of  $M_H$  with a concentration of ingredients in the accelerator-activator MB

$M_H$  is the highest torque achieved during the test and it is an indirect measure of the degree of crosslinking in the rubber network and the modulus of the rubber compound [8]. Figure 4.6 shows the  $M_H$  of the compounds. It exhibits a declining trend as the rubber content in MB increases. According to these results,  $M_H$  is inversely proportional to the cure rate index.

The possible reason for this observation is, if the curing happens slowly, there is a time to form more crosslinks in the rubber network [5]. But when the cure rate is higher, the state of cure will be achieved quickly and hence the number of crosslinks formed during vulcanization could be less. Consequently,  $M_H$  is decreased with the cure rate index improvement. Another reason for this may be due to the reduction of  $M_L$  in MB used compound and according to that  $M_H$  also could be reduced because the whole cure graph shifted to the down words [8].

Table 4.3: Effect of ingredient concentration in MB on physical properties

Property	Units of Measurement	Control	R10	R25	R50	R75	R100
Hardness	Shore A	65	65	64	64	64	64
Tensile Strength	MPa	21.5	22.0	22.3	25.0	21.6	21.3
300% Modulus	MPa	5.6	5.1	5.1	5.2	5.2	4.9
Elongation at Break	%	380	404	398	396	398	394
Specific Gravity	No units	1.110	1.113	1.101	1.108	1.101	1.108
Rebound Resilience	%	67	66	65	65	66	66

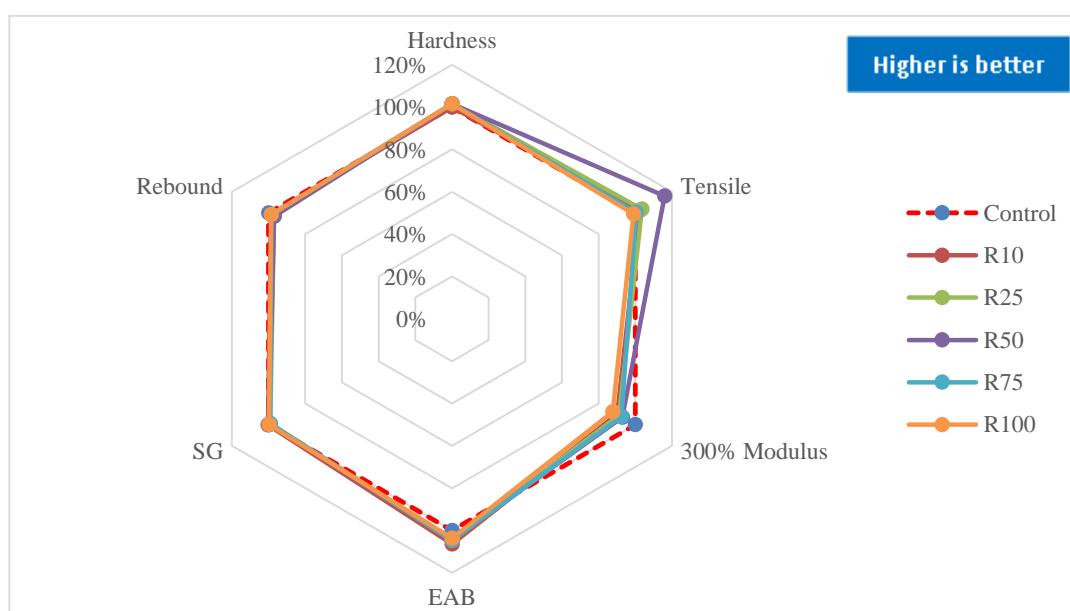


Figure 4.7: Physical property comparison with accelerator-activator MB concentration

The modified curing system has no significant influence on the physical properties of the middle compound. The mechanical and physical properties of corresponding vulcanizates are shown in Table 4.3. Hardness & specific gravity has almost the same results, while tensile strength and elongation at break exhibits a slight improvement with the accelerator-activator MB incorporated vulcanizates than the vulcanizate prepared using normal mixing. It may be due to higher molecular break down in MB

mixing as well as 1<sup>st</sup> stage mixing. As a result, fillers could be easily incorporated into the polymer network due to short chains in the polymer network. Due to higher incorporation, rubber to filler interactions may be higher and it improved the tensile & elongation at break [16]. Rubber concentration of MB does not significantly influence the tensile & elongation at break properties according to the results yielded.

300% modulus has a reduction in MB incorporated compounds compared to the Control. It is in par with the behavior of M<sub>H</sub> and it may also be due to the slight reduction of crosslink density during vulcanization as a result of the high cure rate. The concentration of the ingredients in the accelerator-activator MB does not cause a significant variation of 300% modulus.

Rebound resilience also has a slight reduction in MB incorporated vulcanizates compared to the Control. This could be due to the low degree of crosslinks when a higher cure rate was registered. Higher crosslink density gives good dynamic properties while lower crosslink density yields poorer dynamic properties [17].

Based on the curing characteristics of the compounds, R25, R50, R75 & R100 show the higher cure rate index, but R50 & R100 have higher values compared to the other two versions. Scorch time of R100 is poor than the R50. As in the second part effect of pre-vulcanization inhibitor (CTP) on cure rate & scorch time of compounds prepared by varying the CTP was studied. R50 MB compound was selected for the next study considering favorable curing characteristics and physical properties. Poor scorch time makes some barriers to the processability of the compound and also needs to add more CTP for the recipe which is not economical and makes blooming problems in the solid tire industry. Also, M<sub>H</sub> and 300% Modulus of R100 has poor performance than R50. By considering all factors, R50 was selected for future work.

#### **4.2 Effect of pre-vulcanization inhibitors on scorch time of accelerator-activator MB incorporated rubber compounds**

For this study, the R50 compound was selected as discussed in section 4.1. In order to achieve the required scorch time, pre-vulcanization inhibitors (CTP) were added at

different concentrations as presented in Table 3.4. Cure characteristics of these samples are tabulated in Table 4.4.

Table 4.4: Effect of pre- vulcanization inhibitors on cure characteristics

<b>Rheological Parameter</b>	<b>Units of Measurement</b>	<b>Control</b>	<b>R50/I0</b>	<b>R50/I1</b>	<b>R50/I2</b>	<b>R50/I3</b>	<b>R50/I4</b>
<b>M<sub>L</sub></b>	dNm	2.23	1.94	1.95	1.90	1.98	1.94
<b>M<sub>H</sub></b>	dNm	20.75	18.75	19.32	19.13	19.32	18.27
<b>t<sub>s2</sub></b>	Min: Sec	3.24	2.22	2.46	2.55	3.11	3.15
<b>t<sub>90</sub></b>	Min: Sec	9.25	5.45	6.07	6.30	6.53	6.55
<b>Cure Rate Index</b>	No units	16.6	29.6	29.9	27.9	27.0	27.3

When CTP was added to rubber compounds, an increase in scorch time could be observed and it is proportional to the level of CTP added to the compound (Figure 4.8). This suggests that CTP has an influence on the effect of activator-accelerator complex on the scorch time. It is reported in the literature that CTP molecules could react rapidly with TBBS (accelerator). As a result, there is a depletion of the accelerator available for curing reaction and thereby delaying the vulcanization process [7]. Similarly, CTP molecules may react with already formed activator-accelerator complexes and delay the curing process. The effect of the low level of CTP (less than 0.2 pphr) on the cure rate index is insignificant [6]. The scorch time for R50/I0 and R50/I1 have almost the same cure rate index. Further, results show that the cure rate has been reduced at a significant level once the CTP content is higher than 0.2 pphr. It also shows that both compounds which have more than 0.3 pphr have achieved the safety scorch time limits without further reduction in the cure rate index. Considering the excess use of CTP and associated cost, the R50/I3 compound could be selected as the best compound among the candidate's compounds to be used in the solid tire middle compound with improved cure rate index compared to the Control.

