

**ENHANCING THE CUSHIONING EFFECT OF SOLID  
TIRE CUSHION COMPOUNDS BY INTRODUCING  
THERMALLY EXPANDABLE MICROSPHERES**

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## DECLARATION

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## ABSTRACT

Solid tire industry is a rapidly growing industry all over the world with a very high demand for different kinds of material handling equipment manufacturing companies. In this case, resilient tires are playing a major role. Resilient tires are widely used in different kinds of applications especially in material handling equipment like forklifts. Mostly this equipment will be used in different environmental conditions like severe sun light, heavy rain, extreme wind, etc. In addition to that, this equipment will be running on different kind of ground conditions like metal yards, concrete pavements, and severely damaged floor conditions etc. When it comes to the tire manufacturer, it is their responsibility to produce tires as per the customer requirement in order to satisfy the basic needs of the customer. In this case, “Resilient tires with good comfort” is one of the key requirements which is coming from the tire users. Base, Cushion & Tread are the three main components of a resilient tire. Base component is the part which is mounted to the vehicle whilst the Tread part will be in contact with the ground surface during motion. Cushion part will act like a bridge between base and tread by delivering perfect comfort to the machine operator. When it comes to the material handling vehicles like forklifts, they are heavy duty machines and operator comfort is very important during running conditions. In order to facilitate a perfect comfort, function of the cushion part plays the major role which can be described technically as “*Cushioning Effect*”. Even though it is important that the factor cushioning effect of a resilient tire, there are some limitations and challenges to overcome for tire manufacturers to optimize the cushioning effect whilst maintaining other tire properties at the desired levels. Main challenge is to keep the cushioning property at its optimum level and maintain the other physical properties like tensile, hardness, modulus, elongation, tearing, etc. In general, cushioning effect is gained by using a blend of semi-reinforcing carbon black with different particle sizes. Since the use of this blend has many limitations, a serious requirement is there to find a better solution to enhance the cushioning effect of resilient tires whilst maintaining other required properties at the specified levels. This study is an effort of enhancing the cushioning effort of resilient tires by incorporating *Thermally Expandable Microspheres (ThEM)* into the cushion compound. New compounds were produced by introducing variable ThEM quantities and compared with the regular cushion compound. A series of compound and tire tests were performed in order to identify the perfect formulation with better performance.

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**CHAPTER 1**  
**INTRODUCTION**

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## 1.1 Resilient tires & the cushioning effect

Historically, forklift operators have not had much choice when choosing tires. In the past, forklifts were simple machines. Today, machines are becoming more advanced and complex, and as a result, more complex tires are increasingly needed. Forklifts today are truly beautiful machines. They can lift heavier loads, travel at higher speeds and cover greater distances than in the past. All this cause, forklifts to be useful across a more diverse range of applications. When the “Forklift” topic is taking up to the forum, solid resilient tires are playing one of the most critical and major roles in it. Elastic tires (also known as solid tires or inflated solids) were developed as a non-inflatable solution for pneumatic tires. The two-layer elastic tire is composed of an inner tube heel layer and an outer tread layer. The inner tube heel layer is composed of a hard rubber compound, and the outer tread layer is made of a wear-resistant rubber compound, thereby extending the tire life. Three-layer elastic tire has a third intermediate layer. These three-layer tires are characterized by the addition of a softer rubber compound layer to absorb shocks to the greatest extent, thereby mimicking the cushioning effect of a pneumatic tire and reducing the internal temperature of the tire (technically reducing heat build-up). In simple words, “cushioning effect” can be described as “comfort”. Cushioning effect of solid resilient tires is one of the most critical factors which should be considered with high priority during the designing stage of the tire. In this case, the most challenging part for the compound developer is to keep the cushioning effect at a maximum possible level whilst maintaining other required properties at their desired levels. When compare resilient tires with pneumatic tires in terms of cushioning effect, pneumatic tires have higher cushioning properties than that of resilient tires. Hence, there is a major problem exists in terms of vehicle comfort among the resilient tire users all over the world. Lower the vehicle comfort may result in low productivity of the vehicle drivers, risk factor will be very high of having health problems like fatigue due to frequent shocks and many more indirect impacts. Generally, cushioning effect of a standard resilient tire will be achieved by using a blend of semi reinforcing Carbon Black with different particle sizes (Ex: N330 & N550). Purpose of using this

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type of fillers is to create a porous structure inside the cushion part (middle part) of the tire which gives the cushioning effect to the tire.

## 1.2 Cushion compounding ingredients and their functions

### 1.2.1 Natural rubber

Natural rubber is an elastic substance derived from wood milk, especially from rubber trees and ficus. Technically, natural rubber is an elastomer. Natural rubber is also known by the names of Indian rubber, elastic rubber and rubber. Natural rubber raw materials come from the rubber tree sap. The goal of tapping a rubber factory is to assemble rubber latex. In this case, make an incision in the bark of a rubber tree and collect milk in a cup. After assembly of latex, natural rubber turns into useful rubber. First, acid was added to the latex so that the pectin solidified like jelly. The latex thus obtained was then lyophilized and crushed into rubber pieces and suspended for drying. In 1839, Charles Goodyear invented a more sophisticated method to make rubber more durable and elastic. This is the process of "vulcanization" of rubber, which was technically explained in 1.3.1. Raw natural rubber is sticky, easily deformed in heat and brittle when cold. In this state, it cannot be used for the manufacture of products with good elasticity. Vulcanization prevents the independent movement of polymer chains. As a result, vulcanized rubber deforms when stress is applied, but when the stress is removed, the product returns to its original shape. Natural rubber is the main raw material used in the tire industry.

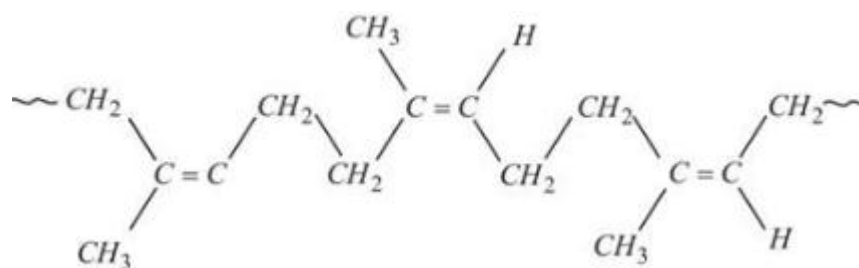


Figure 1: Straight chain polymer of cis- 1, 4 polyisoprene

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## **1.2.2 Carbon Black**

Carbon black is a general-purpose reinforcing filler and light stabilizer used in rubber compounds. Carbon black can give the tire strength and toughness, as well as improve tear, abrasion, and fatigue when bending rubber, as well as improve traction and durability. If carbon black is not added, the tire can drive less than 5,000 miles. Carbon black consists of oil and consists of irregular, branched, strongly spherical subunits. The dispersed carbon black aggregates themselves form a network in a polymer medium. As the filler content increases, the network circuit becomes shorter, and the number of weaves between two stitched bonds decreases. Individual molecules can be adsorbed on several parts of the soot surface, so the bonded rubber is essentially stationary. Reactive groups, including acid groups, phenolic groups and lactone groups, have been identified on the surface of carbon black that affect adsorption. Carbon black can not only improve the "strength" of rubber, but also affect the characteristics of vulcanization. Carbon black reduces the induction time of vulcanization and reduces the cure rate as the number of surface acid groups in carbon black increases. This mechanism, apparently, is one of the competitive reactions between rubber and a filler from an activator of zinc oxide. Carbon black has many surface groups (due to an oxygen content of about 3.5%), while furnace black has a small number of surface groups. Carbon black acts as a catalyst to initiate sulfurization. The onset of soot increases with load. Recently, there has been a tendency to replace carbon black with silicon dioxide to increase tire rolling resistance and increase tire mileage, as well as reduce automotive fuel consumption.

### **1.2.2.1 Reinforcing Carbon Blacks**

The maximum amount of carbon black is used as a reinforcing filler in rubber products, especially in tires. Pure styrene-butadiene vulcanizates have a tensile strength of not more than 2 MPa and low wear resistance but mixing it with 50% carbon black can improve its tensile strength and wear resistance, as shown in the table. It is often used in elastomers in the aerospace industry for aircraft vibration control components, such as engine mounts. In fact, all rubber products that are

important for tensile and abrasion properties use carbon black, so they are black. Where physical properties are important but a colour other than black is required, such as white tennis shoes, soot is replaced by precipitated or smoky silica. Silica-based fillers have also gained a market share in car tires because they have lower rolling losses, which provides a better compromise in fuel efficiency and wet handling. Traditionally, siliceous fillers have poor wear-resistant properties, but the technology is gradually improved to such an extent that they can correspond to the wear-resistant properties of Carbon Black

Table 1: Certain types of Carbon Black used in tire industry

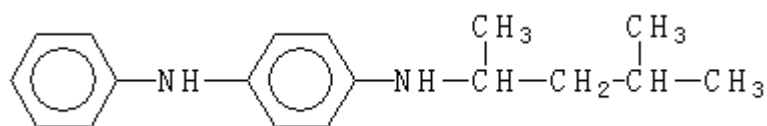
Name	ASTM designation	Particle Size in nm	Tensile strength in MPa	Relative laboratory abrasion	Relative road wear abrasion
Super Abrasion Furnace	N110	20–25	25.2	1.35	1.25
Intermediate SAF	N220	24–33	23.1	1.25	1.15
High Abrasion Furnace	N330	28–36	22.4	1.00	1.00
Easy Processing Channel	N300	30–35	21.7	0.80	0.90
Fast Extruding Furnace	N550	39–55	18.2	0.64	0.72
High Modulus Furnace	N660	49–73	16.1	0.56	0.66
Semi-Reinforcing Furnace	N770	70–96	14.7	0.48	0.60
Fine Thermal	N880	180–200	12.6	0.22	–
Medium Thermal	N990	250–350	9.8	0.18	–

### 1.2.3 Antioxidants

Antioxidants are substances that are added in small amounts to easily oxidized hydrocarbons, such as rubber, plastics, foods and oils, to inhibit or slow down the

oxidation process while oxidizing. Antioxidants act in two different ways. Among the main antioxidants (also known as free radical scavengers), antioxidant activity is achieved by donating electrons or hydrogen atoms to derivatives of free radicals. These antioxidants are usually hindered amines (p-phenylenediamine, trimethyldihydroquinoline, alkylated diphenylamine) or substituted phenolic compounds with one or more large functional groups, such as tertiary compounds, usually at positions 2 and 6. Butyl. Butylated hydroxytoluene (BHT) is a common example of hindered phenolic antioxidants. The reaction sequence in the SN1 mechanism is  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3$  (without SN1), so tert-butyl is replaced by a phenolic antioxidant compound. The main antioxidant is a free radical scavenger, which can combine with peroxy radicals and disrupt the autocatalytic cycle. In secondary antioxidants (also known as peroxide decomposers), activity is achieved by removing oxidation catalysts and preventing the initiation of oxidation. Examples of antioxidants such as a peroxide decomposer are trivalent phosphorus and divalent sulfur-containing compounds such as sulfides, thiodipropionates and organic phosphates. When primary antioxidants are used with secondary antioxidants, a synergistic effect is expected, since primary antioxidants are not very effective in oxidative degradation by ultraviolet radiation. Chelating agents are sometimes added to remove metallic impurities that may cause decomposition.

P-phenylenediamine is used as a starting compound in vulcanization accelerators and antioxidants in the rubber industry. PPD was chosen because of its high temperature stability, high strength, and chemical and electrical resistance.



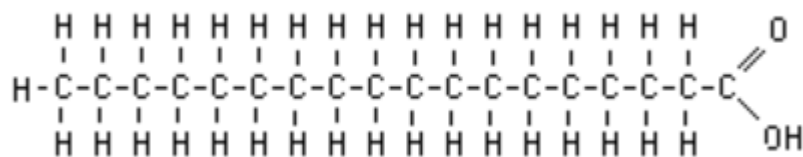
*Figure 2: Chemical structure of 6PPD*



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#### 1.2.4 Activators

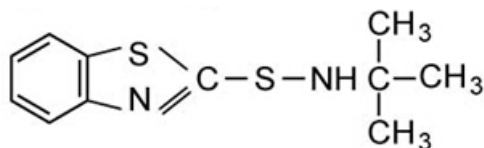
Zinc oxide is an inorganic compound with the chemical formula ZnO. ZnO is a white powder that is insoluble in water and is widely used as an additive in various materials and products, including rubber, plastic, ceramics, glass, cement, lubricants, paints, ointments, adhesives, sealants, pigments, food products, Battery and a first aid kit. Zinc oxide used in the rubber industry ranges from 50% to 60%. Zinc oxide is used with stearic acid to vulcanize rubber. ZnO additives also protect rubber from fungi and UV rays. Stearic acid (SA) is involved in almost all rubber compounds. It is used in relatively low amounts (up to 3.0 phr) but has a multifunctional effect on their properties and processing. Checked SA's function as a softener and filler dispersant in rubber mixtures. As a softener, SA influences the viscosity of filled compound. Processing is facilitated because of its decrease during mixing. Such influence of SA on rheological properties of rubber compounds is manifested in some uncommon results of the apparent viscosity, determined at low shear rate values. These results could be explained when examined in common with the experimental results for the dispersing influence of SA onto fillers and the amount of bond rubber. Based on the rheological properties of rubber compounds in dependence of the SA amounts within, a method is proposed for determining the optimal SA amount as a dispersing agent. Contemporary science considers SA an effective activator (along with ZnO) of sulphur vulcanization of non-saturated rubbers. With regards to the mechanism accelerated sulphur vulcanization, most of the presently proposed hypotheses suggest that at the conditions of the process a reaction occurs between SA and ZnO which results in forming zinc stearate. SA salt probably participates in the formation of an activating complex with the appropriated accelerator and sulphur which provokes the crosslinking of rubber macromolecules. Studies on vulcanization of rubber with zinc stearate as activator show that vulcanized rubber has good performance. Chemical structure of Stearic Acid is shown in Figure 3 below.



