THE EFFECT OF PRE-VULCANIZATION TIME AND VULCANIZATION TEMPERATURE ON INTER-LAYER ADHESION AND PHYSICAL PROPERTIES OF MIDDLE AND TREAD LAYERS OF SOLID TIRE

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This thesis submitted in partial fulfilment of the requirements for the degree Master of Science in Polymer Technology

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February 2020

DECLARATION OF THE CANDIDATE & SUPERVISOR

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ACKNOWLEDGEMENT

First, I would like to extend my profound appreciation to my supervisor Prof. B. A. J. K. Premachandra for all the support and encouragement that he provides me during the master's degree program. I would also like to extend my gratitude to him for continuous support as the course coordinator; you have been an ever-present beacon of support, encouragement, and advice.

Besides my advisor, I would like to thank the rest of my thesis committee: Dr. (Mrs). Shantha Egodage, Dr. (Mrs.) D. G. Edirisingha for their encouragement and insightful comments.

Further, I would like to express my sincere gratitude to the management of Camso Loadstar (Pvt) Ltd for offering tests and laboratory facilities. My special thanks go to Mr. Anurasiri Gunasekara who provides me the support and guidance during the research. I wish to show my appreciation to all the staff who helped to conduct the testings at Camso Research & Development Center.

I would like to acknowledge professors, lecturers, and staff of chemical and process engineering, University of Moratuwa, for coaching and support during the master's degree program.

Finally, I would like to thank my wife, mother, sister, and friends for the support, devotion, and understanding throughout the research period.

Abstract

Resilient solid tires are used for industrial vehicles. Three-layer resilient tire composed of heel, middle and tread layers; the integrity of layers is empirical throughout the service life. This thesis investigated inter-layer adhesion capacity between middle and tread layer. The two compounds were pre vulcanized into 6 levels (0%,20%,40%,60%,80%, and 100%) at 100 °C, by changing the Pre-vulcanization time. Primary vulcanized sample was vulcanized secondarily at 150 °C and 170 °C; inter-facial bonding strengths were compared.
Increased secondary vulcanization temperature decreased the inter-layer adhesions. Based on adhesion strength, manufacturing limitations and physical properties, the optimum primary vulcanization level selected. To develop acceptable bonding at 0% pre vulcanization of middle layer, the tread layer could pre vulcanized up to 80% at 150 °C secondary vulcanizing temperature and up to 20% at 170 °C. At 20% pre vulcanized middle layer, tread layer could pre vulcanized up to 60% and 20% at secondary vulcanization temperature of 150 °C and 170 °C respectively. At 40% pre vulcanized middle layer, tread layer could pre vulcanized up to 40% at 150 °C secondary temperature; but at secondary temperature of 170 °C, tread layer bonded well only at 0% degree pre vulcanization.

In conclusion, 40% of middle and tread layer pre vulcanization levels are suggested as optimum pre vulcanization level at secondary vulcanization temperature of 150 °C, 20% of middle and tread layer pre vulcanization levels was the optimum for secondary vulcanization temperature of 170 °C. Out of two secondary vulcanization temperatures, 170 °C and 20% of middle and tread layer pre vulcanization levels suggested as the optimum pre vulcanization level.

Keywords: Interfacial bonding, pre cure, vulcanization temperature, rubber to rubber bonding

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

6PPD	N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine
ASTM	American society for testing and materials
B.C.	Before Christ
BR	Polybutadiene rubber
CAGR	Compound annual growth rate
FEA	Finite element analysis
LCV	Light commercial vehicle
M&HCV	Medium and heavy commercial vehicle
M_H	Maximum torque
M_I	Initial torque
M_L	Minimum torque
MOR	2-(4-Morpholinothio) benzothiazole
NR	Natural rubber
ODR	Oscillating disc rheometer
OTR	Off the road
pphr	parts per hundred rubber
PVI	Pre vulcanization inhibitor
RPA	Rubber process analyzer
RSS	Ribbed smoked rubber sheet
SBR	Styrene butadiene rubber
t_{90}	Optimum cure time
ts_2	Scorch safety

1. INTRODUCTION

1.1 History of the tire

About 15,000 to 750,000 years ago, circular shaped logs were used to move heavy objects easily. People placed circular shaped logs and a sledge under a heavy object and pulled the sledge over one log to the other. As the log wears, it gradually changed shape similar to a big bone. Subsequently, the wood is cut between two ends to create the axle, which was the very primitive solid wheel [1]. The first use of solid wheels for transportation was in 3500 B.C. [2] . Along the time, leather and iron strip tops were added to the solid wheel. In 1839, Charles Goodyear was credited for the discovery of the vulcanization process [3]. Early rubber did not hold the shape. But vulcanization made the rubber, a perfect material for tires and other engineering applications. Vulcanization is a process of heating rubber with sulphur, to transform it into a firm, flexible material. Soon after the discovery of the vulcanization process, tires were made with solid rubber, the origin of today's solid tire. These tires were strong; absorbed shocks; resisted abrasions and cuts. Initially, these tires were heavy and did not provide a smooth ride. But solid tires have attracted significant attention due to its unique wide range of applications.

Later, in 1845, Robert William Thomson patented the pneumatic tire, which used rubber and enclosed air to reduce vibration [4]. However, this concept was never carried out to the manufacturing process, until John Boyd Dunlop was patented for the first pneumatic bicycle tire in 1888.

1.2 Global tire market

The Global tire market is worth around 3.1 billion units in 2018 at 4.3% CAGR. The tire industry market is projected to reach 3.9 billion units by 2024 [5]. Depending on vehicle type, the global tire market is broadly classified into six categories: passenger car tire; light commercial vehicle (LCV) tire; medium and heavy commercial vehicle (M&HCV) tire; two-wheeler tire; three-wheeler tire; the OTR (off-the-road) tire. OTR's tire business revenue is $ 19 billion.

The OTR business sector mainly includes material handling and construction applications. The type of solid tire selected for this study is related to the field of material handling. The tire business is now very competitive, and in addition to small players around the world, many multinational companies are trying to invade each other's position. Tires with enhanced product performance provide a competitive advantage, not only to maintain existing market share but also helps to conquer new markets.

1.3 Types of tires

The tires can be classified according to the structure: pneumatic and solid tires. Pneumatic tires are inflated hollow tire that retains its shape due to the air pressure. They may be equipped with an air chamber or tubeless. The semi-pneumatic tire also hollows shaped tire, but not pressurized like a pneumatic tire. Due to its lightweight, semi-pneumatic tire is commonly used for lawn mowers, shopping carts, and wheelbarrows puncture-proof shock-absorbing ability. Solid tires are fully rubber filled construction and will be discussed further detail in section 1.4.

1.4 Solid tire

Solid tire is composed of several layers of different thicknesses and compounds, which form a composite structure. Due to its extremely stable, puncture-resistant, and maintenance-free characteristics, they are commonly used in forklifts, ground support equipment, and other material handling applications. Solid tire ensures the lowest operating costs on the harshest of jobsites. They are designed to maintain the longevity; three times than the pneumatic tires, as they are made of special rubber compounds supported by the geometrical design. Typically, the tensile and tear strength are more than twice that of a pneumatic tire to support harsh road surface applications.