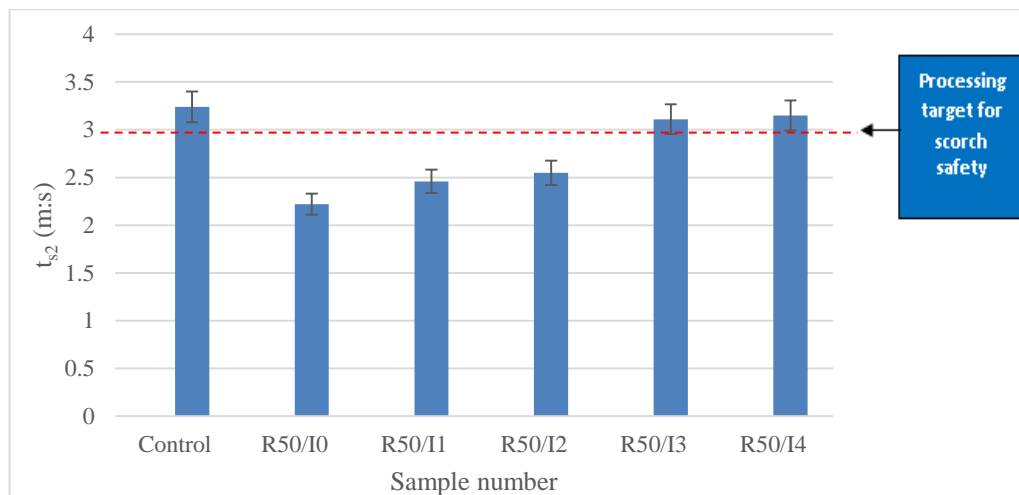


Figure 4.8: Behavior of  $t_{s2}$  with the amount of pre-vulcanization inhibitor (CTP)

Other rheological properties ( $M_L$  &  $M_H$ ) and physical properties of CTP added compounds that are tabulated in Table 4.5 did not show any significant difference in their performance with the CTP content. This is in line with the literature reported in the use of CTP in rubber compounds [6].  $M_L$  &  $M_H$  shows the same trend when it was used accelerator-activator MB which had the same observation during experiment 01. Improvement of tensile & elongation at break and slight reduction of modulus when accelerator-activator MB usage is already reported in this experiment as well (Figure 4.9). It confirms the explanations made earlier.

Table 4.5: Effect of pre- vulcanization inhibitors on physical properties

Property	Units of Measurement	Control	R50/I0	R50/I1	R50/I2	R50/I3	R50/I4
<b>Hardness</b>	Shore A	65	64	65	64	64	64
<b>Tensile Strength</b>	MPa	20.6	24.0	22.9	23.3	23.9	23.6
<b>300% Modulus</b>	MPa	5.7	5.3	5.3	5.4	5.3	5.3
<b>Elongation at Break</b>	%	378	442	410	404	450	432
<b>Specific Gravity</b>	No units	1.108	1.106	1.113	1.106	1.106	1.110

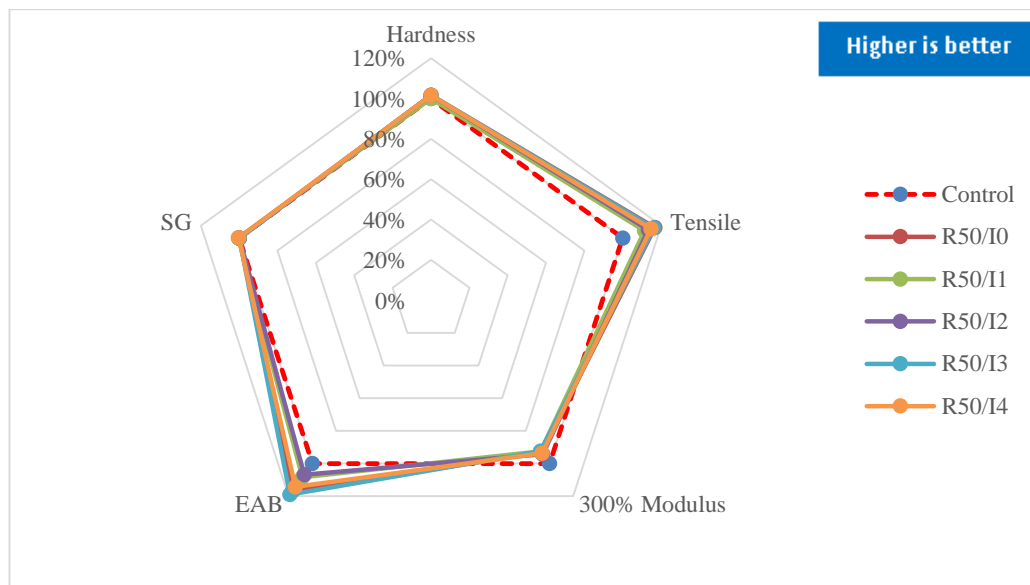


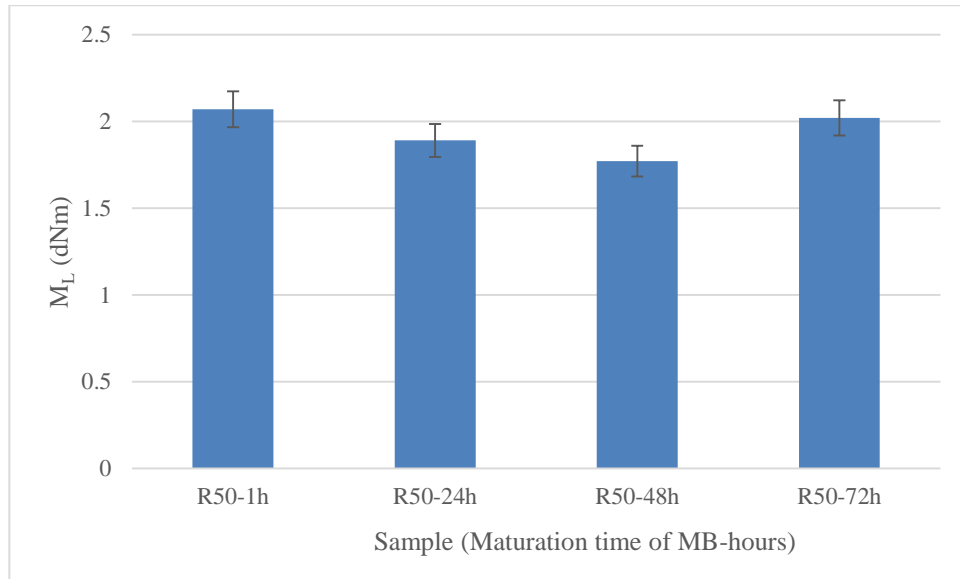
Figure 4.9: Physical property comparison with the amount of pre-vulcanization inhibitor (CTP)

### 4.3 Effect of maturation time of accelerator-activator MB on cure characteristics

It was identified that cure rate improvement with the accelerator-activator MB due to the formation of accelerator-activator complexes during the MB mixing. The effect of the maturation time of the MB on the cure rate index is discussed in this section.