*Figure 3: Chemical structure of Stearic acid*

### 1.2.5 Accelerators

An accelerator is defined as a chemical that is added to a rubber compound to increase the rate of vulcanization and allows vulcanization to proceed at lower temperatures with greater efficiency. Accelerators also reduce the amount of sulfur needed for vulcanization, thereby improving the aging properties of rubber vulcanizates. Accelerators can be classified by their chemical categories, for example, aldehydes, amines, guanidines, thiophosphates, sulfenamides, thioureas, thiram, dithiocarbamates, xanthates. Sulfenamide accelerators include CBS (n-cyclohexyl-2-benzothiazole sulfenamide), TBBS (N-tert-butyl-2-benzothiazole Sulfenamide), MBS (2-(4-Morpholiniothio)-Benzothiazole), DCBS (N,N'-dicyclohexyl-2-benzothiazole sulfenamide), etc., which are the most popular in the tire industry due to their delayed action and the faster curing speed provided during the vulcanization of vulcanizing rubber mixture. These accelerators provide a wide range of crosslink densities depending on the type and amount of accelerator used and exhibit flatness and reversible curing effects. A gradual increase in the dosage of the sulfenamide accelerator shows an improvement in cure delay, cure rate and cure state. The chemical structure of TBBS is shown in Figure 4 below.

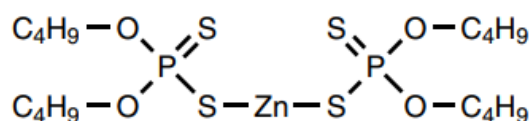


*Figure 4: Chemical structure of TBBS*

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### 1.2.6 Secondary accelerators

ZBPD is used as the secondary accelerator in this research. ZBPD can be technically extended to O, O-dibutyl zinc dithiophosphate. ZBPD is a fast curing auxiliary accelerator for natural rubber. ZBPD is mainly used as a non-blooming natural rubber, a relatively low cost, accelerator in fast curing systems. ZBPD does not fade or stain. ZBPD can be used in NR at levels of 1.0 to 4.0 phr (based on pdr-75%) in combination with sulfenamide, thiazole and thiuram as auxiliary promoters. When used in NRs to enhance stress tolerance, care must be taken when choosing the level of ZBPD to achieve the best compromise between burn and stress tolerance. Since ZBPD is colorless and does not fade, it can be used in translucent, fast-curing NR blends. The chemical structure of ZBPD is shown in Figure 5 below.



*Figure 5: Chemical structure of ZBPD*

### 1.2.7 Pre-Vulcanization Inhibitors (PVI)

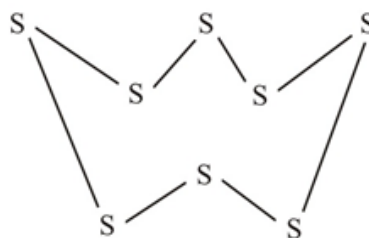
Chemical name of the most widely used PVI in tire industry is N-(Cyclohexylthio)phthalimide. Purpose of using this chemical is to avoid premature vulcanization during processing. Retarders are often added to the cure system. These compounds increase the induction time by reacting with the active accelerator fragment which slows down or temporarily prevents zinc salt formation. Retarders, which are also called pre-vulcanization inhibitors (PVI), are often compounds that readily react with the accelerator (fragments) and only slowly release them. To function as a retarder, the associated polysulfides should also not readily react with the polydiene to produce sulphur bridges. A compound that meets both requirements is N-(cyclohexylthio) phthalimide (CTP). Good retarders do not interfere with the crosslinking process. Its main function is the slow and controlled release of accelerator fragments or (sulfinyl) free radicals without any adverse effects on curing

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and physical rubber properties. -Most effective for sulfinamide accelerators, but can also be used with thiazole, guanidine, thiuram and dithiocarbamates. PVI is particularly useful for improving the efficiency of factory processing operations such as mixing. Calendaring, extrusion and forming. In addition, it provides improved raw meal storage stability and can be used for single stage mixing and recovery of partially cooked compounds. PVI is not stained but may discolour slightly in light or white items. In many compounds, PVI produces a linear response between Mooney scorch and dose levels. Therefore, the processing safety of a compound can be adjusted by changing the dose of PVI. PVI is usually used at 0.1 to 0.4 phr. Higher amounts may slightly reduce the cure modulus. If necessary, the modulus loss can be adjusted by adding sulphur. It is recommended to use up to 40% of the amount of PVI. The reaction of PVI with sulphur and a promoter produces phthalimide. Since phthalimide is less soluble in rubber, blooms may appear on the surface of some compounds. Compounds containing less than 0.6 phr PVI generally do not bloom.

### 1.2.8 Vulcanizing Agent

Sulfur is a chemical element with the symbol S and atomic number 16. It is rich, multivalent and non-metallic. Under normal conditions, the sulfur atom forms a cyclic eight-atom molecule of the chemical formula S<sub>8</sub>. Elemental sulfur is a bright yellow crystalline solid at room temperature. Sulfur is burned in a blue flame to form sulfur dioxide, which has a suffocating pungent odor. Sulfur is insoluble in water, but soluble in carbon disulfide and to a lesser extent in other non-polar organic solvents such as benzene and toluene.



*Figure 6: Chemical structure of Sulphur*

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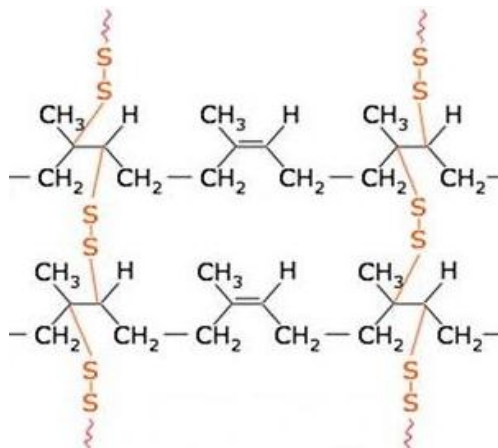
### **1.3 Rubber compounding**

A rubber mixture or composition refers to the addition of certain chemicals, to the crude rubber to achieve the desired properties. Well-known chemicals are crosslinkers, enhancers, anti-degradants, and dyes. Crosslinking agents are necessary to establish crosslinking in order to bind to each other at the molecular level, thereby increasing strength and elasticity. Unformulated elastomers behave like high molecular weights, but with low elasticity and strength. By formulation, long-chain molecules are chemically linked together to form a network and transform the material from a viscous liquid to an elastic solid. This is what happens during vulcanization or curing, which increases strength and modulus and reduces hysteresis. The reinforcing agent of the rubber composition can be used as a stress reliever, and it must have a high specific surface area. This means that the particle size should be less than 1 micron. Typical fillers are carbon black and silica. The size of the primary particles can be as little as 0.1 microns, and the specific surface area is hundreds of square meters per gram of filler.

#### **1.3.1 Rubber vulcanization**

Vulcanization is a chemical process invented by Charles Goodyear to cure rubber. Vulcanization traditionally refers to the processing of natural rubber with sulfur, which is still the most common example, but the term has also evolved to include other (synthetic) rubbers that cure in various ways. Therefore, vulcanization can be defined as curing of an elastomer. In this case, the terms “vulcanized” and “cured” are sometimes used interchangeably. It works by forming cross-links between different parts of the polymer chain, which increases rigidity and durability, as well as other changes in the mechanical and electrical properties of the material. As with the curing of other thermosetting polymers, vulcanization is usually irreversible. Of course, the most common vulcanization method depends on sulphur. Sulphur itself is a slow curing agent that does not treat synthetic polyolefins. Accelerated vulcanization is carried out using various compounds that can alter the crosslinking kinetics, and this mixture is often referred to as cured packaging. The main polymers for sulphur vulcanization are polyisoprene (natural rubber) and styrene-butadiene

rubber (SBR), which are used in most tram tires. Cure packaging is tailored for substrates and applications. The site of reaction / solidification is the allylic hydrogen atom. These CH bonds are adjacent to carbon-carbon double bonds. During the vulcanization process, some of these C-H bonds are replaced by a chain of sulphur atoms linked to the site of solidification of another polymer chain. These bridges contain from one to several atoms. The number of sulphur atoms in the crosslinking strongly affects the physical properties of the final rubber product. Short stitches give rubber better heat resistance. Crosslinking with a large number of sulphur atoms gives the rubber good dynamic properties, but lower heat resistance. Dynamic characteristics are important for bending movements of rubber products, for example, for moving the sidewalls of running tires. Without good deflection properties, these movements can quickly form cracks and ultimately lead to the destruction of rubber products.



*Figure 7: Chemical structure of vulcanized rubber*

### 1.3.2 Mixing of rubber & other ingredients

Vulcanizable polymers cannot be used without mixing. Various additives (such as hardener systems, protection systems, amplifiers, cheapeners and other processing aids) must be mixed with the polymer or polymer mixture to form a uniform homogeneous mass for all these ingredients, which will make the process satisfactory and after curing will give the product ideal performance with minimal time and effort. Due to the partial elasticity and very high viscosity of rubber, high-powered,

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robust machines, such as mixing mills or internal mixers, are required to achieve the mixing of additives into polymers. The ingredients are in the form of liquid, solid powder or solid agglomerates.

The mixing of the solid contents with the solid polymer is carried out in stages. During the separation process, large pieces or agglomerates will be broken into smaller aggregates suitable for incorporation into rubber. For example, soot particles with a size of 250-2000 microns are divided into aggregates with a size of 100 microns. These aggregates are then absorbed or incorporated into the rubber to form a coherent mass. During the mixing process, the shear of the rubber creates a shear stress in the rubber mass, which in turn exerts a shear stress on these aggregates and breaks them down to a final small size. If carbon black is used, it is about 1 micron. To size. At the micromolecular level, this phase is also called enhanced mixing or homogenization. Distribution or homogenization or extensive mixing at the micromolecular level is the movement of agglomerates / particles from one point to another without changing the shape of the particles to increase the randomness of the mixture. Inclusion of ingredients is a very slow process. Another way to reduce the time of administration is to use powder rubber. In a simple belt mixer, rubber powder can be mixed with other ingredients. Seal the powder material in another machine and feed it into the internal mixer. Due to the large surface area of the powder rubber, it is very quickly incorporated into the polymer, and only a very short mixing cycle in the internal mixer is enough to achieve mixing. Even after all ingredients have been added, the dispersion / distribution of ingredients remains incomplete. With due attention to cutting and folding operations on the mixer or simply to expanding the mixing cycle in the internal mixer, good distribution is relatively easy to achieve. However, the dispersion depends on the shear stress created in the polymer, so prolonged mixing may not provide good dispersion. Not only the mixing cycle time, but also the order in which the ingredients are added to the rubber must be carefully thought out. Viscosity decreases with stirring, which is necessary for smooth processing of raw materials. Soot dispersion has a profound effect on the physical properties of vulcanized rubber. Non-dispersed soot (usually considered an agglomerate of soot larger than 9 microns) plays a granular role. Under tension,

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cracks may appear in these places. As the degree of dispersion decreases, destructive properties such as tensile strength, tensile strength and, therefore, abrasion resistance, decrease.



*Figure 8: Industrial Banbury mixer*

### **1.3.3 Milling (Two roll mill)**

Stress, which is applied by rotating wheels will be used for this milling process. Factors to be adjusted during the milling operations are gap between rollers, speed difference between rolls and feed rate. The moulding of rubber begins with the grinding process. After the Banbury mixing cycle is complete, the rubber is placed in the mill. The grinding process forms the rubber into flat long strips by forcing the rubber through two fixed rollers that rotate in different directions and at different speeds.





*Figure 9: Industrial two roll mill*

Samples will be taken out from the sheeted-out compounds and sent for initial testing (basic rheometer testing & physical testing) for verification prior to release them for production. Once the test results are in line with the specification, compounds will be sent for tire building machines for green tire building and finally for tire curing. This study is mainly focused on enhancing the cushioning effect of solid resilient tires whilst maintaining the other critical required tire properties within the specifications. To achieve this goal, Thermally Expandable Microspheres (ThEM) will be used and studied the resilient tire cushioning compound behaviour.