Today's solid tire is a masterpiece of applied technology with an improved performance like rolling resistance and comfort. Unlike a pneumatic tire, the solid tire entirely is a rubber object with associated drawbacks such as less comfortability and thermal performances. In order to achieve desired performances, the tire designers introduce different rubber layers to the solid tire.

Solid tyres are broadly classified into three main categories: resilient, press-on and cured-on tyres. A press-on tire is composed of single or double layers that are bonded to a steel band. The two-layer tire is made with a tread and middle compound while a single layer contains a tread compound. Press-on tires are popular due to the ability to handle high loads with greater stability, are widely used in passenger boarding bridge and ground support equipment.

Cured-on tyre is moulded or vulcanized directly into the wheel casing, forming an integral unit which is attached to the axle. They are used for the free rolling wheels and typically do not use for high load applications.

The resilient tire is composed of two or three layers depending on its intended application. Steel rings are often used as reinforcement to ensure the grip with the wheel. The two-layer tire is made of a heel compound, which is a hard rubber and a tread compound: the outer layer built to wear resistance. The three-layer resilient tire is featured with a third middle layer: maximize the cushioning effect with enhanced thermal performances. The resilient tire selected for this study is in a configuration of the heel, middle and tread layer. Each layer plays a different roll to guarantee enhanced performance. The integrity of these layers is vital to maintain the desired service life.

1.4.1 Resilient tire components and their functions

Three layer resilient tire was selected for this study and layer configuration is presented by below Figure 1.1

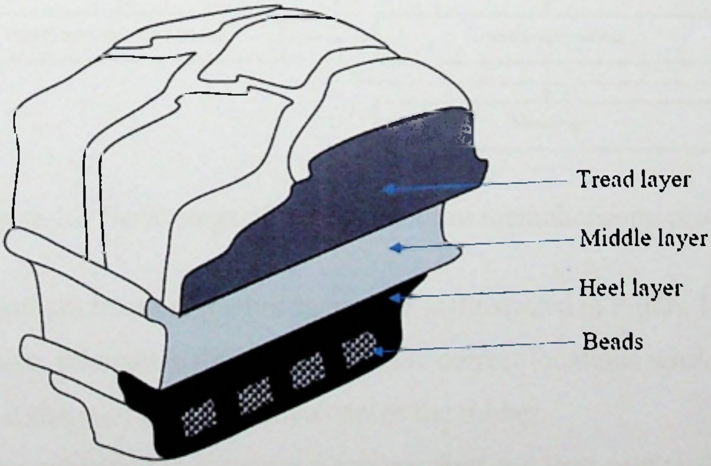

Figure 1.1 Components of a three-layer resilient tire

The objective of the tread is to provide an appropriate level of traction against the road surface while providing a low level of wearing rate and heat generation within the tire.

Due to harsh road surface applications of resilient tires, they need to offer the greatest possible resistance to tearing and tensile failures. The tread layer is in contact with the road surface, is often formulated by using natural rubber and synthetic rubbers like SBR, BR.

The middle layer with low heat build-up and high rebound resilience provide lower rolling resistance and thermal stability to the tyre. Also, this segment provides a cushioning effect for the resilient tire, hence the shock absorbing ability of the tire is improved.

A combination of high hardness, high compression set, and high modulus heel layer which reinforced with steel bead rings ensure better grip in between the rim.

Each component expected to maintain the continuity over the service life in order to avoid pre-mature failure of the tire.

1.5 The resilient tire manufacturing process

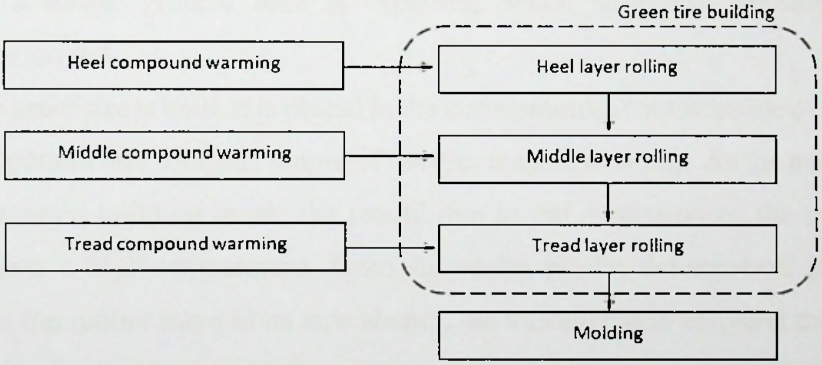

Figure 1.2 Basic steps of the resilient tire manufacturing process

Typical, the resilient tire manufacturing process is illustrated in Figure 1.2. In the green tire building step, relevant materials apply at the correct locations while the third step, define the final shape of the tire and vulcanize the rubber.

Compounds are subjected to a warming process first and then sent to different rolling stations where two roll mills used to apply each component to the green tire. This process is called a green tire building or tire rolling that each layer applies to the right position using a special drum. Green tire rolling starts with heel rolling and followed by middle and tread rolling. Generally, warming temperature is around 90-100 °C and the rolling compound temperature at this stage is around 100-105 °C. so that sufficient activation energy is available to start curing reactions at this stage. Generally, the time between warming starts to insert green tire into the mould is considered as process time for green tire building. The process time is critical as thermal history is induced to each compound during this period. This is the step where pre curing or scorching occurs.

Pre vulcanization is an invariable process in the present solid tire manufacturing processes that occurs at an early stage. It substantially affects the accumulation of plastic material during the process of heat and time, can also be called the heat history of the rubber material. The thermal history of the rubber more than a long, more than high temperature, the pre vulcanization level also gradually increased. Even though some extent of pre vulcanization is possible during the resilient tire manufacturing stage, the pre cure degree should be regulated and minimized to avoid its influence on product performances. In order to maintain high flexibility during the manufacturing process, a longer process time is expected, which adversely increases the pre vulcanization risk.

After the green tire is built, it is placed in the curing mould. On the inside of the mould, the tread pattern and complex shapes of cavities may be existing. As the heated mould closes pressure building inside the mould due to the expansion of the rubber after getting into a high temperature. From its sticky plastic deformation state (when deformed the rubber stays in its new shape), the vulcanization converts the rubber to an elastic deformation characteristic, (when the rubber returns to its initial state when applied strain stops). To ensure the quality of the surface finish and the performance of the tire, a lesser degree of pre vulcanization of each layer is required. Curing is carried out usually around 150 °C. But due to high production efficiency, a high temperature curing is a common phenomenon for any tire industry.

It is obvious that the continuity in contact with each layer should be maintained throughout the desired service life. Due to different thermal histories of the heel, middle, and tread assemblies, the bonding strength between each part might get affected.