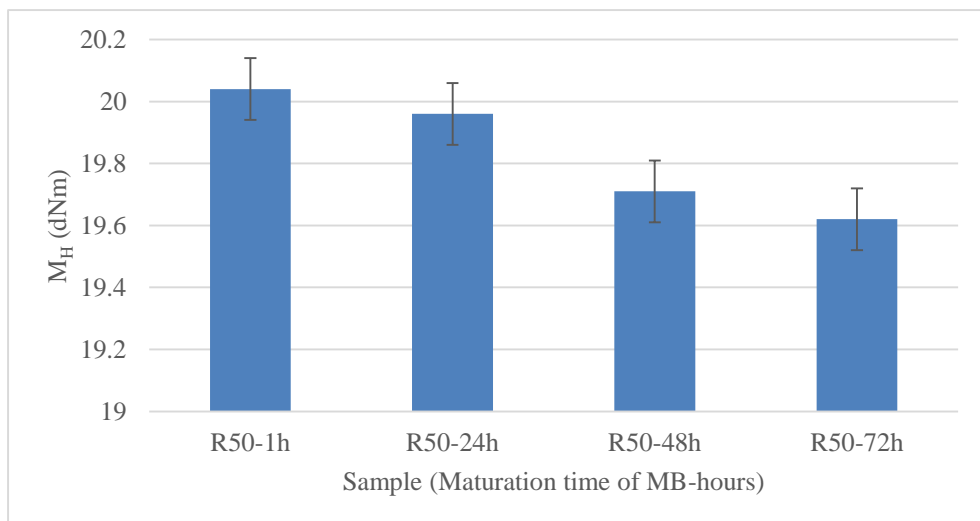
Table 4.6: Effect of maturation time of accelerator-activator MB on cure characteristics

Rheological Parameter	Units of Measurement	R50-1h	R50-24h	R50-48h	R50-72h
$M_L$	dNm	2.07	1.89	1.77	2.02
$M_H$	dNm	20.04	19.96	19.71	19.62
$t_{s2}$	Min: Sec	2.30	2.33	2.44	2.29
$t_{90}$	Min: Sec	6.58	7.05	7.26	7.02
Cure Rate Index	No units	22.39	22.06	21.28	21.98



*Figure 4.10:* Behavior of  $M_L$  with maturation time of accelerator-activator MB

From 1 hour to 48 hours, there is a gradual drop of  $M_L$  and this is maybe due to the oxidation of the rubber chains with the time. The oxidation was happened due to the heat, that generated during the MB mixing stage and that heat is retained inside the MB rubber sheet. But after 48 hours of maturation, there is a slight improvement in  $M_L$ . This may because of storage hardening of natural rubber which happens due to carboxylate ends of amino acids are involved to form ester or amide linkages [18]. Consequently, accelerator-activator MB undergoes storage hardening and hence  $M_L$  may have increased.



*Figure 4.11:* Behavior of  $M_H$  with maturation time of accelerator-activator MB



$M_H$  also has a gradual drop with the maturation time of MB as shown in Figure 4.11. It is also confirmed that rubber molecules have undergone oxidation with the time due to generated heat as explained earlier and therefore,  $M_H$  has reduced.

There is no significant effect of maturation time on  $t_{s2}$ ,  $t_{90}$  and cure rate index according to the results obtained in this experiment. The results yielded are presented in Figure 4.12.

All the compounds of the R50 series (which used accelerator-activator MB) have the same improvement of tensile & elongation at the break while dropping modulus as observed in experiments 01 & 02 (Figure 4.13). But this behavior is not affected by the maturation time of the accelerator-activator MB.

This observation suggests that the reaction between accelerator & activator by forming its complexes may not be significant time-dependent one. These chemicals are reacted during the MB mixing stage when the heat is there at the system. Therefore, it could be concluded that no significant reactions related formation of the activator-accelerator complexes occur with the maturation time.

After considering these results and the practical aspects such as compound handling and capacities in the mixing plants, 24 hours maturation time for MB is selected for further research.

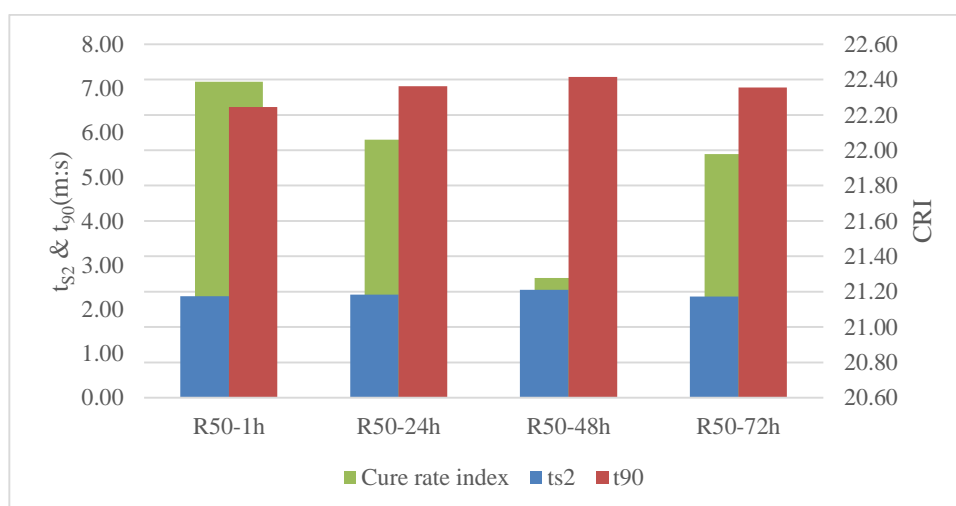
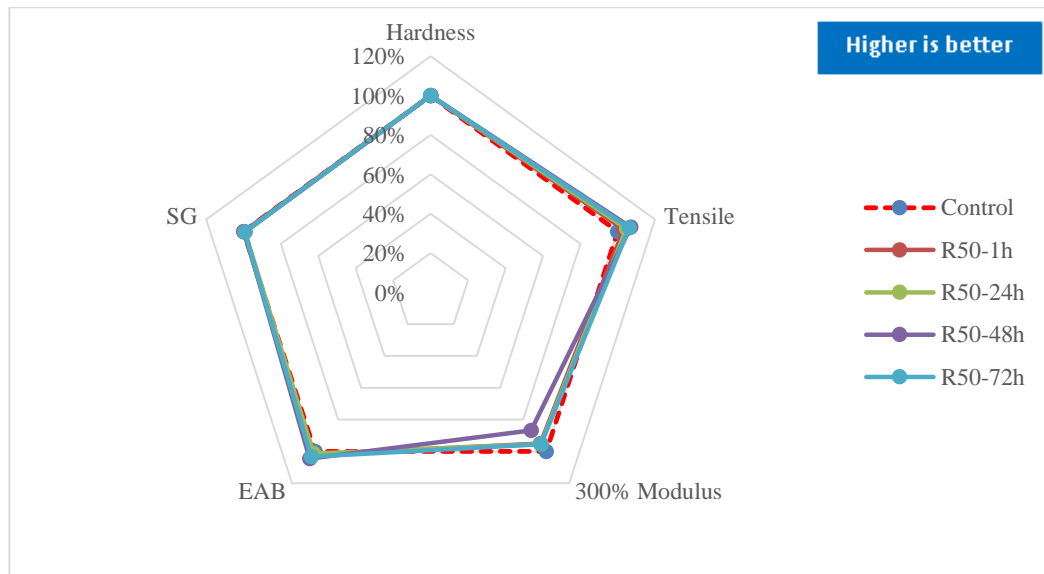