#### **1.4 The objectives of this study**

- Creating a porous structure inside the cushioning component of the solid resilient tire by using Thermally Expandable Microspheres (ThEM).
- Control/minimize the heat build-up inside the resilient tire with newly formed cushion compound by using ThEM.
- Enhance the cushioning effect of solid resilient tires without doing any changes in desired other critical properties of the cushioning compound as well as in the tire.

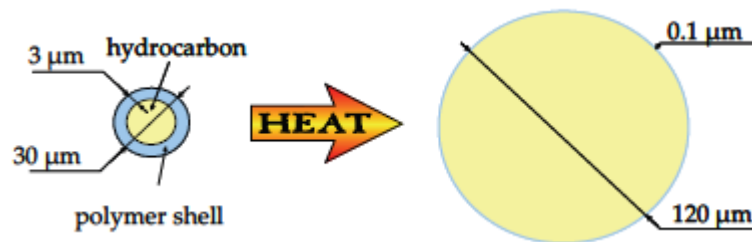
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**CHAPTER 2**  
**LITERATURE REVIEW**

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## 2.1 Concept of ThEM

Microspheres expanding upon heating are polymer particles with a core / shell structure that expand upon heating. The core of the microsphere contains low-boiling saturated hydrocarbons, and the shell consists of an airtight thermoplastic polymer that prevents the release of hydrocarbons. At ambient temperature, the polymer shell is stiff. However, polymer shells soften when heated, and hydrocarbons increase internal pressure. Over time, the microspheres swelled like balloons, with a sharp increase in volume.



*Figure 10: An illustration of the general concept of ThEM*

After cooling the microspheres, the polymer shell solidifies in an expanded state, retaining its volume. Thus, the density of the microspheres can be reduced from about 1100 kg m<sup>-3</sup> to about 30 kg m<sup>-3</sup>. However, continuous heating as the microspheres expand ultimately causes them to shrink, as hydrocarbons are gradually lost, and pressure drops. [8] These microspheres are prepared by suspension polymerization, in which hydrocarbons are encapsulated as the polymer forms. Mixing polymer shell-forming monomers with hydrocarbons; dispersing the mixture in water to form an emulsion; the emulsion is heated in the presence of an oil-soluble initiator; therefore, the monomers polymerize and at the same time encapsulate the hydrocarbons, forming a shell. The properties of the microspheres depend on such parameters as the composition of the polymer shell, the boiling point of the hydrocarbon, and the size of the microspheres. Unique expansion characteristics are usually determined by thermomechanical analysis (TMA) and are defined by the start temperature ( $T_{\text{start}}$ ) of the expansion, the temperature at which the maximum

expansion occurs ( $T_{max}$ ), and the maximum probe displacement (used to measure the increase in sample volume). [8].

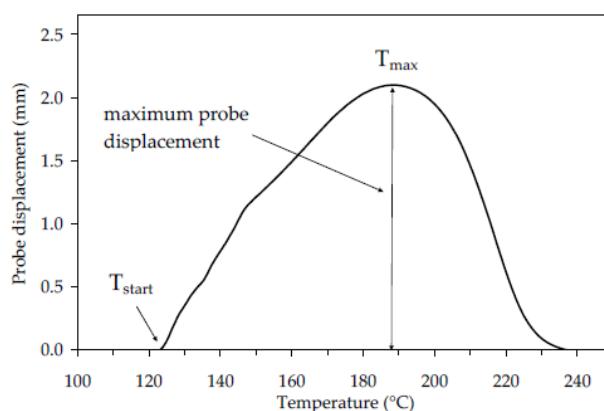


Figure 11: The expansion behaviour of microspheres.

## 2.2 Characteristics of Thermally Expandable Microspheres (ThEM)

Characteristics of the Thermally Expandable Microspheres (ThEM) used in this study are shown in below Table 02.

Table 2: Specification table of ThEM

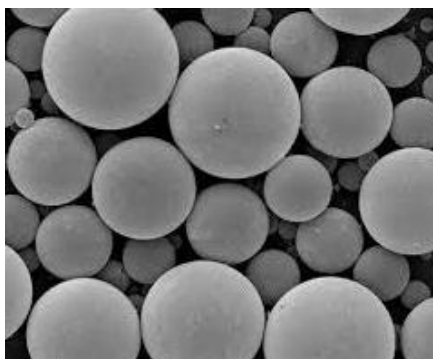
Average particle size	36 – 44 $\mu\text{m}$
Expansion start temperature ( $T_s$ )	120 – 130 $^{\circ}\text{C}$
Maximum expansion temperature ( $T_{max}$ )	160 – 180 $^{\circ}\text{C}$
True specific gravity after expansion	$0.013 \pm 0.005$
Density, before & after expansion	1.0-1.2 $\text{g}/\text{cm}^3$ , 0.01-0.03 $\text{g}/\text{cm}^3$

## 2.3 Special features of ThEM

One of the identical features of this ingredient is formation of uniform cells and hence it will be helpful to have uniformly distributed cell structure inside the cushion

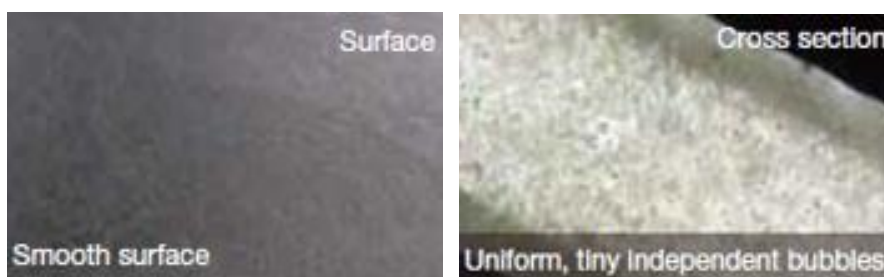
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compound. Scanning Electron Microscope (SEM) image of a uniformly formed cell structure is shown in Figure 10 below.



*Figure 12: SEM image of a uniformly formed cells*

In addition to the above feature, there are many more special features are identified in this special ingredient such as smooth and refined finish, reduction of expansion loss so that only a small amount of ThEM needs to be added, Easy to control the processing temperature, Perfect particle size distribution compared to conventional agents, Smooth surface & tiny, uniform independent bubbles. SEM images of the cross section & the outer surface of a ThEM used compound are shown in Figure 11 below.

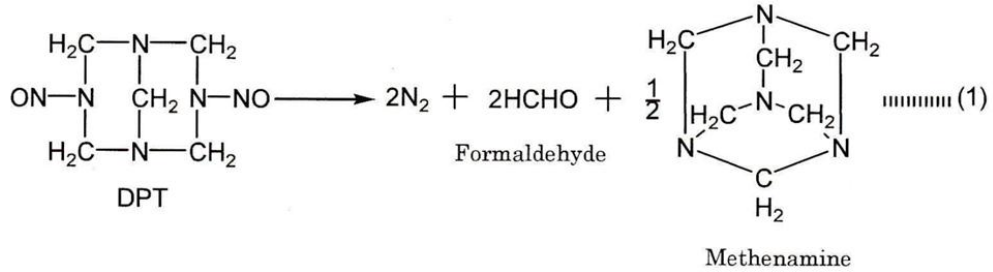


*Figure 13: Surface & cross-sectional micro images*

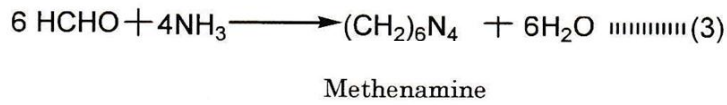
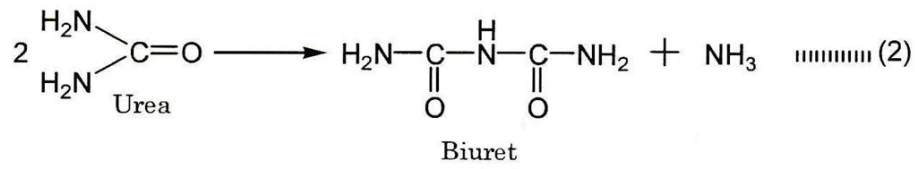
In order to enhance the reaction ability of the ThEM, a ThEM promoter was used together. Reaction between ThEM and the promoter is shown below.

## 2.4 Reaction between ThEM & the ThEM promotor

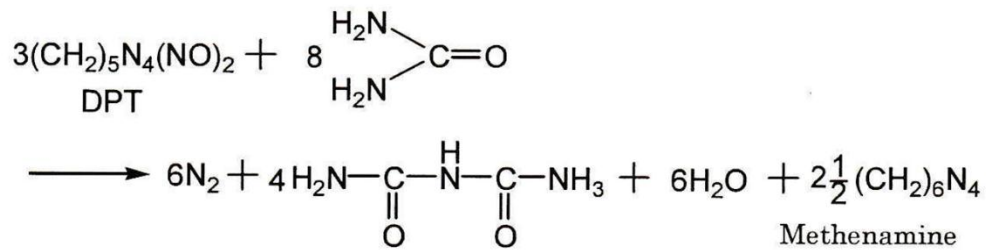
- Decomposition reaction of ThEM



- Decomposition reaction of ThEM promotor



- Combination of ThEM & the ThEM promotor



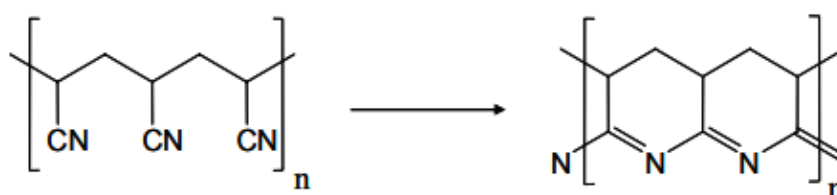
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## 2.5 Properties of ThEM

The general function of thermally expanding microspheres seems quite simple. The polymer shell softens when heated, and internal pressure causes swelling of the particles. However, the ability of microspheres to expand strongly depends on the barrier layer, and the mechanical properties of the polymer shell retain the blowing agent and are deformed during the expansion process. Acrylonitrile (AN) or vinylidene chloride is the main component in the polymer shell of almost all microspheres. The homopolymers of these monomers are semi-crystalline and have excellent barrier properties. However, the thermoplastic characteristics of these homopolymers are insufficient to explain why copolymers with monomers, such as methyl methacrylate (MMA), methyl acrylate (MA) and MAN, often form a polymer shell. The barrier properties of the polymer shell can be divided into two parts. First, the polymer shell is formed in situ during the polymerization. If the polymer shell is not lumpy and free from defects, the encapsulation of hydrocarbons will be impaired. Secondly, the cohesion of the polymers that make up the shell is important to prevent the penetration of hydrocarbons through the polymer shell. Barrier properties are important. Not only for unexpanded microspheres, the thickness of the polymer shell decreases significantly during the expansion process, which further emphasizes the importance of barrier properties. [3] If the barrier properties of the shell are sufficient to prevent the release of hydrocarbons from the microspheres; the expansion of microspheres depends on the viscoelasticity of the polymer shell. To expand the microspheres, the internal pressure must exceed the yield strength of the polymer shell. The glass transition temperature ( $T_g$ ) of the polymer shell is the main parameter for determining the expansion temperature of the microspheres. The shell is solid below  $T_g$ , which can effectively prevent the expansion of microspheres [8]. However, around  $T_g$ , the shell softens, and the plasticity of the polymer shell increases the reason microspheres can expand. Therefore, the  $T_g$  of the shell polymer is closely related to the  $T_{\text{start}}$  expansion parameter. A huge expansion of the microspheres is possible because the polymer shell is deformed by plastic flow. Important factors for the ductility of the polymers that make up the shell of the microsphere are composition, molecular weight, degree of crosslinking, and

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crystallinity. A more comprehensive description of these briefly outlined polymer properties can be found in "Polymer Properties" by D.W. Van Krevelen. Polymer degradation in the shell is another parameter that cannot be ignored when using microspheres in some applications, as processing temperatures in excess of 200 °C are sometimes required during the foaming process of thermoplastics, for example. Due to the cyclization reaction between nitrile groups in the polymer, this degradation can cause discoloration or affect the mechanical properties of the microsphere shell [6].



*Figure 14: A cyclization reaction occurs in polyacrylonitrile (PAN) at elevated temperatures*

## 2.6 Applications of ThEM

Microspheres have extraordinary expansion capabilities, making them valuable to the industry in many applications. For example, they can be used to reduce weight, change product properties (such as thermal, acoustic, and electrical insulation properties) and save materials. Microspheres are used in coatings to achieve 3D patterns on wallpaper or to enhance surface characteristics such as matting or non-slip and weight reduction [1]. In car body primers, 50% by weight can be saved. % Material with improved corrosion resistance and noise reduction. Other advantages of using microspheres are increased firmness and elasticity with light weight. Using the internal forces created by the pressure created by the encapsulated hydrocarbons, the glue line can be broken, which facilitates its removal, for example, of automobile windshields. Thermoplastic materials (such as PVC, TPE, PE, PP, TPU, etc.) can be foamed using microspheres using traditional polymer processing methods (such as extrusion or injection moulding). Since the microspheres used in this processing



technology usually appear as a dry powder or as the main Bach, foaming products can be obtained without special equipment [8].