For the resilient solid tires, the highest number of recent customer claim history is reported as bonding failure between two assemblies of middle, tread, due to pre-vulcanization of middle and tread layers [6]. The weaker bond between the two layers led to failures in the dynamic conditions of tire application. These pre-mature failures occur within the design life of the tire which increases the downtime of forklifts. Depending on the tire building process parameters such as green tire temperature and process time could induce different pre-vulcanization for the middle and tread layer. One aim of this study was to investigate the highest pre-vulcanization level that ensures acceptable adhesion level between the tread and middle layer of a resilient tire. Furthermore, enhancing the vulcanization temperature might be economically advantageous since the vulcanization time is drastically reduced with an increase in vulcanization temperature. Hence, enhancing the vulcanization temperature might save a significant amount of energy. The determining factor of the physical properties of a rubber vulcanizate is the crosslinking density and the form of cross linking. The quality and the number of crosslinks is associated with vulcanization temperature [7]. The study sample has been initially subjected to primary vulcanization; as the second step the vulcanization completed at 150 °C and 170 °C, which is called secondary vulcanization. Therefore, previously explained goals were extended to find the highest primary vulcanization level at secondary vulcanization temperatures of 150 °C and 170 °C.

1.6 Research objectives

General objective

- To prepare different middle layer and tread layer rubber compounds with different pre vulcanization levels for evaluating their interface bonding strength according to secondary vulcanization temperatures

Specific objectives

- Find the optimum level of pre vulcanization for acceptable interfacial bonding strength at elevated secondary vulcanization temperature
- Find the optimum level of pre vulcanization for acceptable interfacial bonding strength at low secondary vulcanization temperature
- Find the optimum level of pre vulcanization that ensures selected physical properties with the acceptable interfacial bonding strength

2. LITERATURE REVIEW

2.1 Compounding of rubber

Rubber compounds are generally obtained by mixing different rubbers starting with a base polymer, followed by mixing all the other additives. The choice of materials is directly related to the tire performance requirement and the desired property of the compound. The non-vulcanized compound is the output of the mixing process [8].

A typical tire contains rubber (45%), inert filler (25%), specialty chemicals (15%) and fabric (15%). That may be rather dissimilar for forklift tires due to different applications and tire anatomy. Compounder has his main responsibility to develop a formulation to achieve required performances with optimum properties maintaining minimum cost.

2.1.1 Rubbers

The major material used in the tire is elastomers. Elastomers contain long chains which are a combination of repetitive units called monomers. So, it has a high molecular weight. The final properties of the compound determine the selection of monomer, polymerization technique and architecture of the polymer backbone.

The source of natural rubber is the hevea brasiliensis tree. Natural rubber exhibits excellent fatigue performances. There are advantages of natural rubber when compare with synthetic rubber are low heat build-up and excellent hot tearing resistance.

Today, Synthetic rubbers like polyisoprene have been offered comparable benefits similarity to natural rubber. The tread of passenger cars is commonly manufactured using styrene-butadiene rubber which is a synthetic rubber. Most of the tread compound contains 10% to 20% of butadiene rubber (BR) in the compound formulation to obtain a good balance of performance. BR exhibits good wear resistance and maximum resilience.

2.1.2 Fillers

Fillers are used as a reinforcing agent of gum polymers. There are many types of fillers like low reinforcing clays, mineral fillers, carbon black, silica, etc. [9]. One of the most popular fillers in the tire industry is carbon black. In a polymer-carbon black network, the influence of viscoelastic property depends on the particle size, shape, structure, interaction with each other and polymer chain [10]. Effective reinforcement can be achieved by greater polymer to filler interaction than the filler to filler interaction. Fine particle size may offer a good grip and wear resistance, but it increases the difficulties in processing and energy loss.

Silica is useful due to its good tear resistance property, for off-the-road applications. The major difference of interaction property of carbon black and silica filler is to filler interaction is strong in silica than the polymer to filler. Aramid, natural fibres like rice husk, chopped steel stands and etc were used as fillers in the rubber industry.

2.1.3 Anti-degradants

Different kinds of antioxidants and antiozonants were used for internal and external components to protect the tire.

2.1.4 Curatives

Vulcanizing agents used in the rubber industry can be identified as peroxides, sulphur or insoluble sulphur. Rhombic sulphur is the mostly used agent because it is cheaper and the most practically available chemical. Sulphur is soluble in NR at levels up to 2.0 pphr. If the concentration is higher than mentioned, insoluble sulphur must be used to prevent the migration of sulphur to the compound surface, this is called sulphur blooming.

In importance, the accelerators second only to sulphur in the vulcanization process. They accelerate the slow rubber-sulphur reaction and increase the rate of reaction. Hence, increases productivity.

2.2 Compound mixing

Generally, internal mixers are used to prepare rubber compounds. Two rotors inside the internal mixer chamber generate high shear forces and disperse ingredients in the polymer. Homogeneity of the compound is achieved by the generated shear forces. After mixing the compound is pelletized. These raw materials are subjected to quality checks in different aspects like rheological characteristics and random physical properties.

2.3 Rubber to rubber interface bonding strength

Rubber to rubber bonding is very important for a solid tire as it is configured with several layers. The integrity of a solid tyre during service life depends upon the ability of three layers to stay bonded to each other even under extreme conditions of stresses [11].

Several studies have conducted in the field of rubber to rubber interfacial bonding strength. The study of Bhowmick reports that a similar degree of crosslink required the same value for the work of de-attachment. Further Insite shows, at a given degree of crosslinking the strength of adhesion, is lower when the molecular lengths are shorter. It is attributed to the work of fracture of an elastomeric network increases with the molecular weight of the network stands [12].

The effect of interfacial bonding of elastomers was studied by gent and co-workers [13]- [14]. They reported that the threshold mechanical strength of interfacial adhesion between two layers was directly proportional to the degree of crosslinking. It was explained, an increase in crosslink density causes an increase in the interfacial bonding strength.

The peeling strength is a kind of characteristic of adhesion that is sensitive to rubber's intrinsic properties. Yue Wang showed that the peeling force is greatly influenced by the chemical nature of the two interface layers [15]. He explained that crosslinking density, molecular weight, and impurity percentage were directly influenced the peeling strength. The influence of molecular weight directly proportional to the modulus; as molecular weight increases, the modulus also increases. When modulus increases more energy consumed to create a new surface, so peeling strength increases. On the other hand, chain mobility and diffusion rate reduce with an increase in modulus, which lowers the peeling strength. The influence of modulus on adhesion is determined by the dominant factor of these factors [15]. Raevskii and voyutskii proposed that peel force increased as the crosslink density is increased at the interface [16].

Thickness and width of the adhesive layer are sensitive to the peeling strength as the increase of this dimension of layers required more energy for peeling. In the experiment's dimension, uniformity of samples is essential to achieve more accurate competitive results. Above and beyond, peeling strength is also influenced by humidity, flaws, and defects at the interface which diminishes the peeling strength. In experimental conditions, the bonding surface should be carefully protected from impurities and maintain the same temperature over all testings for data accuracy and preciseness [15].

Debye proposed that the adhesion between two layers is mainly influenced by interfacial chemical crosslink, the extend of interdiffusion of two adhering members and the van der waals forces. It cannot compromise the factors like the chemical nature of the elastomer and additives [17].