Figure 4.12: Behavior of  $t_{s2}$ ,  $t_{90}$  & cure rate index with maturation time of accelerator-activator MB



*Figure 4.13:* Physical property comparison with maturation time of accelerator-activator MB

Based on the results obtained from the experiments, 01, 02 & 03 R50/I3-24h recipe was selected which had 50 pphr of TSR 20 in MB mixing, 0.3 pphr of CTP and 24 hours MB maturation for the experiment 04 to study the other compound properties.

#### **4.4 Comparison of the curing characteristics of rubber compounds and properties of the rubber vulcanizates prepared using new process & conventional process**

For this study, R50/I3-24h recipe which has 50 pphr of rubber (TSR 20) in the accelerator-activator MB and 0.3 pphr CTP were selected and compare the curing characteristics including the cure rate index, physical, mechanical and dynamic properties of solid tire middle compound in between conventional curative mixing methods and proposed curative mixing method.

##### **4.4.1 Effect on curing characteristics**

Curing characteristics of the Control and selected sample were reproduced here for completeness of the discussion. The behavior of  $M_L$  &  $M_H$  are shown in Figure 4.14 and it is inlined with the results obtained on experiment 01 & 02. The reduction of

$M_L$  &  $M_H$  with the accelerator-activator MB usage is already discussed in section 4.1. Further investigations on crosslink density show a reduction that will discuss under section 4.4.2.

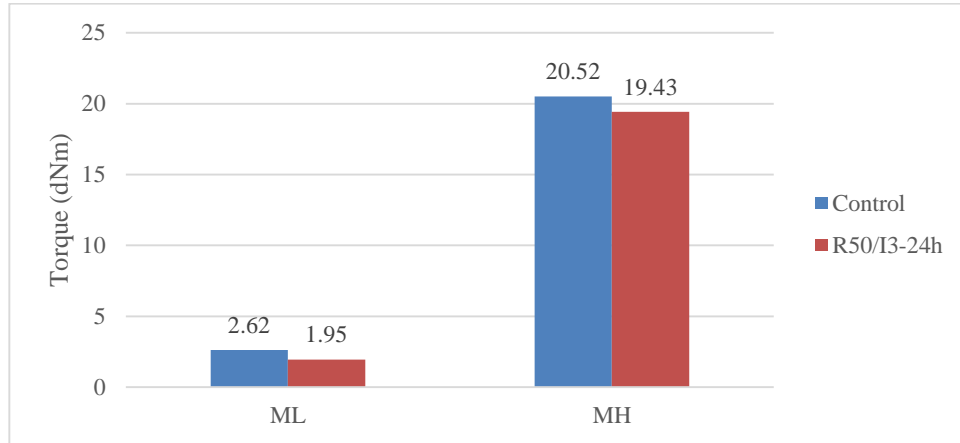


Figure 4.14: Effect of curative mixing methods on  $M_L$  &  $M_H$

Molecular weight estimation test ( $G''$  value at 100 °C temperature, 10% strain, and 1 Hz frequency) was conducted in RPA to verify the rubber chain break down during mixing and  $M_L$  results.  $G''$  which is known as viscous modulus is increased with the chain length because of long chains create more resistance when rubber chains flow past each other [19]. According to the results which show in Figure 4.15 Control has higher  $G''$  than the R50/I3-24h and therefore, the chain length of Control is higher. It confirms that the R50/I3-24h has a higher rubber molecular breakdown due to both MB and 1<sup>st</sup> stage mixing stages [19].

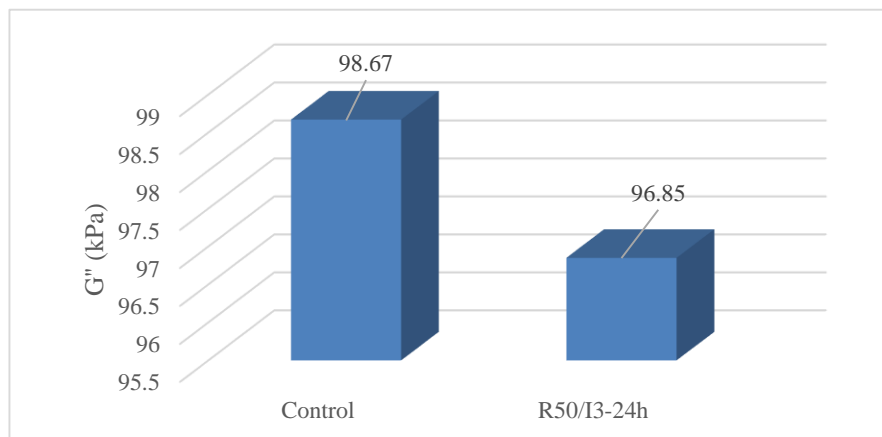


Figure 4.15: Effect of curative mixing methods on  $G''$  in RPA

Scorch time, optimum cure time and cure rate index of Control & R50/I3-24h is illustrated in Figure 4.16 and there is the same behavior as previous experiments. There is a 52% improvement in the cure rate index due to the reduction of  $t_{90}$ .