## 2.7 Studies carried out on ThEM

### 2.7.1 Enhancing HDPE Insulation with Polymeric Microspheres

Increasing the efficiency of a soldier's ration heating program is an investment that will allow him to successfully complete his mission. Researchers at the Army's Nadick Soldier Research, Development, and Engineering Centre have recently worked to improve the thermal insulation packaging of US rations. The team conducted a three-year study investigating the benefits of filling packaging materials with polymer microspheres to improve their thermal insulation and other properties. Measurements performed with C-Therm's TCI thermal conductivity analyser showed that the thermal conductivity of the package was reduced by 80% only when the microsphere load was 1%. These results show how filling polyolefin films with microspheres can improve the thermal insulation of quantitative packaging and, in turn, heat the entrance of war fighters faster by increasing the heating efficiency [16].

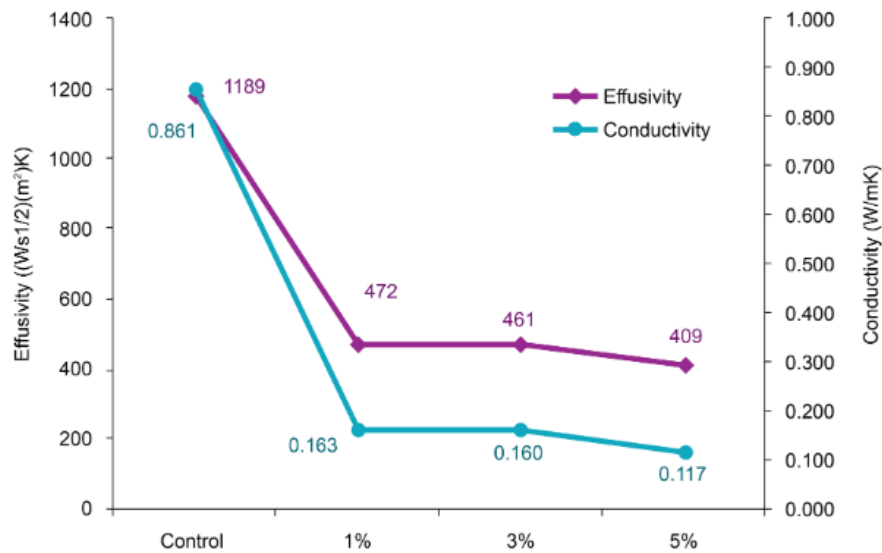


Figure 15: Thermal analysis of high temperature profile blown multi-layer microsphere loaded HDPE

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## **2.8 Development of microporous rubber foam material with ThEM**

A foamed rubber having a plurality of micro voids comprising micro spheres incorporated therein characterized in that the microspheres are expanded during heating and vulcanization of the rubber and the volume fraction of the expanded microspheres is 35-80 % in the foamed rubber. The microspheres may be thermoplastic microspheres filled with a volatile liquid. The microspheres may have an unexpanded diameter of 5 to 10  $\mu\text{m}$  and an expanded diameter of between 300  $\mu\text{m}$  and 1000  $\mu\text{m}$  [5]. Also disclosed is a method of manufacture of a rubber comprising the steps of: providing a rubber; incorporating additives; adding and mixing microspheres into the rubber composition; and heating the rubber to effect vulcanization. The vulcanization of the rubber may be delayed allowing for expansion of expandable microspheres during heating, such a delay may be achieved by adding a delayed action accelerator or a retarder to the rubber. The composition which can be vulcanized to form a microporous vulcanized rubber comprises an elastomer material which is substantially uniformly dispersed in 0.5 to about 80% by volume of hydrated sulfuric acid per 100 parts by weight of the elastomer material. Magnesium particles and 1 to about 100 parts of discrete fibres. A fibre having a diameter in the range of about 0.0005 to about 0.004 inches and a length in the range of about 0.005 to about 0.250 inches, and a sulphur-containing vulcanizing component sufficient to convert an unvulcanised composition to the vulcanized rubber when cured, wherein Fibres increase liquid absorption and dispersion of the resulting vulcanized rubber [15].

## **2.9 Porous structures with ThEM and its applications**

Porous microspheres have external pores on the surface or internal pores (usually interconnected) in the core, and the active substance can dissolve or disperse in the surface or core of the microsphere. In the 1950s, cross-linked polystyrene with a macroporous structure in the dry state was obtained by a new polymerization method. Until the 1990s, porous microspheres were considered suitable materials for potential applications, including drug carriers, high-speed chromatography, cell delivery, and tissue regeneration (such as stents) [11], with little progress. Compared

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to traditional microspheres, they have many unique characteristics, such as the special characteristics of drug absorption and drug release kinetics, large specific surface area and low density. Porous microspheres differ from traditional microspheres in surface and internal pores. Porosity plays an important role in determining the efficiency of the capacity and kinetics of release. The diameter, quantity and structure of pores are key factors affecting the performance of porous microspheres [4]. Most applications of porous microspheres are based on porous structures (pores, pore sizes, surface areas, etc.). New areas have been discovered in which microspheres can be used. Jiang et al. A super-hydrophobic surface of a lotus-like sheet was obtained using a porous microsphere / nanofiber composite membrane by the electro-hydraulic kinetic method. A charged stream of polystyrene / dimethylformamide solution was pumped onto a metal plate using a nozzle, and a porous structure formed as the solvent evaporated. In other areas, porous microspheres can be used for delivery to the stomach as well as anode materials for high-performance lithium-ion batteries to create a porous structure inside an elastic tire. IM will be introduced into the cushioning composition. The expectation of a porous structure inside the tire is an enhancement of the cushioning effect, and this will be studied in detail in this study.

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**CHAPTER 3**  
**EXPERIMENTAL**

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### 3.1 Materials

The following materials were used as per the compounding formula used in Table 03.

SLR 20 (Natural Rubber)  
N330 (Carbon Black)  
N550 (Carbon Black)  
6PPD (Antioxidant)  
TMQ (Antioxidant)  
Zinc Oxide 99.5%  
Stearic acid  
TBBS (Accelerator)  
DCBS (Accelerator)  
Vocal S-75 (Secondary accelerator)  
PVI (Retarder)  
Sulphur (Vulcanizing agent)  
ThEM (Thermally Expandable Microspheres)  
ThEM Promoter

### 3.2 Instruments

The following instruments were used for the preparation and characterization of the samples.

Banbury mixer  
Two roll mill  
MDR (Moving Die Rheometer)  
Tensile meter  
Dumbbell cutter  
Tear sample cutter  
Hardness meter  
SPG (Specific gravity) meter  
Hydraulic press  
Dispegrader

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Rebound tester

Compression moulding hydraulic lab press

### 3.3 Preparation of vulcanized rubber samples

Formulations for the preparation of vulcanized natural rubber are shown in Table 3 below. Altogether 6 compounds were prepared including the control compound sample. The control correspond sample was labelled as Regular and others were labelled as Test 2, Test 3, Test 4, Test 5 & Test 6.

Table 3: Formulations used for the preparation of compound samples

Ingredient	Amount (pphr)					
	Regular	Test 2	Test 3	Test 4	Test 5	Test 6
1 <sup>st</sup> Stage						
SLR 20	100.0	100.0	100.0	100.0	100.0	100.0
N330	12.5	12.5	12.5	12.5	12.50	12.5
N550	27.0	27.0	27.0	27.0	27.00	27.0
6PPD	1.0	1.0	1.0	1.0	1.0	1.0
TMQ	1.0	1.0	1.0	1.0	1.0	1.0
Zinc Oxide 99.5%	3.75	3.75	3.75	3.75	3.75	3.75
Stearic acid	1.50	1.50	1.5	1.5	1.5	1.5
2 <sup>nd</sup> Stage						
TBBS	0.95	0.95	0.95	0.95	0.95	0.95
DCBS	0.3	0.3	0.3	0.3	0.3	0.3
Vocal S-75	0.8	0.8	0.8	0.8	0.	0.8
PVI	0.4	0.4	0.4	0.4	0.4	0.4
Sulphur	1.3	1.3	1.3	1.3	1.3	1.3
ThEM	0.0	4.0	5.0	6.0	7.0	8.0
ThEM promoter	0.0	4.0	4.0	4.0	4.0	4.0

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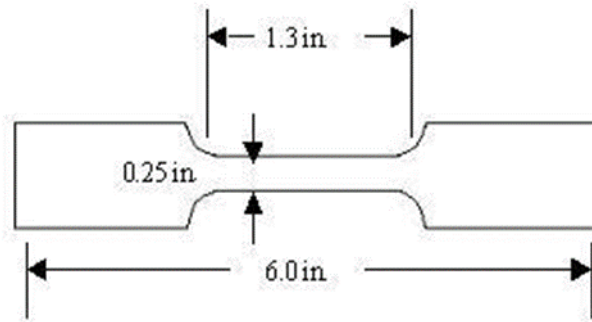
### **3.3.1 Compounding**

Compounding was carried out in two stages named 1<sup>st</sup> stage compounding and 2<sup>nd</sup> stage compounding. Converted the pphr value into Kilo grams or grams and weighed the material separately by using electronic balance. As mentioned in Table 03, 1<sup>st</sup> stage compounding ingredients (SLR 20, N330, N550, 6PPD, TMQ, Zinc oxide & Stearic acid) were mixed inside the Banbury mixer (lab mixer) following up the correct sequence. First, SLR 20 was added with Stearic acid and let them mix for 3 mins. Secondly, N330 & N550 were added at the same time and let them mix for another 4mins. Other remaining materials were then added as the last step of the 1<sup>st</sup> stage compound preparation and let all the material mixed for another 3 mins. Therefore 1<sup>st</sup> stage mixing cycle was 10 mins inside the Banbury mixer. 2<sup>nd</sup> stage compound mixing process was performed in the two-roll mill by adding 2<sup>nd</sup> stage materials (TBBS, DCBS, Vocal S-75, PVI, sulphur, ThEM & ThEM promoter). 2<sup>nd</sup> stage mixing cycle was 4 mins.

### **3.3.2 Forming & vulcanization of rubber compounds**

In order to test the curing performance, sample test pieces need to be produced. Sample preparation was done on test plates with 2 mm ± 0.2 mm thickness in order to perform tensile & tearing tests. These test plates are vulcanized in a mould and typically have four cavities, each with a cavity of 150 x 150 mm. Vulcanizing conditions are, 140 °C (curing temperature) for 30 min (curing time). Cylindrical test pieces are used for compression set, relaxation, abrasion and compression testing, and can also be produced in moulds. Curing conditions of hardness test sample preparation is 150 °C (curing temperature) for 17 min (curing time). There are two common sizes, a so-called small test piece with a diameter of 13 mm and a height of 6.3 mm and a large test piece with a diameter of 29 mm and a height of 12.5 mm. In this study, samples with a diameter of 13 mm and a height of 6 mm were prepared. The samples used for hardness testing are shown in Figure 17 below. The test piece is punched out from the test piece for testing of tensile strength, tear strength and tensile deformation. When punching out the specimen, it is very important to use a sharp punch or knife on a soft surface. Poor cutting edges or punches with a notch

may cause cracks in the test piece, which may give incorrect results. The standard tensile sample is shown in Figure 16 below. hardness was also used to measure specific gravity (SPG) of the sample as well as used in dispegrader to observe the porosity level inside the sample.



*Figure 16: Standard test sample for tensile test*



*Figure 17: Samples prepared for hardness test*

### **3.3.3 Resilient tire production for testing**

Industrial two roll mill was used to produce green tires as shown in Figure 18 below. All the 3 components were built by using this industrial two roll mill. First, Base compound was placed on collapsible drum in the two-roll mill and at the same time, bead wires were also placed. Then the rest of the base compounds were rolled out on the beads until the specified base weight is achieved.





*Figure 18: Use of expandable drum for green tire building*

As the next step, a bonding layer was applied on top of the prepared base component in order to enhance the strength between base and the cushion part. Then the cushion compound was applied on top of the bonding layer as the same way which used to prepare base component.

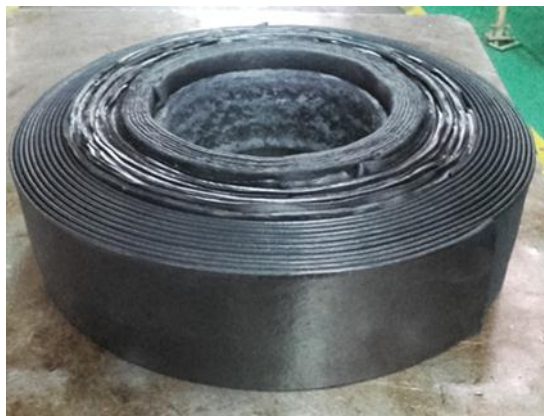


*Figure 19: Cushion layer applied green tire*

Finally, tread compound was rolled on top of the cushion compound and the final green tire (product before curing is called as green tire) looks like in Figure 20

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below. Green tire was cured under  $130\pm 3$  °C for 2 hours. (Curing time was calculated based on  $T_{90}$  which was extracted from rheological graph)



*Figure 20: Produced green tire*

### **3.4 Laboratory Tests**

General testing lab equipment were used to measure rheological parameters as well as physical parameters during this study. Moving Die rheometer (MDR) was used to measure minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), scorch time ( $T_{s2}$ ) & curing time ( $T_{90}$ ) of the 2<sup>nd</sup> stage compounds prepared. Testing conditions of MDR is, 151 °C for 30 min. Followed-up the methodology described in ISO/TS 289-4:2017(en) for MDR testing. Durometer was used to measure Hardness of the compound. Sample preparation which was used to measure hardness of the compound was described in 3.3.2 and it is the method described in ISO 48-7:2018 standard. Specific gravity hydrometer was used to measure specific gravity (SPG) of the compound. Same sample which was prepared for hardness measurement was used to measure SPG of the compound. Rebound tester was used to measure resilience of the compound and followed-up the methodology described in ISO 4662:2017 standard. Tensometer was used to measure tensile, modulus & elongation of the compound. Followed-up the methodology described in ISO 37:2017 standard for tensile testing.