In the practical application, rubber compounded with fillers and other additives. Fillers in the rubber compound can influence the chemical and mechanical properties of the vulcanizates. So, it should be worthwhile to study their influence on interfacial adhesion. Rhee and Andriese have reported that high filler loading can decrease the interfacial adhesion. It was attributed to the formation of bound rubber, which is increases with surface area and carbon black loading. The bound rubber suggested that reduce the wettability of the rubber compound hence the adhesion also declined [18].

When there is a strong bond between two layers, stress can be transferred across the interface by physical bond, chemical bond (like crosslinks) or entanglements. If a failure occurred from the bond between the two layers, the energy required to apply on the surface should be greater than the work of adhesion between two layers [19].

Kausch and Tirrell found that molecules near the interface do not necessarily have to fully interpenetrate between two layers to make high strength interface bonding. Portions of the chain may be sufficient interpenetrate because they can resist mechanical separation [20]. Some studies have attempted to relate the depth of interdiffusion to the strength of the resulting interface [21]. They found that the strength of the interface greatly increases with the depth of interpenetration.

2.4 Vulcanization of rubber

A hundred years ago, Charles Goodyear could find a method of preserving and enhancing the desired properties of rubber. Vulcanization involves changes in both the chemical and physical aspects of the rubber. The most important physical change in rubber during the transformation from raw rubber to vulcanized rubber is the change in plasticity. After vulcanization, rubber turns to very elastic nature but after having been stretched, it quickly returns almost to its original shape. Unlike raw rubber, vulcanized rubber shows usually greater elongation, lesser hysteresis, greater tensile strength, and greater resistance to the action of solvents and heat to tear and abrasion. Vulcanization is a process that increases elasticity while it causes a reduction in plasticity. In other words, it increases the retractile force and decreases the permanent deformation after removal of the deforming force. This is generally accompanied by the formation of a cross linked molecular network.

The theory of rubber elasticity is explained as network density or number of crosslinks that support polymer chains per unit volume of elastomer is proportional to the retractile force to resist deformation. A polymer chain that supports is considered as a linear polymer molecular segment between network junctures. An increase in the number of crosslinks provides an increase in the number of supporting chains or networks. Thus, vulcanization is a process of chemically producing network junctures by the introduction of crosslinks between polymer chains (Figure 2.1). [22].

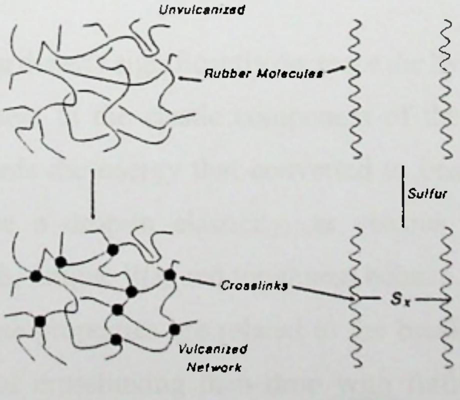

Figure 2.1 Network formation during vulcanization

Source: The Science and Technology of Rubber Ltd

2.4.1 Effects of vulcanization on vulcanizate properties

Significant changes in the vulcanization that are occurred at the molecular level. The long rubber molecules linked together with crosslinks along the polymer chain. Due to crosslink formation in the rubber, it becomes insoluble in any solvent. Essentially rubber cannot be processed by any means using a mixer or extruder; on a mill or calendar; or during shaping, forming or moulding. Thus, it is highly stated that vulcanization should occur at the final stage of the geometric form [22]. If the vulcanization occurred before this step it's called pre vulcanization or pre cure.

Below Figure 2.2 illustrated the effect of vulcanization on properties of vulcanizates.

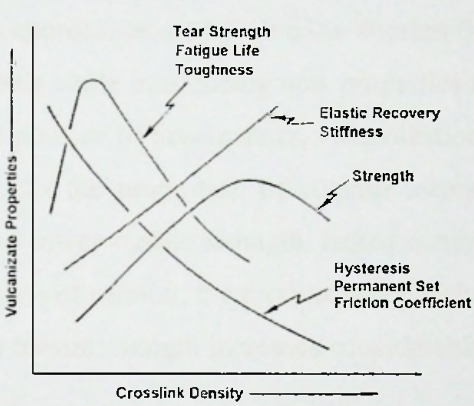

Figure 2.2 Vulcanizate properties as a function of the crosslinking density

Source: The Science and Technology of Rubber Ltd

Increases in crosslinking density significantly decrease the hysteresis which is the ratio of the viscous component to the elastic component of the deformation resistance. Hysteresis also represents the energy that converted to heat. Low hysterias at high crosslink density cause a drop-in elasticity, as viscous or plastic behaviour is decreased. Tear strength, fatigue life, and toughness behave in the same manner with crosslink changes. These properties are related to the breaking energy and increase with a small amount of crosslinking then drop with further increase in crosslink density. The energy required to break increases with increases in both the number of network chains and hysteresis. Since hysteresis drop due to a greater number of crosslinks, the energy-to-break related properties are maximized at some intermediate crosslink density [22].

The dependency of properties that were presented in Figure 2.2 is discussed by means of influence from the crosslink density. They are also dependent on the type of crosslink, the type of polymer, the filler type, and filler loading [22].

Vulcanization can be carried out by mixing sulphur into different proportions with a rubber. Harry L shows that change in vulcanization level is an influence on vulcanization properties. Five to eight parts of sulphur into 100 parts of rubber and heating the mixture at 140 °C will consume about 3 to 4 hours to complete the vulcanization. Modern approaches are involved to shorten the vulcanization time by using organic accelerators while introducing new properties to the vulcanizate. With the addition of a small number of accelerators, vulcanization time can be completed within a few minutes. As the proportion of sulphur increased to 14-18 parts, the vulcanization exhibits a lower tensile strength, hence commercially not viable. But when there are 30-40 parts of sulphur, the product becomes hard and elongation drops to a very low level, but tensile strength increases considerably.

2.4.2 Characterization of the vulcanization process

The crosslink formation start time, rate of crosslinking and the extent of crosslinking are important characteristics of the vulcanization process.