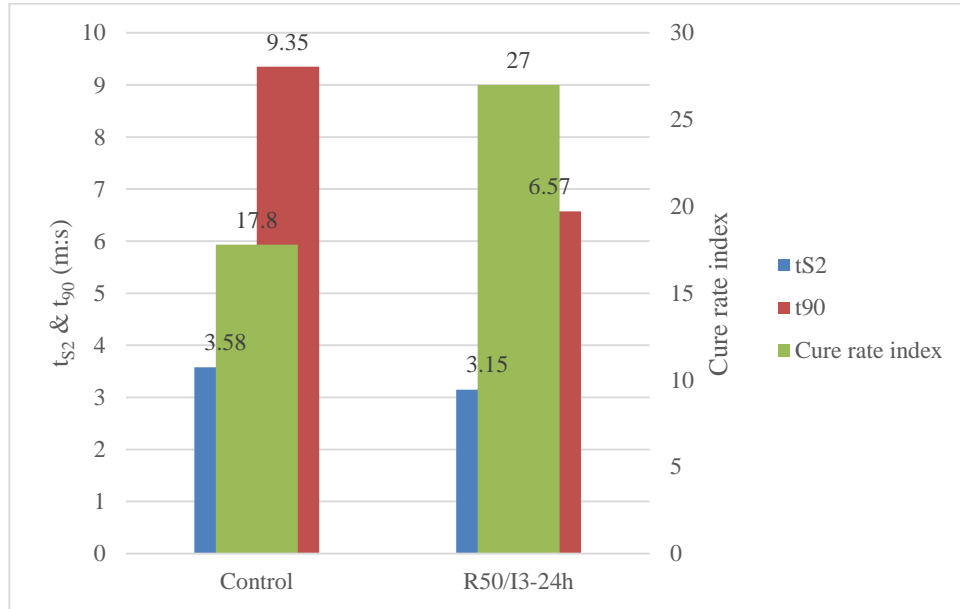


Figure 4.16: Effect of curative mixing methods on  $t_{S2}$ ,  $t_{90}$  & CRI

#### 4.4.2 Effect on crosslink density

The percentage swelling by volume of the Control and the selected sample (R50/I3-24h) are shown in Figure 4.17.

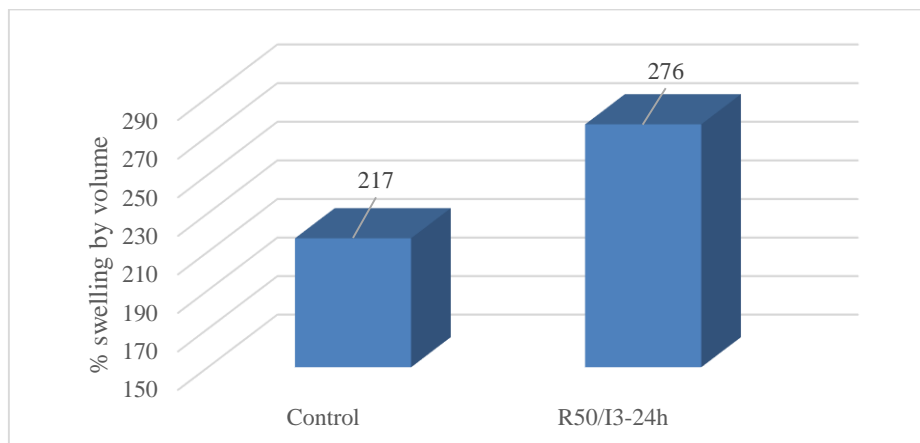


Figure 4.17: Comparison of percentage swelling by volume

R50/I3-24h which has a 52% higher cure rate index also has the highest percentage swelling by volume compared to the Control sample. That means the crosslink density of R50/I3-24h is lower than the Control sample because due to the lower crosslink density, higher free volume in the rubber network. Then p-xylene could be embedded into the free volume and it increases the swelling ratio [13]. This result is inlined with the  $M_H$  results and the proposed reason for this observation already expressed in chapter 4.1. The summary of the explanation is as follows.

Due to the formation of accelerator-activator complexes during the MB mixing cure rate increases and the high cure rate could be achieved. Formed lower crosslink density in the rubber network because it comes to the state of cure quickly than the slow curing. Therefore, the crosslink density of R50/I3-24h is lower than the Control.

To confirm the results of the swelling test, an in-house test was conducted in RPA. Strain sweep was done from a low level to a higher level (0.5 to 140% strain) while frequency and temperature are constant. Figure 4.18 shows  $G'$  (storage modulus) behavior in the RPA test while going strain sweep in a higher range. At the low strain (0.5 to 20%), the filler network is breaking down and then, formed crosslinking networks are breaking down at the high strain (20 to 140%). These network failures are related to the behavior of the  $G'$  during strain sweep [19]. Low  $G'$  means less crosslinking network of the vulcanizate. According to Figure 4.18, R50/I3-24h has lower  $G'$  at the high strain than the Control and hence crosslink density might be lower. Therefore, swelling test results are confirmed by the RPA studies.

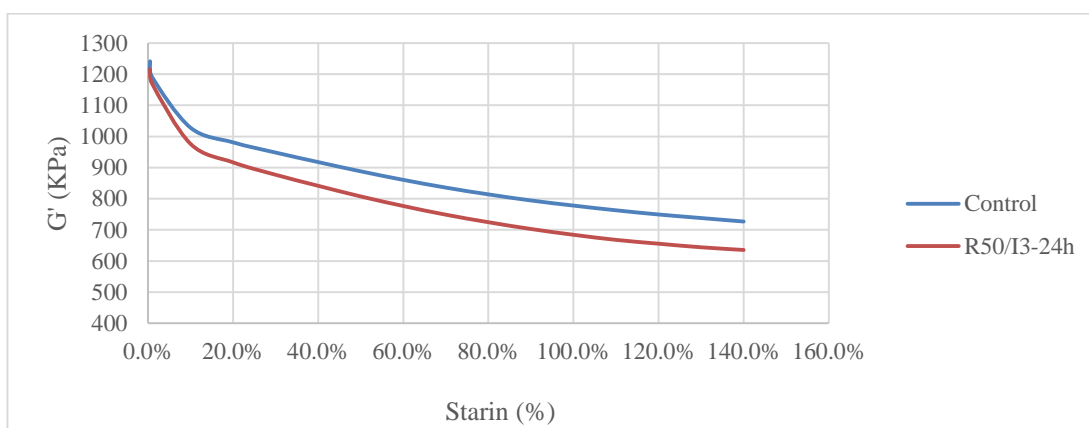


Figure 4.18:  $G'$  behavior in RPA in strain sweep test

#### 4.4.3 Effect on physical/mechanical properties

Physical and mechanical properties of the Control and selected sample were reproduced here for completeness of the discussion. Physical properties for Control and R50/I3-24h are tabulated in Table 4.7. Hardness and the SG are not affected at all by the modified mixing methods. An increase in the cure rate is registered when the modified MB system is used.