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Dispegrader was used to observe porosity level of the compound and followed-up the methodology described in ISO 11345:2006, ASTM D7723.

Initially all the above-mentioned tests were carried out for regular compound which is already used in production (compound #116513). After that, same set of tests were performed to the testing compounds (Test 02, Test 03, Test 04, Test 05 & Test 06) & respective samples with the purpose of having good comparison with the regular compound. Since ThEM has been incorporated with testing compounds, volumetric changes with time was also analysed in order to observe whether expanded micro balloons can influence the geometrical shape of the tire. After completion of all the compound related testing, based on compound test results the most suitable test compound has been selected for the green tire preparation. After comparing all the test results, it has been decided to move forward with Test 03 compound for further studies. Therefore, as per the formulation of Test 03, master batch was prepared in order to produce test tires for the study. The procedure described in 3.3.3 was used for all the test tire production. One tire was produced by using the general cushion compound (control compound) and the other tire was produced by using Test 03 cushion compound for further comparative tire tests. QED test (endurance test for heat build-up analysis), deflection test, ground pressure measurement & footprint tests were carried out to compare tire performances. Another two test tires were produced by using Test 03 compound, in order to perform QED test. QED test was performed as per described in ISO 4666-1:2010(en).

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**CHAPTER 4**  
**RESULTS AND DISCUSSION**

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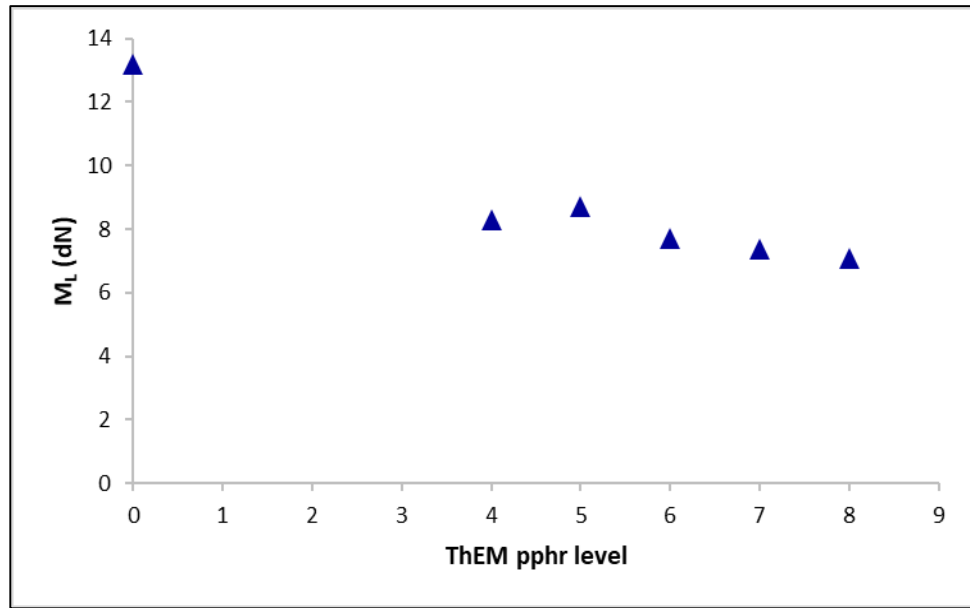
## 5.1 Analysis of cure characteristics

Test results of the rheological test (MDR) are shown in Table 4 below.

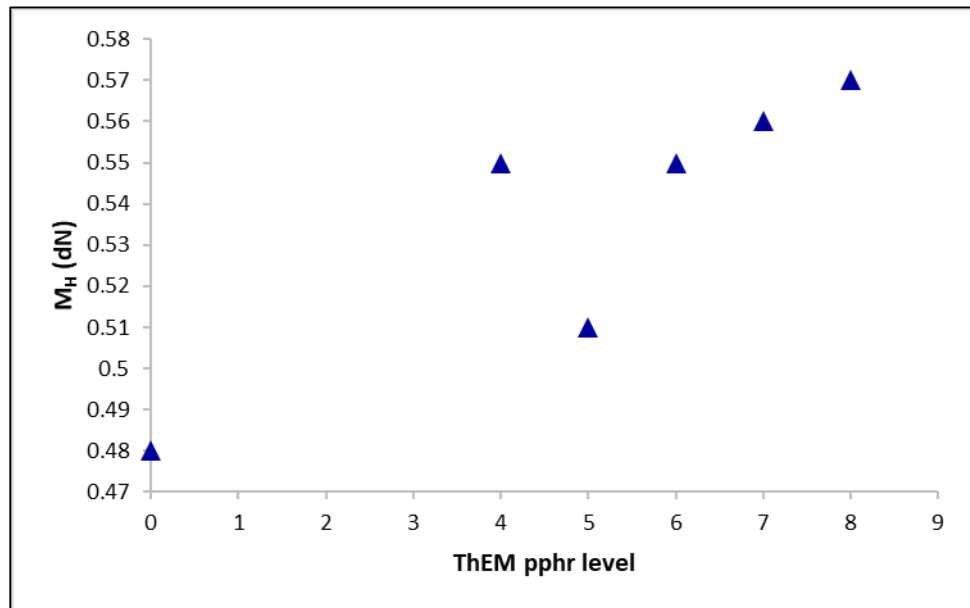
Table 4: Rheological test results of the six compounds

Description	Regular	Test 02	Test 03	Test 04	Test 05	Test 06
$M_L$ (dN)	13.17	8.31	8.73	7.7	7.36	7.09
$M_H$ (dN)	0.48	0.55	0.51	0.55	0.56	0.57
$T_{S_2}$ (Min)	0.89	0.71	0.72	0.72	0.73	0.72
$T_{90}$ (Min)	13.17	8.31	8.73	7.7	7.36	7.09

Graphical representation of all the rheological test results is shown in below charts. Variation of  $M_L$  is shown in Figure 21. As per the test results, there is a considerable drop in  $M_L$  values when compared with the control sample.  $M_L$  is the lowest torque value recorded on the rheology chart. It is a measure of the stiffness of an unvulcanised rubber mixture at a given temperature. Lower the  $M_L$ , lower the stiffness of the compound as per the definition. Therefore, when introducing ThEM into cushion compound stiffness will be reduced and the cushioning compound becomes much softer than ever before. This is a good indication for a better cushioning property. But looking at the chart, we can decide that the stiffness will not reduce with the amount of ThEM used. Even the ThEM amount is increasing, there is no big variations in  $M_L$ . As the curing progresses, the torque further increases. The slope depends on the compound used and the curing system. After a period, the torque usually reaches a maximum and then flattens out. The highest torque recorded on the chart is called  $M_H$  (Maximum Torque). Variation of  $M_H$  is shown in Figure 22 below.  $M_H$  curve shows an entirely different variation compared to  $M_L$  curve when increasing the amount of ThEM.  $M_H$  is gradually increasing with the ThEM amount as per the  $M_H$  curve.



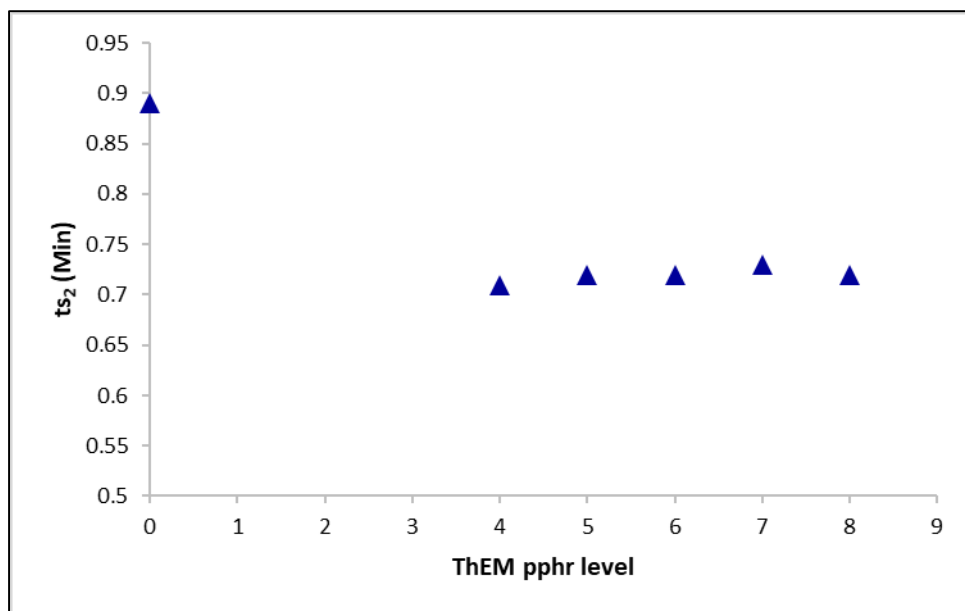
*Figure 21: Variation of  $M_L$*



*Figure 22: Variation of  $M_H$*

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As mentioned previously,  $M_L$  is a measure of the stiffness of an unvulcanised rubber mixture at a given temperature. As curing begins, torque increases. When the torque is increased by 2 units above the  $M_L$  value, the time is recorded, and this time is called  $T_{s2}$ . It is the time from the beginning of the test to the time the torque has increased 2 units above  $M_L$  value. Variation of  $T_{s2}$  is shown in Figure 23 below. When we create a trend line throughout the test results in below chart, it shows an increasing trend with increasing ThEM amount. Reason behind that would be the formation of cell structure inside the cushion compound sample. When heat applies and with the time, cell structure starts to form inside the sample. Which leads to take more time to increase the torque values by 2 units from the  $M_L$ .



*Figure 23: Variation of  $T_{s2}$*

Curing time ( $T_{90}$ ) is calculated as the time required for the torque to reach 90% of the maximum achievable torque. Even though the  $T_{s2}$  variation showed an increasing trend,  $T_{90}$  shows a decreasing trend with increasing the ThEM amount. After the formation of micro balloons, compound becomes much softer as per the  $M_L$  &  $M_H$

charts above. Therefore, it will not take longer time to reach 90% of the maximum torque. Variation of  $T_{90}$  is shown in Figure 24 below.

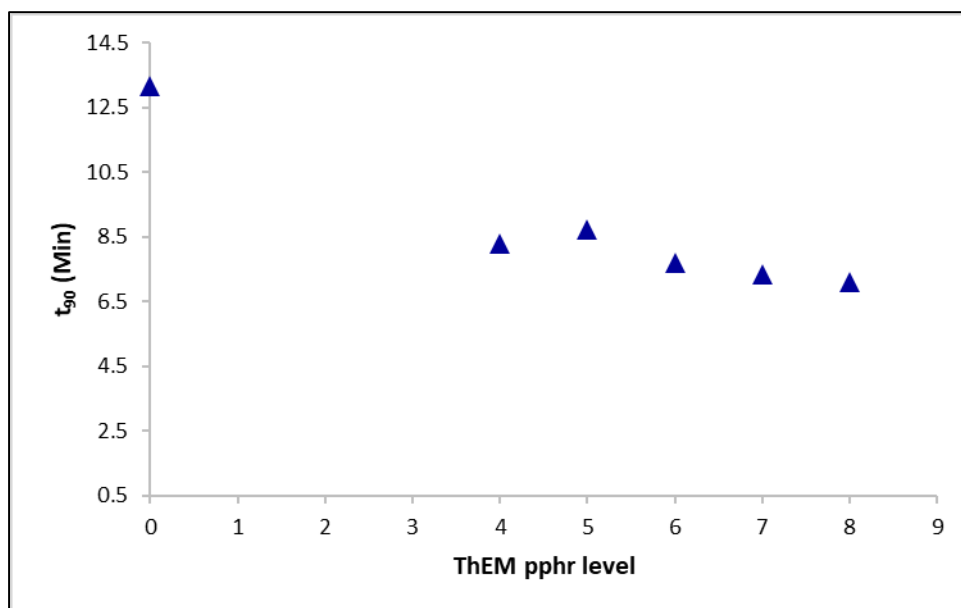


Figure 24: Variation of  $T_{90}$

## 5.2 Analysis of physical properties

Test results of the physical tests (Tensile, Hardness, SPG, Resilience & Volumetric change) are shown in Table 5 below.