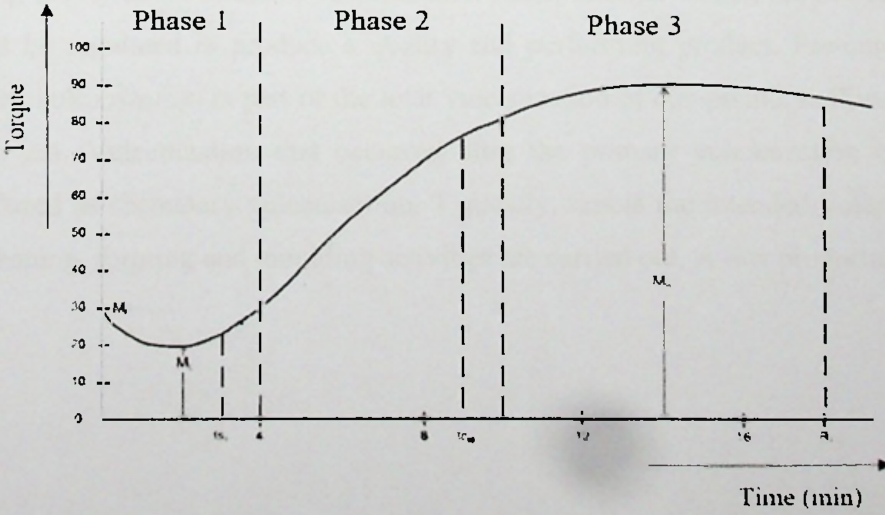

Figure 2.3 Typical rheometer graph for rubber vulcanization

The typical torque vs. time response curve for rubber compound is given in Figure 2.3. During the rheometer test, as the discs touch the compound, the curve starts with an initial large torque. When the rubber heats up, the torque decreases due to a drop-in viscosity of the rubber. Eventually, viscous liquid is transformed into a viscoelastic solid with cross-linking formation. In this region, the torque exhibits an increment which reflects the domination of cross-link formation over possible chain scission. If the torque reaches a maximum followed by a reduction of torque, the process is known as the reversion. Depending on the nature of cross-link and the amount chain or crosslink scission, the torque can be either kept increasing (marching) or remain constant (plateau) at the highest level. Both compounds used for this work have shown the marching curve.

Torque vs time response curve presented in Figure 2.3 comprised three phases. Phase 1 gives and an indication of the processing behaviour of the rubber compound. In this region, the compound is safe because vulcanization is not initiated yet. Before the intended vulcanization starts compound is allowed for shaping and flowing in the mould. Phase two describes the curing characteristics and phase 3 gives an indication of the physical properties of the rubber compound. As illustrated in Figure 2.3 rheometer results can analyse as torque values and time values.

As explained earlier vulcanization that occurred during the processing stage is not desired because it reduces the flow properties of the compound which reduces the shaping ability at the intended vulcanization stage. In other words, the pre-cure level should be regulated to produce a quality and performing product. Pre-cure or the primary vulcanization is part of the total vulcanization of compound, is illustrated in Figure 2.4. Vulcanization that occurred after the primary vulcanization could be considered as secondary vulcanization. Typically, this is the intended vulcanization that shaping, forming and moulding activities are carried out. A low proportion of

Pre- vulcanization over total vulcanization is preferred, as pre-vulcanization increases the viscosity of the compound during the processing stage.

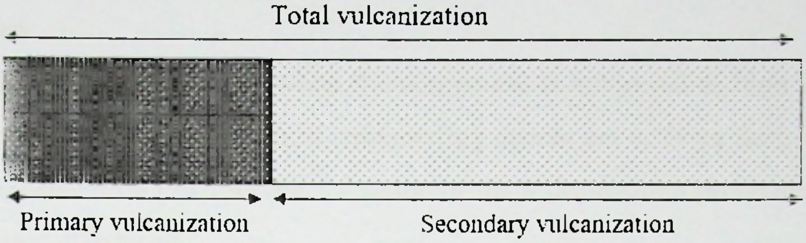

Figure 2.4 Primary, secondary and total vulcanization

Major torque values are M_I, M_L, and M_H. M_I is the initial torque recorded at the beginning of the test. M_L is the minimum torque that displays in the rheometer curve. As the compound absorbs heat under pressure, due to viscosity drop torque also falls. The lowest value that recorded is called M_L which is a measure of viscosity and stiffness of the compound. M_H is the maximum torque record during the test. The Thermoelectricity of the compound is derived from the difference of initial viscosity & minimum viscosity. This is an indication of the degree of crosslinking formed during the vulcanization process. As illustrated in Figure 2.3 the torque increment is not linier over time. This suggested that the crosslinking formation rate is not constant over the vulcanization process.

Hanafi and Salmiah reported that the difference between the maximum and minimum torque indicates the crosslinking density rise during the test period [23]. They suggested that if the same compound exhibits an increase in the difference between M_H and M_L (M_H - M_L), it is a demonstration of an increase in crosslinking density.

Typical time values commonly used in industry are ts_2 and t_{90}. ts_2 is the induction time, after attaining the minimum torque, as torque rises, time taken to rise two units above M_L is known as ts_2. Scorch resistance or scorch time is the resistance to premature vulcanization. Further, it can explain as prolong the time for initiation for vulcanization. There must be enough time to permit mixing, shaping, forming and flowing rubber in the mould cavity of rubber before the intended stage of vulcanization. After the necessary delay, a rapid formation of crosslinking expected. Scorch resistance is typically measured by the time required, at a given temperature, for the onset of crosslink formation, as indicated by an abrupt increase in viscosity. Reduction in ts_2 of a compound under temperature is an indication of the start of vulcanization. t_{90} is the optimum cure time that is the time at which 90% of cure has taken place.

Nabil and Ismail explain that when the compound is subjected to high temperature during processing on two roll mill sulphurating agents get activate during and occur partial vulcanization [24]. As the activation of the vulcanization process ts_2 of partial vulcanizates is reduced.

2.4.3 Effect of vulcanization temperature

Ru Liang Fan and co-workers reported that an increment in vulcanization temperatures the vulcanization reaction follows the classical law of kinetics of a chemical reaction [25]. They show that t_{90} or optimum cure time which is a measure of the vulcanization rate decreases as the curing temperature increases for natural rubber-based compounds. Prolong curing time or an increase in temperature exhibit distortion of properties like tensile strength, hardness, and modulus. But this behaviour was noted in a situation like over curing for $10 \times t_{90}$. The distortion in the properties is mainly attributed to chain scissions or is associated with the nature and density of the crosslinks. The study has shown that structure changes in the rubber backbone did not occur to any measurable extent even at higher vulcanization temperatures. The property distortion should be attributed to changes in the type of crosslinks generated and to the decrease in crosslink densities with the effect of high temperature vulcanization and prolong curing [25].

T. Kurian and the team reported that crosslinking density decrease with an increase in vulcanization temperature. They describe this fact from the decrease in M_H - M_L results from the rheometer. Molecular changes also can affect the overall viscosity reduction might affect the decrease in maximum torque. The decrease in crosslinking density at high temperatures is further explained. Polysulphidic crosslinks are thermally unstable and convert to monosulphidic and disulphidic form with pro-long heating. These are shorter linkages than polysulphidic form. The typical initial crosslinking form is polysulphidic when longer curing time it converts to short forms. This happens mostly in low temperatures. Compared to low temperature curing at high temperature polysulphidic form stay as it is. Hence the crosslink density is low [7].

2.5 Problem statement

Resilient tires are very popular in applications such as Forklifts, ground support equipment, other material handling applications. Pre-mature failures in forklifts cause increased down time of forklift and for safety risk. The highest recent claim rate is reported from the resilient three-layer segment is interface failure of the middle to tread due to the pre-cure of each layer [6]. Figure 2.5 presented failed tire pictures.