Table 4.7: Effect of curative mixing methods on physical properties

Property	Units of Measurement	Control	R50/I3-24h
Hardness	Shore A	65	65
Specific Gravity	No units	1.112	1.110

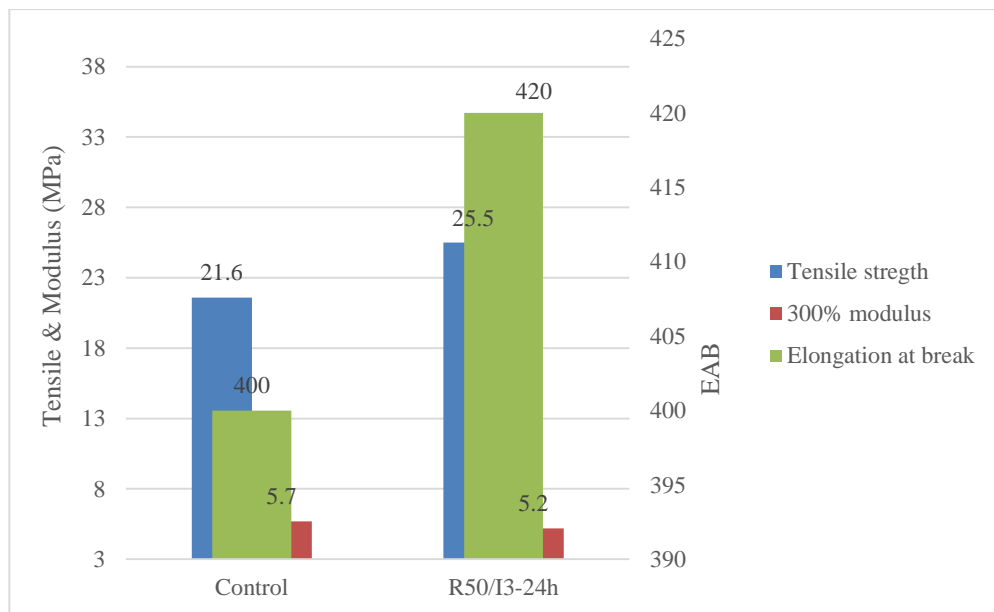


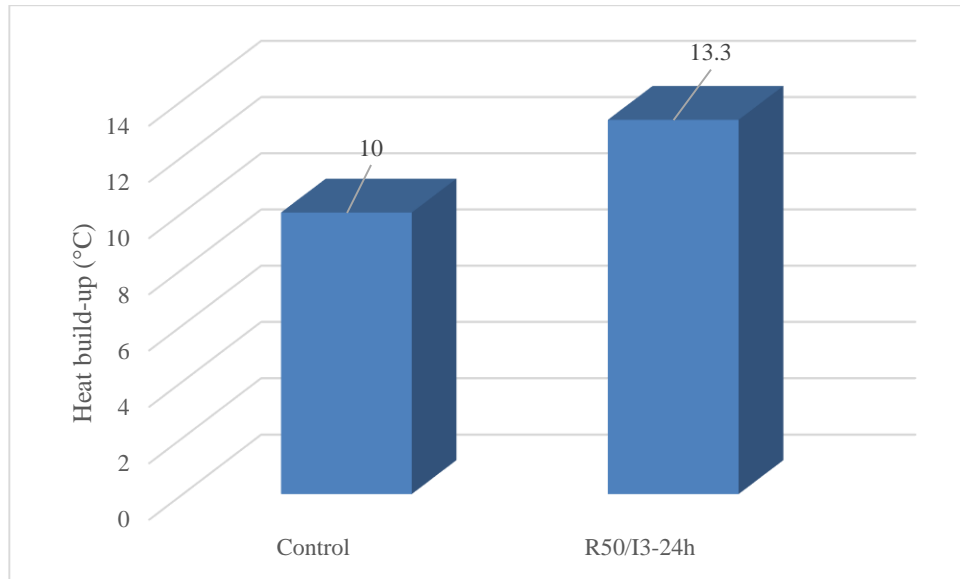
Figure 4.19: Effect of curative mixing methods on tensile, modulus & EAB

Tensile strength & EAB demonstrate a slight improvement for R50/I3-24h and the reason was explained in chapter 4.1. Modulus has a slight reduction and it confirms the  $M_H$  reduction and crosslink density reduction. When the crosslink density reduced, the tightening of rubber chains also reduced compared to the rubber

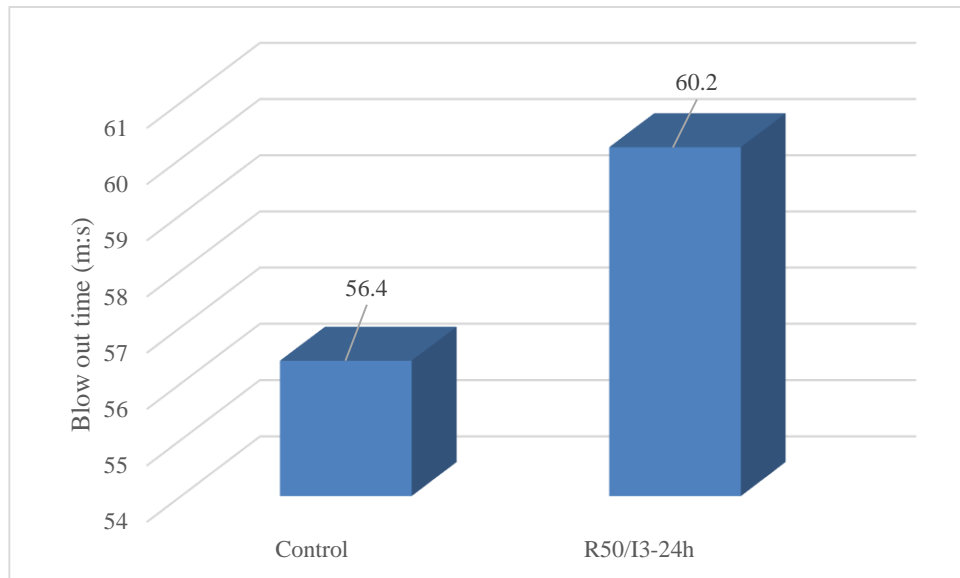
vulcanizates with a higher crosslink density. Consequently, resistance to deformation under the load is reduced and explained the reduction in modulus.

#### **4.4.4 Effect on dynamic properties**

The effect of cure rate improvement on dynamic properties is discussed in this section. Hysteresis of the vulcanizates (Control & R50/I3-24h) is presented in terms of heat build-up (section 3.5.6). It could be seen that R50/I3-24h has slightly higher heat build-up (Figure 4.20) showing its reduced elastic characteristics. This may be due to the low crosslink density of the vulcanizates. However, when the mechanical properties are considered these vulcanizates have shown better properties than the Control. As explained in section 4.1 it may be due to the better filler dispersion in the vulcanizates. With regard to the hysteresis which is a dynamic property, it could be proposed that crosslink density has become predominant in determining the set properties. Vulcanizates having mono-sulfidic bonds are less flexible than the poly-sulfidic bonds and hence heat generation could be higher in this system [5]. Therefore, it could be proposed that the R50/I3-24h system has a higher percentage of mono-sulfidic crosslinks than the Control one. This is further supported by the high blow out time registered for the R50/I3-24h. This explanation is in agreement with the work carried out by John S. Dick who has also reported that low cross-link density and mono-sulfide networks make less flexibility rubber articles [17]. Low crosslink density offers less elastic properties to the vulcanizate and therefore, energy loss during flexing is higher. In addition, shorter rubber chains in R50/I3-24h make a higher number of chain ends and these ends undergo vibration and spatial movements [20] lead into higher hysteresis. It should also be noted that the heat build-up of selected vulcanizate is in the acceptable range for the solid tire middle compound as it is below the recommended maximum temperature rise limit (15 °C). Therefore, this vulcanizate could be used for the manufacture of solid tire middle compounds in industrial applications.