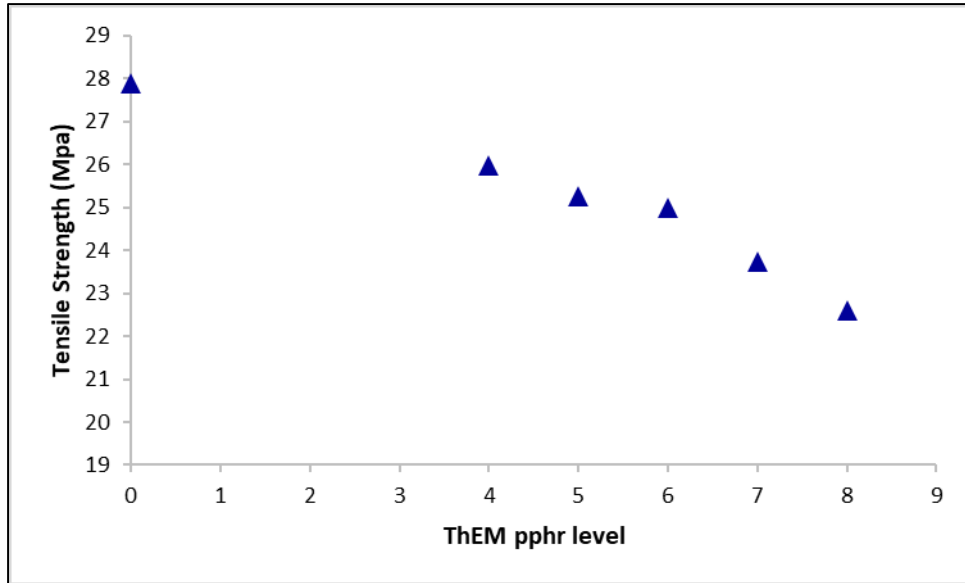
Table 5: Physical test results of the six compounds

Description	Regular	Test 02	Test 03	Test 04	Test 05	Test 06
Tensile Strength (N/mm <sup>2</sup> )	27.88	25.97	25.26	24.98	23.75	22.59
Elongation @ Break (%)	383.44	369.78	370.24	363.88	359.53	355.28
Tearing Strength (N/mm)	64.55	59.32	61.78	59.55	56.78	55.11
Hardness (Shore A)	65	64	61	61	58	55
Specific Gravity	1.138	1.002	0.893	0.761	0.696	0.6
Resilience (J/mm <sup>3</sup> )	52	53	57	60	61	63
% Increment in Vol.	0	3.19	17.95	36.15	47.63	71.25



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### 5.2.1 Variation of tensile strength

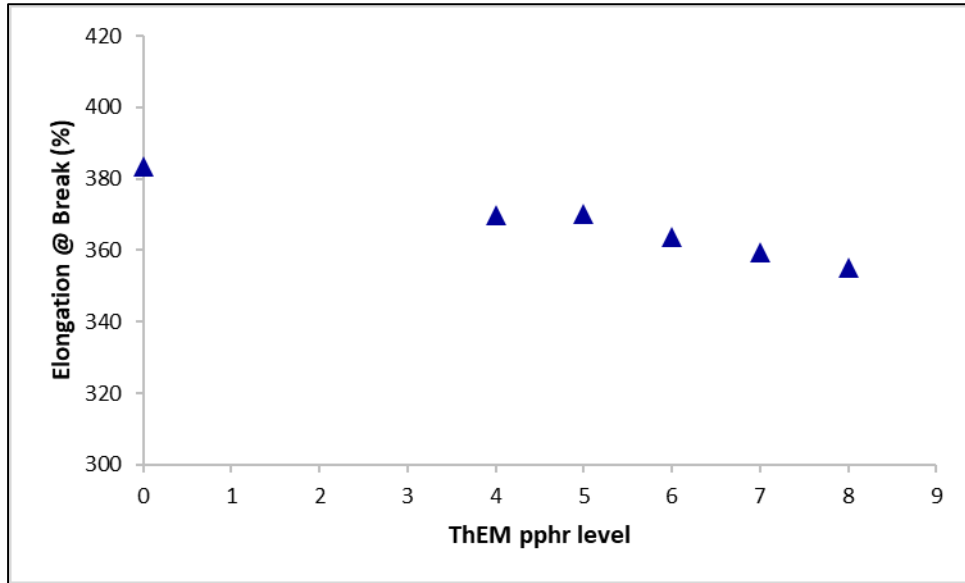


*Figure 25: Variation of Tensile strength*

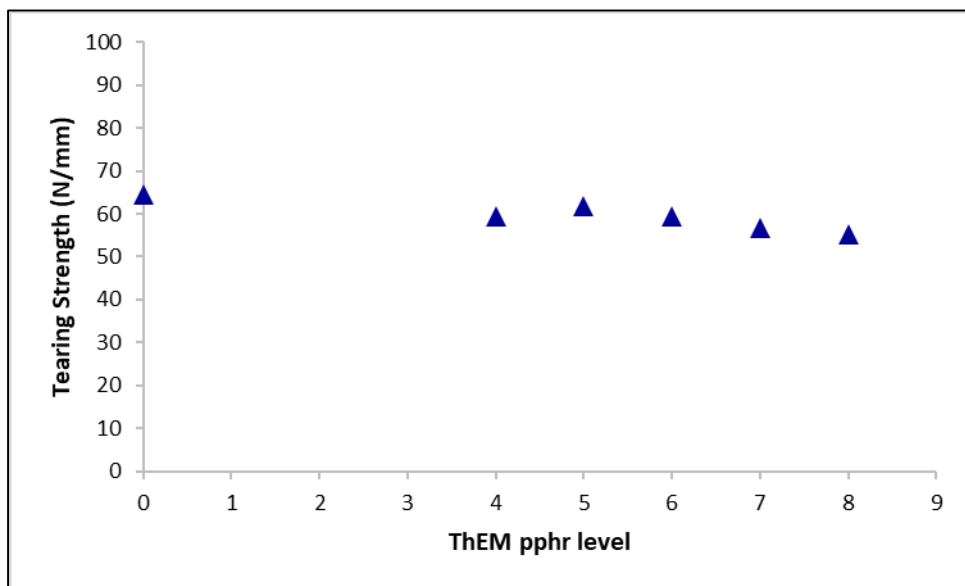
As per the tensile variation graph above, it shows a decreasing trend in tensile property with increasing ThEM amount. Reason for this reduction would be the formation of micro balloons inside the compound. Tensile test will be done by applying two vertical forces in opposite directions. That force will be transferred into these micro balloons and destroy the cell structure by less force which leads low tensile strength for the compounds which were produced by using ThEM.

### 5.2.2 Variation of elongation at break & tear strength

Elongation & tearing results are also measured by using this technique (applying vertical forces on the sample) and hence, the same explanation can be considered as the reason for negative impact in elongation & tear strength as shown in below Figure 26 & Figure 27.



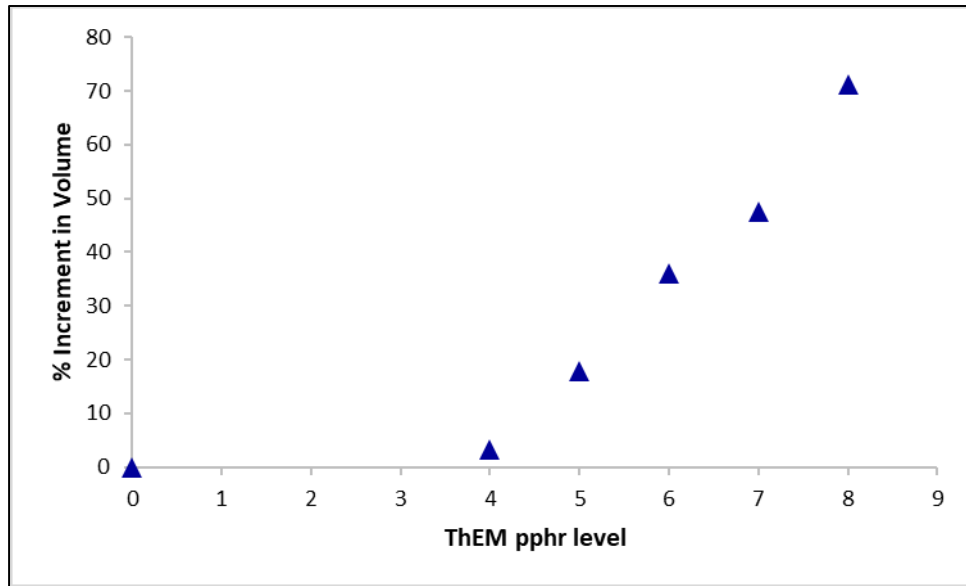
*Figure 26: Variation of Elongation at break*



*Figure 27: Variation of Tear strength*

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### 5.2.3 Variation of % increment in volume



*Figure 28: Variation of % increment in volume*

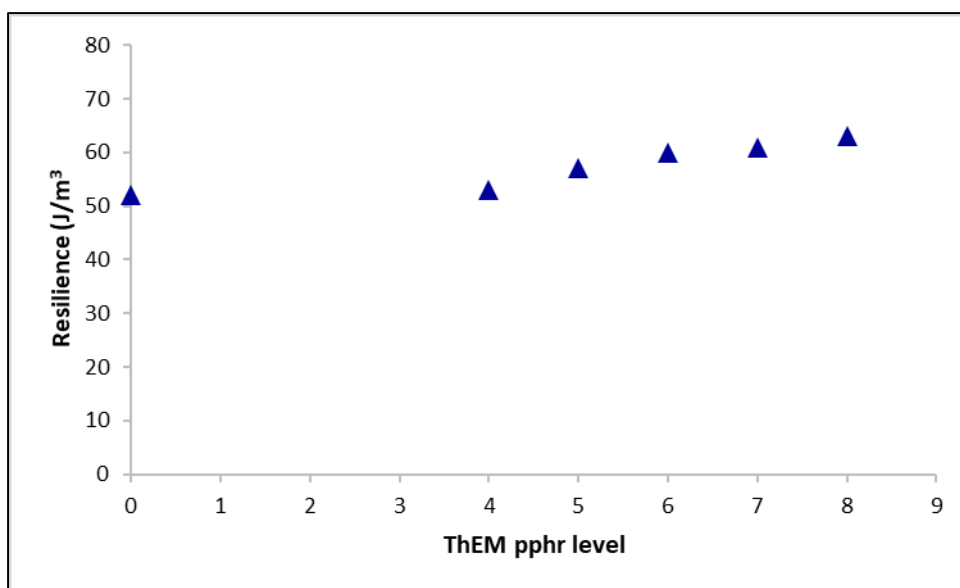
In this case, volumetric changes need to be considered as lot of voids are created inside the compound as ThEM are in cooperated with the compound. When heat is applied, microspheres starts to expand and takes some volume. When heat is gradually increasing, parallely volume is also getting increased. Therefore, when compare the volume of regular sample and the ThEM mixed sample, sample volume is slightly high in ThEM mixed samples. As per the above chart, volume is getting increased with increasing the amount of ThEM since the portion of porous structure created inside the compound due to microspheres are higher from Test 02 sample to Test 06 sample.

### 5.2.4 Variation of Resilience

As per the definition of resilience, resilience is the percent of energy required for a deformed piece of rubber to rebound back to its original shape after a deformation. Resilience and the cushioning effect have very close relationship as resilience is increasing, proportionately cushioning effect is also increase. Expectation of introducing ThEM to the rubber compound is to enhance the cushioning effect of the compound by creating a porous structure inside the compound. Theoretically, porous

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structures will help to enhance the resilience property and it is verified by Figure 29 below.