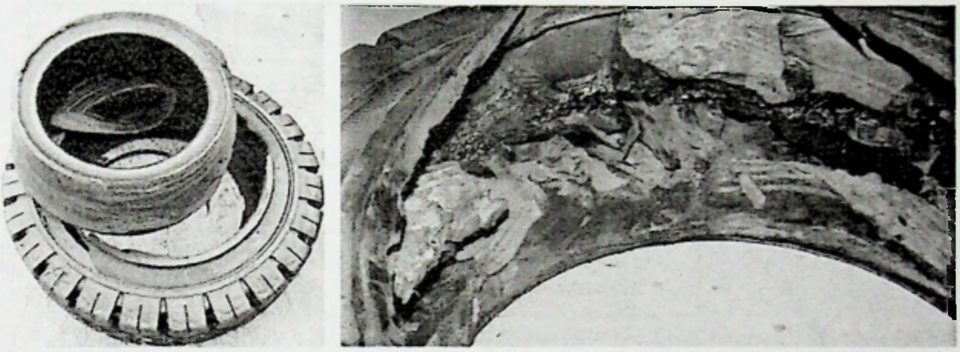

Figure 2.5 Resilient tire middle to tread premature failure

Resilient tire manufacturing process associated with high temperature processing at compound warming and tire rolling stages. Each layer including middle and tread layers are subjecting for thermal history induction over the processing time. Even though pre vulcanization is associated phenomena to current resilient tire manufacturing set ups pre curing should regulate at a level that won't affect product performances. Increasing demand and price competitiveness in the tire industry is always seeking opportunities to work in high temperature which increased the risk of high degree pre cure.

There was no previous study on the topic of investigation on maximum pre cure level that can reach without influencing product performances. Hence, this investigation is essential to find the maximum pre vulcanization level of the middle and tread layer without affecting the product performance of the solid tire.

3. MATERIALS & EXPERIMENTAL TECHNIQUES

This experiment was designed to evaluate the influence of interrupted rubber vulcanization. In order to achieve interrupted vulcanization, the vulcanization process has to be conducted in two steps: the first is identified as primary vulcanization (pre vulcanization); the second step is secondary vulcanization.

The flow diagram illustrates the basic steps of interlayer bonding strength evaluation (Figure 3.1)

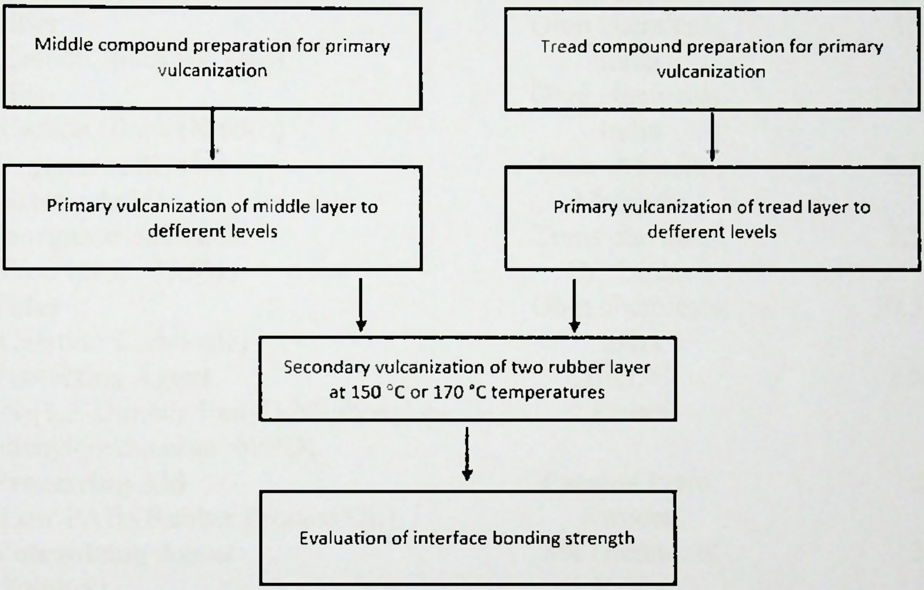

Figure 3.1 Basic steps of the experiment

3.1 Materials and compounding

The formulation presented in Table 3.1 and Table 3.2 was used for compounding the middle and tread layers respectively.

Table 3.1 Formulation of middle layer compound

Component	Origin	Parts (pphr)
Elastomer (Natural Rubber TSR 20)	VOC rubber, Sri Lanka	100
Filler (Carbon Black (N 330))	Ohm chemicals, India	15
Filler (Carbon Black (N 660))	Ohm chemicals, India	12.5
Organic Activator (Stearic Acid)	Creo chemical, Malaysia	2.5
Inorganic Activator (Zinc Oxide 99.5%)	Trans chemical, Sri Lanka	3.5
Filler (Calcium Carbonate)	Ohm chemicals, India	30.5
Protecting Agent (N-[1,3-Dimethylbutyl]-N'-phenyl-p-phenylenediamine -6PPD)	HKDC, China	2.5
Processing Aid (Low PAHs Rubber Process Oil)	Panama Petro, Sweden	8
Vulcanizing Agent (Sulphur)	Mk chemicals, Korea	2
Accelerator (2-(4-Morpholinothio) benzothiazole-MOR)	WR Chems, Malaysia	1.2
Retarder (CTPI)	WR Chems, Malaysia	0.2

Table 3.2 Formulation of tread layer compound

Component	Origin	Parts (pphr)
Elastomer (Natural Rubber TSR 20)	VOC rubber, Sri Lanka	100
Elastomer (Polybutadiene rubber)	VOC rubber, Sri Lanka	30
Filler (Carbon black (N550))	Ohm chemicals, India	55
Organic Activator (Stearic Acid)	Creo chemical, Malaysia	3
Inorganic Activator (Zinc Oxide 99.5%)	Trans chemical, Sri Lanka	5.5
Protecting Agent (N-[1,3-Dimethylbutyl]-N'-phenyl-p-phenylenediamine -6PPD)	HKDC, China	1.5
Processing Aid (Low PAHs Rubber Process Oil)	Panama Petro, Sweden	4.5
Vulcanizing Agent (Sulphur)	Mk chemicals, Korea	2
Accelerator (2-(4-Morpholinothio) benzothiazole-MOR)	WR Chems, Malaysia	1.1
Retarder (CTPI)	WR Chems, Malaysia	0.3

The rubber compound was prepared using a laboratory-scale internal mixer and mixing mill. Farrel BR1600 Banbury mixer was used for compound mixing with a friction ratio of 1:1.16. A fill factor of 0.55 was used during mixing. The mixing cycle used in the compounding of middle and tread compounds is described in Table 3.3 to Table 3.6. The lump taken from the internal mixer was then sheeted out on a two-roll mill to a thickness of about 3.5 mm, for which two laboratory-scale mills (size 200 mm x 400 mm) were used with a friction ratio of 1:1.2.

After mixing, sheeted rubber was kept for 24 hours at 30+/- 2 °C for conditioning.