*Figure 4.20: Effect of curative mixing methods on heat build-up*



*Figure 4.21: Effect of curative mixing methods on blow out time*

Blow out time indicates the stability of rubber network upon the flexing. Heat is generated during flexing causes network failure which depends on the type of crosslinks found in the vulcanizate. A rubber vulcanizate is highly vulnerable to failure if polysulphides bonds are predominant in the network, as S-S bond energy is lower than the S-C bond energy. Therefore, the poly-sulfidic crosslinking network is less heat resistant while mono-sulfidic bonds have the highest heat resistance [5]. According to the blow out times presented in Figure 4.21, R50/I3-24h has a higher



blow out time than the Control sample qualifying the select the vulcanizates for the use of the intended application (solid tire middle compound). This may be due to the presence of a higher percentage of mono-crosslinks in the vulcanizates.

#### 4.4.5 Effect on visco-elastic properties

DMA was carried out to compare the visco-elastic properties of Control and selected vulcanizate.  $G'$  (storage modulus),  $G''$  (loss modulus) and  $\tan \delta$  (loss modulus/storage modulus) were measured.

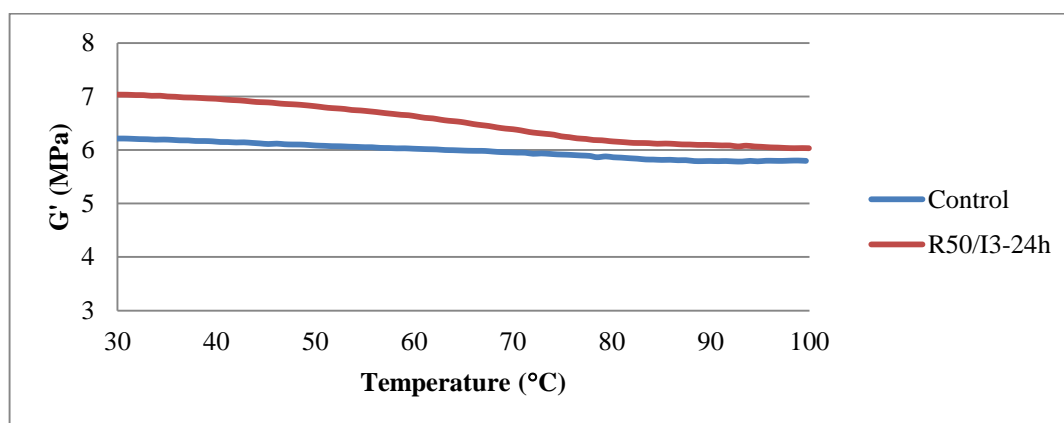


Figure 4.22: Behaviour of storage modulus ( $G'$ ) – Temperature sweep

Lower crosslink density was observed in R50/I3-24h vulcanizate and therefore, it has less resistance to deformation. Therefore, the tightening of the NR backbone chain is less in R50/I3-24h compared to the Control. The storage modulus of the compounds which is shown in Figure 4.22 confirms the flexibility of these vulcanizates.

Figure 4.23 shows that the loss modulus of the R50/I3-24h has higher values than Control. As proposed earlier, due to the lower crosslink density and the possible mono sulfidic crosslinking network may responsible for the observed high loss modulus. In addition, when the rubber chains are shorter, the number of chain ends in the system is increased. Under the stresses, chain ends could vibrate, oscillate freely and change their spatial arrangement contributing higher hysteresis and loss modulus [20].

Tan  $\delta$  is the ratio of loss modulus to storage modulus and it could be seen that it is higher in R50/I3-24h. This observation suggests that rolling resistance of R50/I3-24h is inferior to the Control. However, it should not that rolling resistance of the solid tire is not governed completely by the dynamic properties of the solid tire middle compound. Therefore, it could be assumed that the dynamic properties of the selected vulcanizate may be in the accepted range when the difference of the DMA properties between the Control & selected vulcanizate is considered.