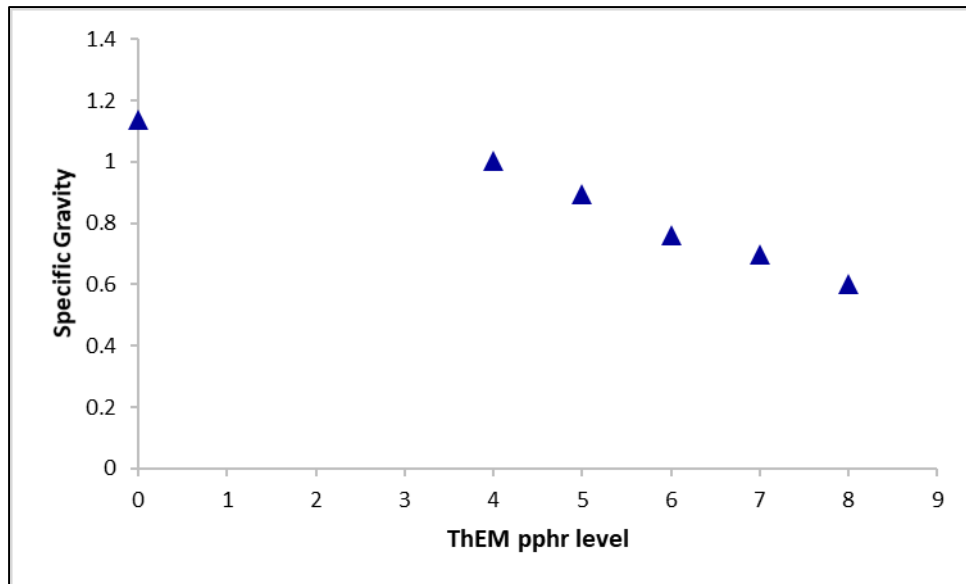
*Figure 29: Variation of Resilience*

### **5.2.5 Variation of specific gravity & Hardness**

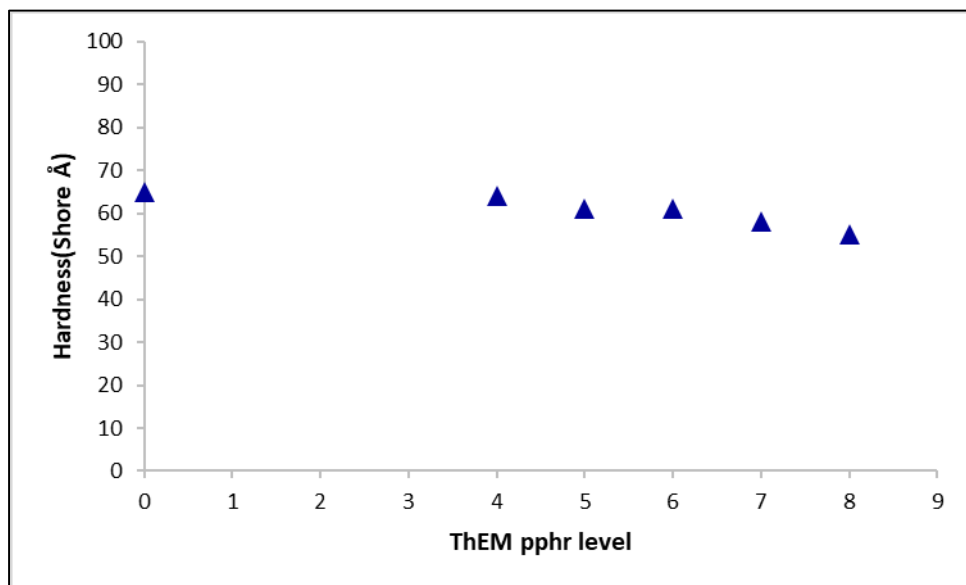
Specific gravity is called relative density and is the ratio of the density of a substance to the density of a reference substance. Equivalently, for the same given volume, it is the ratio of the mass of the substance to the mass of the reference substance. As described in 4.2.3, as the amount of ThEM added increases, the volume increases. Therefore, according to the definition of specific gravity, there is an inverse relationship between specific gravity and sample volume. Figure 30 below will prove this.

The hardness of the rubber mixture is measured by a Shore A durometer; the higher the hardness, the harder the compound. Elastomer hardness is measured by standard size and shape impact gauges based on indentation depth. Cushioning effect and the hardness property have an inversely proportional relationship. When hardness is getting increased, cushioning effect will also be dropped accordingly. That will be proven by Figure 31 below. Reason behind the low hardness of ThEM mixed

compounds is the formation of micro balloons as described previously in many physical property tests like tensile and tearing. The wall of these newly formed micro balloons is not hard enough to withstand against external forces and hence the hardness is getting reduced



*Figure 30: Variation of Specific Gravity*

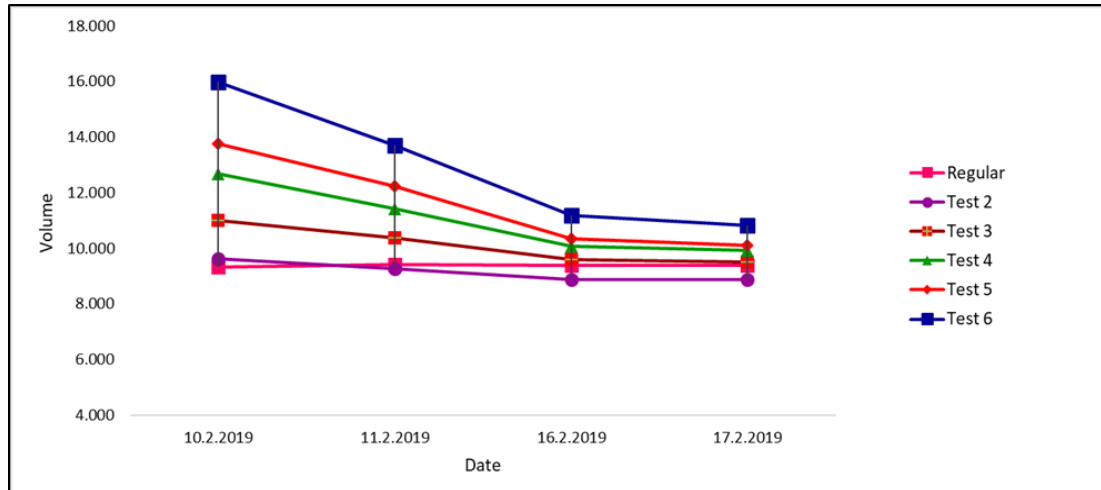


*Figure 31: Variation of Hardness*

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### 5.2.6 Volumetric change with time analysis

As described previously, volumetric change with time analysis has been done and the graphical representation of results are shown in Figure 32 below.



*Figure 32: Volumetric change with time*

### 5.2.7 Testing of aged samples of selected test compound

By considering all the rheological & physical test results, it has been decided to choose Test 03 compound for further studies and test tire production. Reason for select this compound is, most of the test results are much closer with the test results of regular cushion compound with some enhancement in cushioning effect. Prepared samples from the Test 03 compound was aged for some time (1 day, 3 days & 5 days) in ambient temperature and again performed some physical property tests like tensile strength, elongation at break, tear strength & hardness in order to make sure that the existing properties are not changing with the time. Variations of those test results are shown in Figure 33 - 36.

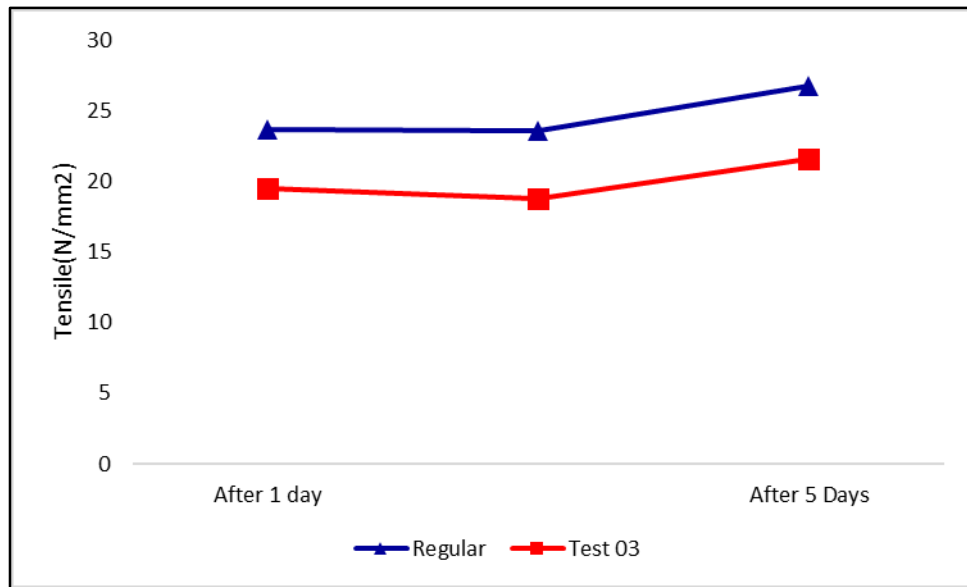


Figure 33: Variation of Tensile strength with time

Trend of varying tensile with time is same as in the regular compound but with less tensile values. Reasons for getting less tensile values for the ThEM introduced compounds were explained in 4.1.1.

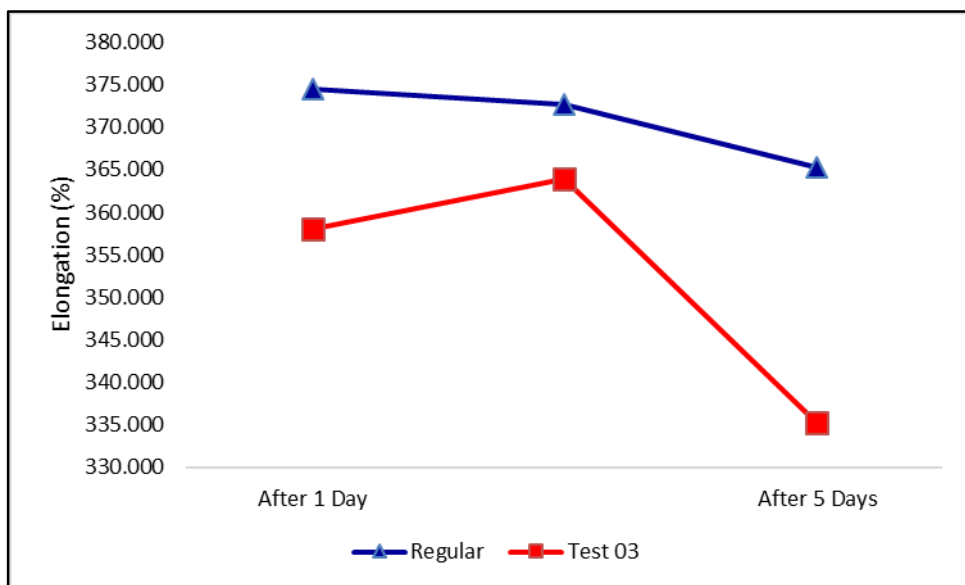


Figure 34: Variation of Elongation @ break with time

Elongation reduces with time as per Figure 34 above and the trend matches with the regular compound. As cured rubber compounds become stiffer with time, tensile properties are increasing whilst decreasing elongation property. Meantime, tearing decreases & hardness increases with time due to the same reason. That will be proven by under mentioned charts.

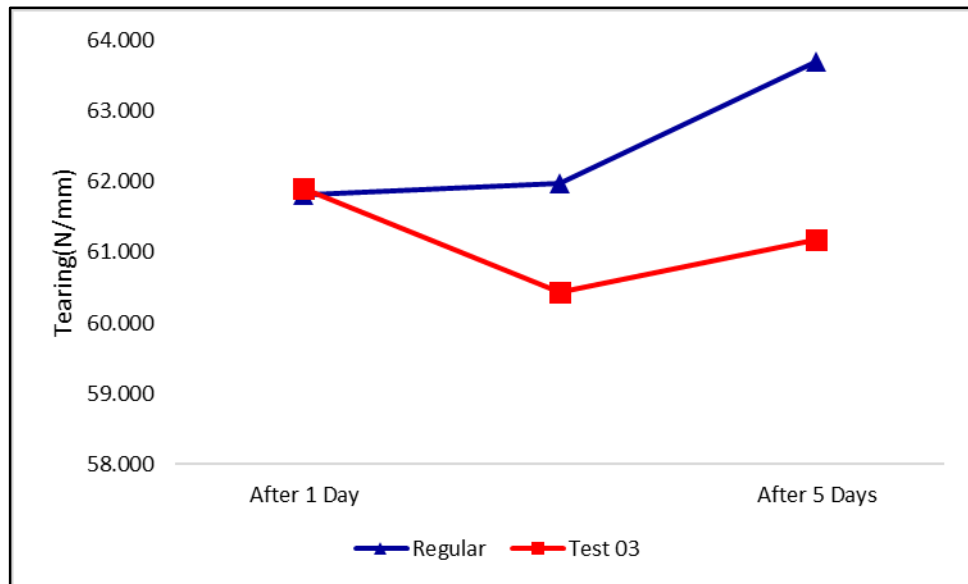


Figure 35: Variation of Tear strength with time

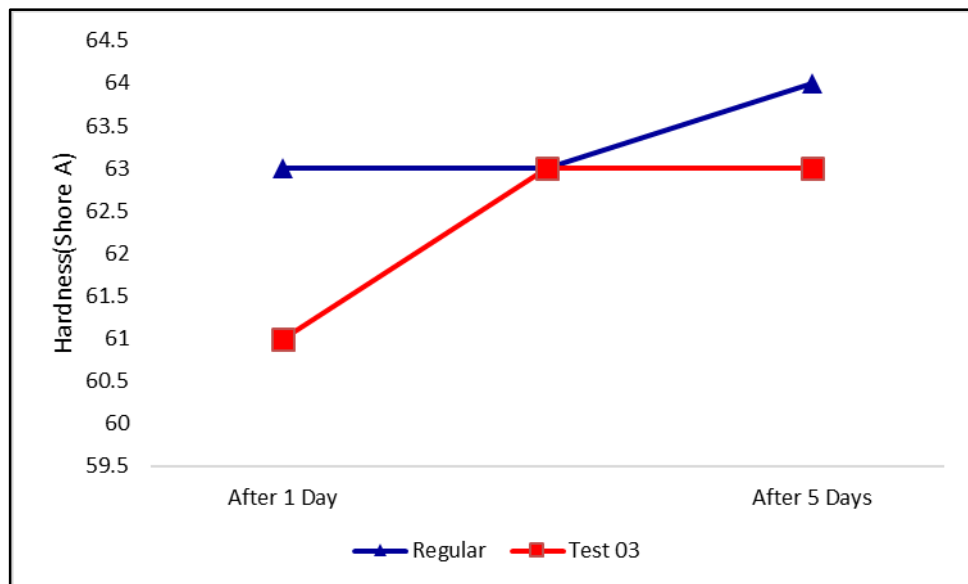


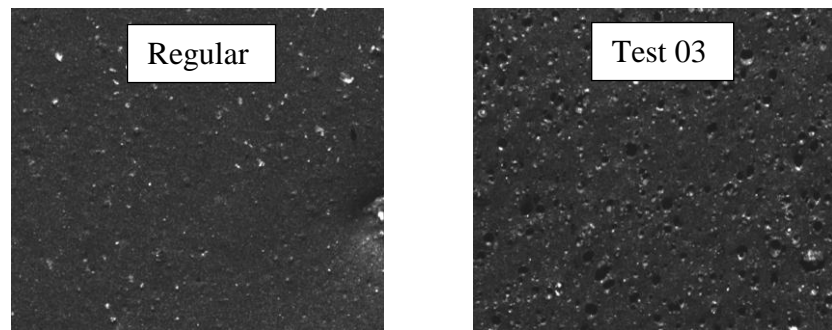
Figure 36: Variation of Hardness with time