Table 3.3 First stage middle compound mixing cycle

Time (Sec)	Description
0	NR
30	Stearic Acid + 6PPD + Processing Oil + Zinc Oxide
30	N 660+ N 330 + Cal. Carbonate
50	Ram Sweep
(30-50)	Dump @ 150 °C

Table 3.4 Second stage middle compound mixing cycle

Time (Sec)	Description
0	1st Stage compound
40	PVI + MOR + Sulphur
(90-120)	Dump

Table 3.5 First stage tread compound mixing cycle

Time (Sec)	Description
0	NR + BR
40	Stearic Acid + 6PPD + Processing Oil + Zinc Oxide
35	N550
30	Ram Sweep
(40-50)	Dump at 150 °C

Table 3.6 Second stage tread compound mixing cycle

Time (Sec)	Description
0	1st Stage compound
40	PVI + MOR + Sulphur
(65-80)	Dump

3.1.1 Compound batch variation.

To ensure the minimum influence of material variation on final comparative results, the material quality and property variation were carefully controlled in this experiment. For that, the same batch of the middle compound was used for all middle samples and the same batch of tread compound was used for all tread samples.

3.1.2 Vulcanization system

Sulphur was used as the vulcanization agent for the vulcanization system. Two types of activators were used: Stearic acid as an organic activator and Zinc Oxide as the inorganic activator. Throughout the study, MOR was used as the accelerator. A pre vulcanization inhibitor was used for both compound types.

3.2 Vulcanization

This research was concerned about Sulphur vulcanization when Sulphur forms covalent bonds between long-chain molecules in the presence of carbon-carbon double bonds. Typically, the vulcanization reaction is completed in a single step. However, in this study, the vulcanization reaction was completed in two steps; in primary and secondary vulcanization processes. Secondary vulcanization was accomplished at two temperatures; 150 °C and 170 °C.

3.2.1 Evaluation of vulcanization time

Vulcanization time was estimated using a commercially available rubber processing analyser (Table 3.9-RPA 2000). In RPA, the un-vulcanized compound is compressed between two plates set at curing temperature by moving lower die with a direct-drive motor. RPA needs to be enabled with a fast temperature controlling ability.

Generally, the optimum cure time is defined by T_{90} value, which represents the time required to reach 90% of maximum torque for plateau or reversion curves. If the sample is having a thickness of around 2 mm, it is possible to take rheometer T_{90} time directly as the cure time. But the dimension of samples used in this study is thicker than 2mm, thus longer curing times should be applied. Therefore, a commercially developed finite element analysis code was used to solve the heat transfer and cure problem. Due to the simplicity of the sample geometry and low thickness, the FEA estimates the state of cure with high accuracy. One-dimensional quasi-equivalent slab was assuemed to the calculation [26]. It was considered the thermal conductivity is a dependent of temperature. Further, time varying boundry condition chemically generated heat production which is a fuction of temperature and state of cure also a concerned for the FEA. These datas that required to feed FEA, are currenly available from past studies [27].

3.2.2 Compression moulding

A calculated amount of rubber compound was introduced into a heated mold for vulcanization; subsequently, the mold is closed under pressure. While the material in the cavity is melting, it was subjected to a force. To apply pressure, an electrically heated ram press was used in this study(

First letter - Secondary vulcanization temperature (L-150 °C and H-170 °C)

First digit – Primary vulcanization level of middle layer
Second digit – Primary vulcanization level of tread layer

Table 3.10). For both primary and secondary vulcanization, the specific pressure on the samples was maintained at 4.5 bar (ASTM requirement is minimum 3.5 bar). Setting temperature for primary vulcanization was maintained at 100±2□C and secondary vulcanization was maintained at 150±2 °C or 170±2 °C.

3.3 Sample preparation

Table 3.8 demonstrates the 3 steps of sample preparation. The three steps include; compound preparation for primary vulcanization, primary vulcanization of the compounds, and secondary vulcanization of the sample. To avoid variation in the curing stage, the same molds and lab press were used at each stage. Only one operator was involved in the sample preparation procedure to avoid human variations.

3.3.1 Compound preparation for primary vulcanization

Compound preparation for primary vulcanization includes steps of thickness reduction of the compound, sizing and introduce fabrick backing. Thickness reduction of the compound was accomplished by using a two-roll mill which consists of two rotating rolls separated by a narrow gap called mill nip. Mill nip was maintained at 3.3 mm with a 1:1.2 friction ratio. Due to the internal friction of the compound, heat is generated during milling. The temperature for all samples was set below 80 °C using the peripheral cooling system of the two roll mill. For each sample preparation, 2 kilograms of pre-blended middle and tread compounds were dropped into the nip gap of the cylinders. As the material processes on the two roll mill, it was folded over repeatedly to reduce the thickness to the desired level while achieving an improved homoginity. Ten passes were sent through two roll mills to reduce the thickness of each sample. Uniform thickness compound sheets and fabric backing were cut to match with mold dimentions.

3.3.2 Primary vulcanization of samples

Primary vulcanization was carried out by a hydraulic, electrically heated laboratory press. A special mold was designed with the cavity dimensions of 7.5 mm x 150 mm x 350 mm. In order to achieve a sufficient internal pressure during secondary vulcanization, the output sample dimension of the primary vulcanization mold should be larger than the secondary vulcanization mold cavity dimensions. During the mold design stage, this was considered as it is essential for proper interface adhesion of two layers. The temperature of the press was adjusted to a curing temperature of 100 °C with a precision of ± 2 °C. A fabric backing was introduced to the opposite side of the adhesion surface. A compressive pressure of 4.5 bar was applied for each sample preparation.

During secondary vulcanization, uniformity of the thickness of primary vulcanizate is also vital to maintain uniform pressure at the interface. To avoid the influence of pressure on adhesion strength, each pre vulcanizate sample should have the same dimension. Pre vulcanizates dimension is an influencing factor in secondary vulcanization pressure. Therefore zero percent primary vulcanized samples were also prepared by squeezing in the primary vulcanization mold at room temperature with the same pressure and achieved the same dimentions. Three bumping cycle was introduced and bumping pressure was increased progressively to ensure the diffusion and to evacuate the air trapped withing the mold and the rubber layers.

Two hundred and sixty grams of the middle compound and three hundred grams of tread compound was used to fill the mold cavity. The weight of the compound was calculated by measuring the specific-gravity of the compound.

$$\text{Volume to be filled} = \frac{\text{compound weight}}{\text{specific gravity}}$$

As described in chapter 2, pre-vulcanization said to occur during the green tire processing time duration. As the process time increases, the degree of pre-vulcanization also increases due to the progression of vulcanization reaction with increased temperature. Therefore it is logical to define the primary vulcanization level based on the time which subjected to the elevated temperature. Hence, the primary vulcanization percentage could be defined as a fraction of total time to full cure.

$$\text{Primary vulcanization level} = \frac{\text{Time spent at elevated temperature}}{\text{vulcanization time for the particular temperature}} \text{x } 100\%$$

In section 2.4.2, the rheometer curve decribes that the curing reaction rate is not constant over the vulcanization time duration. Therefore it is obvious that there is no linier rate of crosslink formation during the processing time. So it is clear that the primary vulcanization percentage defined from the above approach may not tally by the figure with the crosslink density of the vulcanizate, but it represents the level of primary vulcanization. This approach more relevent to the tire industry since the maximum process time that ensures product quality could be directly derrive as an outcome of the research work.