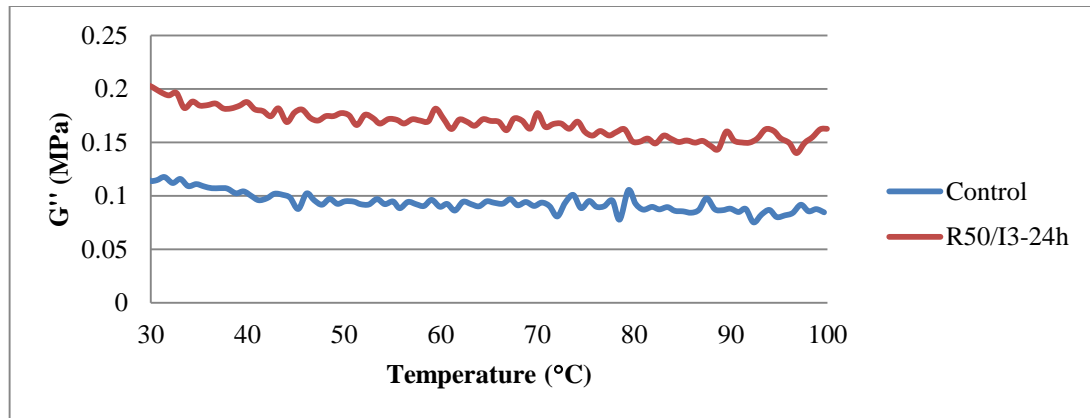


Figure 4.23: Behaviour of loss modulus ( $G''$ ) – Temperature sweep

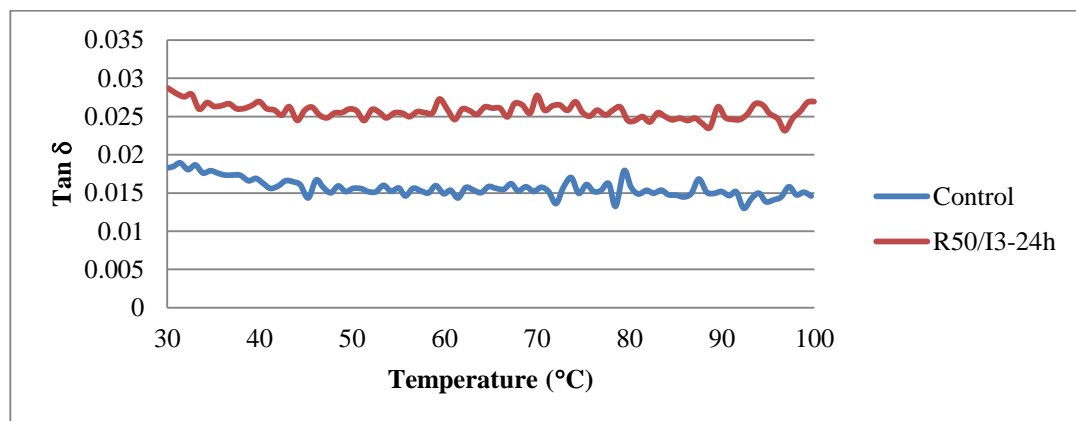


Figure 4.24: Behaviour of Tan  $\delta$  – Temperature sweep

#### 4.5 Impact of cure rate improvement of the new process on the curing cycle of the solid tires

Cure rate improvement is observed in the compound in which accelerator-activator MB was used and hence  $t_{90}$  of the compound is reduced. The reduction of  $t_{90}$  of the solid tire middle compound governs to reduce the curing cycle time of the product (solid tire) because  $t_{90}$  of the middle compound is used to design the curing cycle time. Consequently, energy-saving related to the tire curing and capacity improvement could be achieved from this curing cycle time reduction. Table 4.8 shows the proposed curing cycles based on new  $t_{90}$  of the middle compound and the energy-saving related to the tire curing for proposed curing cycles.

Table 4.8: Energy consumption reduction with the proposed curing cycles of solid tires

Tire size	Current curing cycle time (hrs: min)	Energy consumption for the current curing cycle (MJ/tire)	Proposed curing cycle time (hrs: min)	Energy consumption for the proposed curing cycle (MJ/tire)	Percentage of curing cycle reduction (%)	Percentage of energy consumption reduction (%)
18x7-8	1:40	52.9	1:30	47.0	11	13
7.00-12	2:00	118.4	1:50	107.6	9	10
23x9-10	2:30	120.9	2:15	107.5	11	13
3.00-15	2:45	277.2	2:30	249.5	10	11
12.00-20	3:40	554.4	3:20	499.0	10	11
14.00-24	8:00	705.6	7:10	623.6	12	13

Around 10% of curing cycle reduction could be yield with the  $t_{90}$  reduction from accelerator-activator MB. It impacts the energy consumption of solid tire curing and around 12% energy could be reduced based on new curing cycles. As a result, productivity and the operational cost related to tire curing will be reduced.

## 5. CONCLUSIONS AND RECOMMENDATIONS

The effect of incorporation of accelerators and activators in rubber masterbatch form prior to first stage compound mixing on cure characteristics and physical, mechanical & dynamic properties was studied. The typical solid tire middle compound was selected for the study because the total vulcanization period is governed by the middle compound due to its slow heat transfer and subsequent slow cure rate.

It was found that 52% cure rate improvement along with a reduction in optimum cure time could be achieved through the use of accelerator-activator masterbatch (MB). It was also found that the decrease of concentration of activator-accelerator combination in the MB proportional to the cure rate index improvement and reduction of optimum cure time. In addition to the cure rate improvement, mechanical properties such as tensile strength & elongation at break were improved in the vulcanizates while 300% modulus exhibits a slight reduction. Among the candidate compounds, R50 has shown the optimum properties.

In addition, this system could be used to reduce energy consumption around by 12% and operational costs related to the curing process of solid tires.

The scorch time of the compound was dropped with the incorporation of activators and accelerators in the form of accelerator-activator MB due to the early formation of the accelerator-activator complexes during the MB mixing stage. The incorporation of a Pre-vulcanization inhibitor (CTP) improves the scorch time while maintaining the improvement of the cure rate index to comply with the processing safety. It is also found that the incorporation of 0.3 pphr CTP to the selected compound (R50) yields the optimum curing, physical & mechanical properties.

It was revealed that the formation of activator-accelerator complexes is independent of the maturation period of accelerator-activators MB form.

The crosslink density and hysteresis (heat build-up) of R50/I3-24h vulcanizate that is used accelerator-activator MB exhibited a slight reduction compared to the Control. However, blow-out time had improved with accelerator-activator MB. Viscous part

of the visco-elastic rubber compound had increased and therefore, loss modulus ( $G''$ ) and  $\tan \delta$  of R50/I3-24h was higher than the Control. Therefore, R50/I3-24h rubber compound is recommended to obtain a 52% cure rate improvement and safe scorch time in solid tire middle compounds with a 12 % energy savings.

Based on the findings of the present study, it is recommended further;

- To carry out a study to confirm the mechanism and the network structure of the vulcanizates developed by introducing the new curing ingredient incorporation process
- To study the possibility of reduction of accelerator-activator concentration/combinations while maintaining the required curing characteristics and vulcanizate properties
- To Study the same process for thin wall articles
- To extend the study by building a solid tire with reduced the curing cycle and investigate that the influence of product performance in the term of fatigue life, rolling resistance, heat build-up, etc
- To study on the improvement of dynamic properties of the solid tire middle compound

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# APPENDIX A: MIXING PARAMETER CHART FOR ACCELERATOR-ACTIVATOR MB MIXING (R50)

<b>FABREL</b>	Recipe	RA MB 01	TCU SP	°C			13: 42: 00 12/5/2018			
	Product ID		Sides	35 52						
	Batch	3 of 4	Rotors	35 42						
	Step Advance On	<b>STEP</b>	Door	35 40			Peak kw 7			
Step 1	Operator Instruction	Mode #	Step Time Sec	Mix Time Sec	Total Time Sec	Temp	Energy KWH	RPM	Ram Eff BAR	IRM %
1	Feed polymer Manual acknowledge	1	49	0	49	57	0.04	81.2	0.00	0
2	Ram Down Mix [mastication]	2	50	50	99	88	0.12	82.0	3.48	34
3	Manual acknowledge	1	22	50	121	71	0.14	81.2	0.00	34
4	Ram Down Mix	2	40	90	161	90	0.19	81.8	3.51	70
5	Manual acknowledge	1	14	90	175	87	0.21	80.0	0.00	70
6	Ramp down mixing	2	60	150	235	105	0.29	99.4	3.56	112
7	DUMP	6	3	153	238	105	0.29	99.2	3.35	112
8		0	0	0	0	0	0.00	0.0	0.00	0
9		0	0	0	0	0	0.00	0.0	0.00	0
10		0	0	0	0	0	0.00	0.0	0.00	0
11		0	0	0	0	0	0.00	0.0	0.00	0
12		0	0	0	0	0	0.00	0.0	0.00	0
13		0	0	0	0	0	0.00	0.0	0.00	0
14		0	0	0	0	0	0.00	0.0	0.00	0
15		0	0	0	0	0	0.00	0.0	0.00	0
16		0	0	0	0	0	0.00	0.0	0.00	0
17		0	0	0	0	0	0.00	0.0	0.00	0
18		0	0	0	0	0	0.00	0.0	0.00	0
19		0	0	0	0	0	0.00	0.0	0.00	0
20		0	0	0	0	0	0.00	0.0	0.00	0