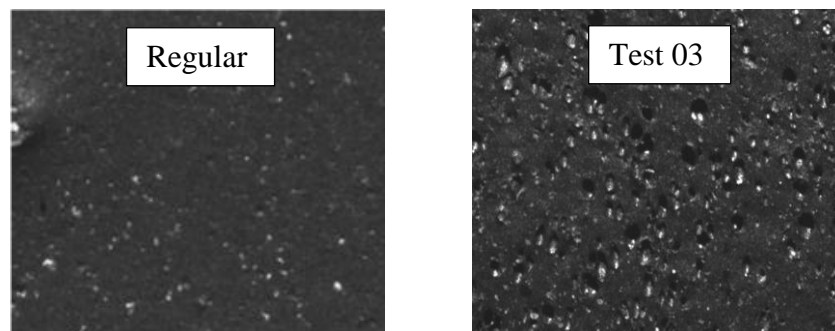
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As mentioned in 4.3.2, samples prepared to measure hardness & SPG of the compounds was used to check the porosity level inside the compounds as below. Dispegrader images of regular and Test 03 samples in different times are shown in Figure 37 below.

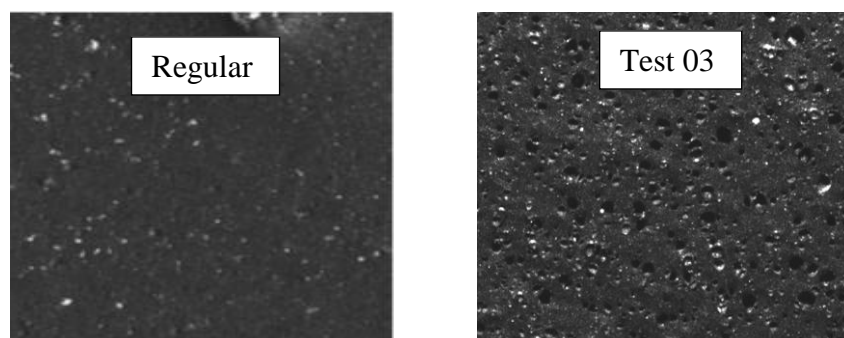
After 01 day:



After 03 days:



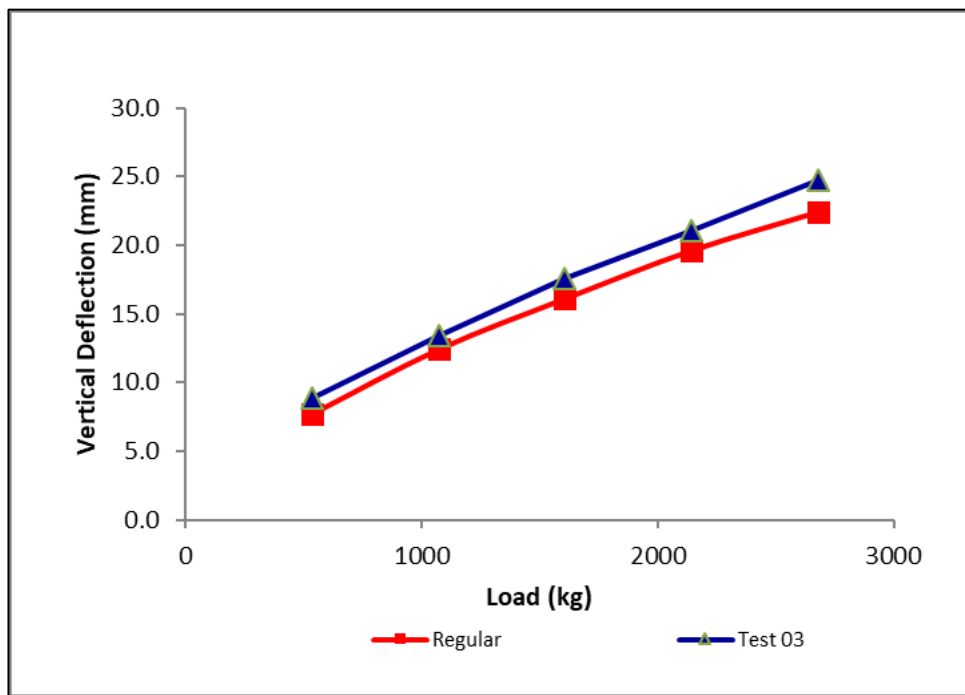
After 05 days:



*Figure 37: Agglomerated views of samples*

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As per the above images, the porosity level of regular sample was remained at the same level even after 5 days. But the porosity level of Test 03 sample is changing with time not only the number of pores inside the compound, but also the size of pores is also getting increased. Even though the cushioning effect can be increased with the formation of porous structure with large pores, there will be a problem with regards on dimensional stability of the tire. Therefore, vertical deflection test & the footprint calculation was done in order to check the dimensional stability of the tire.

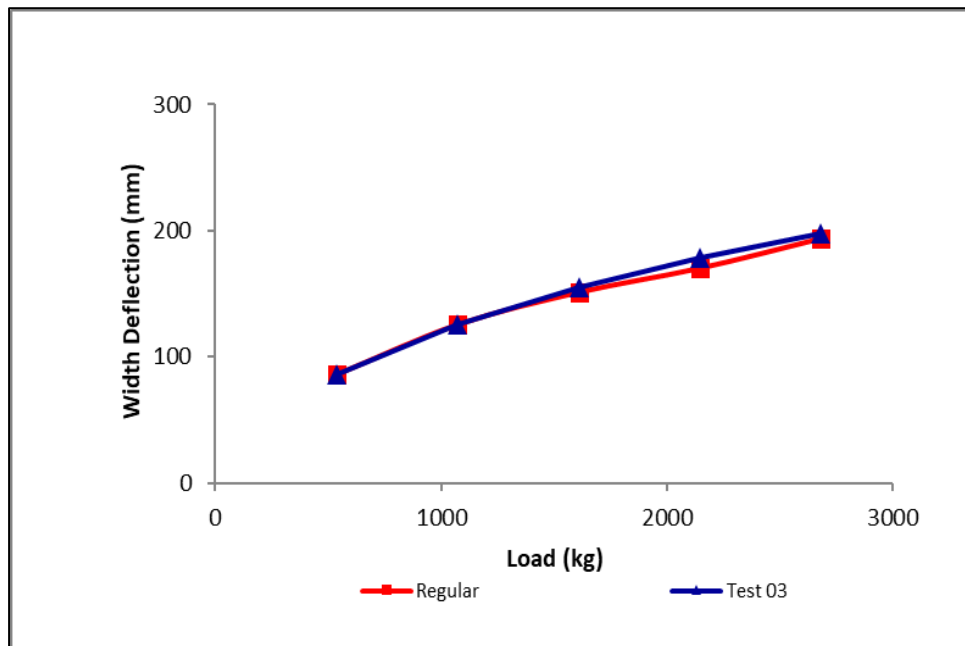


*Figure 38: Comparison of vertical deflection of two tires*

Even though the trend shows same, vertical deflection of the tire which was produced by using Test 03 compound is not much dimensionally stable as the values of vertical deflection shows much higher than the regular tire. Higher the vertical deflection, lesser the tire stiffness. Stiffness is also a one of the important tire properties which requires to perform well during the application. Reason for this higher vertical deflection values would be the formation of cell structure inside the tire and it is not so stronger enough to withstand against the dynamic load. Cell

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structure destroys with the time under dynamic load and hence tire starts to deflect accordingly. That will be proven by footprint analysis as shown in Figure 39 below.



*Figure 39: Analysis of Footprint*

Footprint will be monitored by measuring changes in tire width when the tire is subjected to a load. As per the above chart, tire produced by using Test 03 compound starts to deviate from the regular variation when it comes to high loads like >2000Kg. Again, it was confirmed that the use of ThEM for resilient tires have a negative impact from the deflection point of view.

Endurance test (QED Test) has been performed as the next step to observe heat build-up inside the tire which also have a direct relationship with tire cushioning effect. Higher the heat build-up, lower the cushioning effect theoretically. Test results summary of the QED test is shown in Table 06 below.

As per the QED graph, both test tires show less performance compared to the regular tire. That is because of the breakdown of the cell structure due to dynamic load applied during the QED test. Meantime, it was observed that the tire dimensions were also deviated from the specifications. Meantime, surface damages like flow

marks were appeared due to the breakdown of micro balloons. One of the surface defects appeared on the side wall of the tire is shown in Figure 40 below.

Table 6: QED Test result summary

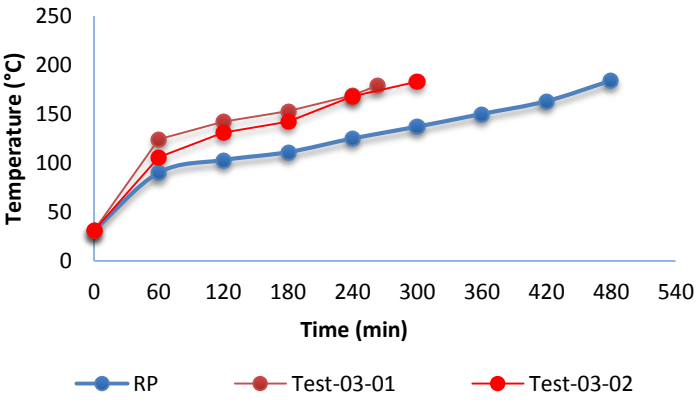
Tire size & Sample No.	Tire test results									
5.00-8/3.0 Elite XP Test 03-01	 <table border="1" data-bbox="627 1021 1345 1189"> <thead> <tr> <th>Test</th> <th>% Expansion of OD</th> <th>% Expansion of Width</th> </tr> </thead> <tbody> <tr> <td>Test 03-01</td> <td>4.77</td> <td>2.89</td> </tr> <tr> <td>Test 03-02</td> <td>5.43</td> <td>4.10</td> </tr> </tbody> </table>	Test	% Expansion of OD	% Expansion of Width	Test 03-01	4.77	2.89	Test 03-02	5.43	4.10
Test		% Expansion of OD	% Expansion of Width							
Test 03-01		4.77	2.89							
Test 03-02	5.43	4.10								
5.00-8/3.0 Elite XP Test 03-02										
5.00-8/3.0 Elite XP Regular production (RP)										



Figure 40: Surface defects on side wall

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**CHAPTER 5**  
**CONCLUSION**

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Hardness is one of the critical physical properties in resilient tires but with incorporating ThEM with the cushion compound resulting in reducing hardness gradually with increasing the ThEM quantity which is one of the major negative points of using ThEM in resilient tires. As per the test results, resilience property is enhanced when increasing the amount of ThEM. Improvements in resilience is one of the expected outcomes and hence that can be taken as one of the positive impacts of use ThEM in cushion compound. Volumetric enhancement was observed in samples as well as in the final cured tire dimensionally. Unstablensness of tire geometrical shapes will be problematic during the real application and hence, that can be taken as a negative impact of ThEM. With the time, it was observed more deviations in shape when compared with the original one. Reason for that would be the breaking of the formed cell structure as those cells are not strong enough. Because of that reason, dimensional variations can be observed even in the cured tire after some time. Not only the volume, but also the tensile, elongation & tearing properties are also getting reduced with time as per the test results. Reason behind that reduction would be the same which have already explained for volumetric reduction (breaking of the cell structure formed). When the prepared test tires were undergoing dynamic loads, it was observed that the side walls of the tires getting very unstable due to the breakage of the developed micro balloons. There were not many deviations highlighted in footprint, ground pressure & vertical deflection when compared with the regular tire. By considering all the above facts, it can be concluded that the use of ThEM with the purpose of having enhanced cushioning properties of resilient tires, shows some positive impact but with very high limitations since the final product will not dimensionally stable and it cannot with stand when it is subjected to a dynamic load. ThEM can be used as a cushioning agent in resilient tires only with an improvement in strength of the formed cell wall.

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