Section 1.5 described that typical warming temperature is around 90-100 °C and the rolling temperature is around 100-105 °C. As explained earlier the primary vulcanization occurre due to elevated temperature during processing time. A common temperature was assumed which represents both warming and rolling temperatures for this study. It was assuemed that in both warming and rolling steps compounds are subjected to a 100 °C pre vulcanization temperature, therefore pre vulcanizate samplese were prepared by curing at 100 °C. Different pre cure levels were achieved by changing the vulcanization time, calculated from 0% ,20% ,40% ,60% ,80% and 100% of optimum cure time of the perticular vulcanizate. Optimum cure time was calculated by considering the t_{90}, thermal conductivity and critical point for the curing. Primary vulcanizate names and pre-vulcanization times of the middle and tread compound tabulated in (Table 3.7, Table 3.8).

Table 3.7 Primary vulcanization time of middle pre-vulcanizates

Sample name	Primary vulcanization time (minutes)
M0	0.0
M20	15.9
M40	31.8
M60	47.6
M80	63.5
M100	79.4

Table 3.8 Primary vulcanization time of tread pre-vulcanizates

Sample name	Primary vulcanization time (minutes)
T0	0.0
T20	17.7
T40	35.4
T60	53.2
T80	70.9
T100	88.6

To stop further vulcanization reaction, after completing the primary vulcanization in the laboratory press, the mold unit was immediately immersed in a water bath maintained at room temperature. Once the mould reaches the ambient temperature, the mold half's was opened and the rubber samples were carefully demolded. Samples were kept in a dust-free air-conditioned environment for 48 hours to remove moisture then sized to 25 mm x 7.5 mm x 130 mm dimensions. For this period, the surface to be bonded was wrapped with clean Mylar film to avoid contamination (Figure 3.2). This approach is very vital because the impuirities, moisture or dust on the bonding interface are directly affected for the interfacial bonding strength [15].

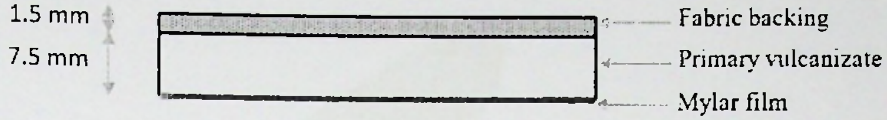

Figure 3.2 Primary vulcanizate

3.3.3 Vulcanization of adhesion samples

After removing protective mylar film, the primary vulcanizate middle and tread compounds were cured together at secondary vulcanization step for the combinations as described in Table 3.9 and

First letter - Secondary vulcanization temperature (L-150 °C and H-170 °C)

First digit – Primary vulcanization level of middle layer
Second digit – Primary vulcanization level of tread layer

Table 3.10. Depending on the secondary vulcanization temperature 150 °C and 170 °C the respective optimum cure time was estimated from the FEA model as 1800 seconds and 372 seconds. For each temperature, 36 different combinations could be obtained by changing the primary vulcanization level of the middle and tread layer. Samples size and sample preparation have followed the instruction of ASTM D413 for the adhesion test. The compression pressure and bumping cycle followed as same as the primary vulcanization step.

The same laboratory press that was used in primary vulcanization was adjusted to (150 °C and 170 °C) the curing temperatures. In this study, the said temperatures were considered as low and high secondary vulcanization temperatures. Secondary vulcanization temperature 150 °C was selected as it is a typical vulcanization temperature in the solid tire industry. Higher temperature vulcanization is one of the interesting areas for making efficient production in the rubber industry. 170 °C selected to evaluate inflence on adhesion properties and give an insite to the industry about the feasibility of solid tire curing at 170 °C. Compare and contrast results at two secondary vulcanization temperatures ;150 °C and 170 °C .

After secondary vulcanization, before the adhesion test, the samples were kept for 48 hours for conditioning. Adhesion sample with dimensions. Figure 3.3 shows a sample prepared for the adhesion test.

Figure 3.3 Adhesion sample with dimensions

Table 3.9 Low secondary vulcanization temperature sample names and primary vulcanization percentages

Sample name	Primary vulcanization time as a percentage of cure time (%)	
	Middle	Tread
L0/0	0	0
L0/20	0	20
L0/40	0	40
L0/60	0	60
L0/80	0	80
L0/100	0	100
L20/0	20	0
L20/20	20	20
L20/40	20	40
L20/60	20	60
L20/80	20	80
L20/100	20	100
L40/0	40	0
L40/20	40	20
L40/40	40	40
L40/60	40	60
L40/80	40	80
L40/100	40	100
L60/0	60	0
L60/20	60	20
L60/40	60	40
L60/60	60	60
L60/80	60	80
L60/100	60	100
L80/0	80	0
L80/20	80	20
L80/40	80	40
L80/60	80	60
L80/80	80	80
L80/100	80	100
L100/0	100	0
L100/20	100	20
L100/40	100	40
L100/60	100	60
L100/80	100	80
L100/100	100	100

First letter - Secondary vulcanization temperature (L-150 °C and H-170 °C)
First digit – Primary vulcanization level of middle layer
Second digit – Primary vulcanization level of tread layer

Table 3.10 High secondary vulcanization temperature sample names and primary vulcanization percentages of composition layers

Sample name	Primary vulcanization time as a percentage of cure time (%)	
	Middle	Tread
H0/0	0	0
H0/20	0	20
H0/40	0	40
H0/60	0	60
H0/80	0	80
H0/100	0	100
H20/0	20	0
H20/20	20	20
H20/40	20	40
H20/60	20	60
H20/80	20	80
H20/100	20	100
H40/0	40	0
H40/20	40	20
H40/40	40	40
H40/60	40	60
H40/80	40	80
H40/100	40	100
H60/0	60	0
H60/20	60	20
H60/40	60	40
H60/60	60	60
H60/80	60	80
H60/100	60	100
H80/0	80	0
H80/20	80	20
H80/40	80	40
H80/60	80	60
H80/80	80	80
H80/100	80	100
H100/0	100	0
H100/20	100	20
H100/40	100	40
H100/60	100	60
H100/80	100	80
H100/100	100	100

3.4 Determination of properties

3.4.1 Rheological analysis

Torque vs. time response curve for middle and tread compounds were obtained from RPA for rheological analysis of primary vulcanizate samples mentioned in Table 3.7 (M0-M100) and Table 3.8 (T0-T100). 150 °C and 170 °C temperatures were tested for rheological properties of ts_2, t_{90}, M_L, M_H. Test duration was extended compared to the curing time, to observe the nature of the rheometer curve after vulcanization. Each sample showed a plateau curve during test time.

3.4.2 Adhesion test

As explained in section 3.3, secondary vulcanized samples were taken for the adhesion test by using an Instron 1195 universal testing machine. Samples widths were measured to the nearest 0.2 mm and recorded. As illustrated in Figure 3.4 two layers were attached to the grip head and maintain specimen in approximately a vertical position during the test to ensure a 180° peel. The force required to cause separation between adhered surfaces was measured from the machine. Testing machine travel at a speed of 500± 50 mm/min until the test piece breaks. 5 measurements were taken to get an average result. (ASTM D413)

Adhesion Strength = F/d

F- Maximum force indicated in the machine at failure,

d– Median thickness of each test piece

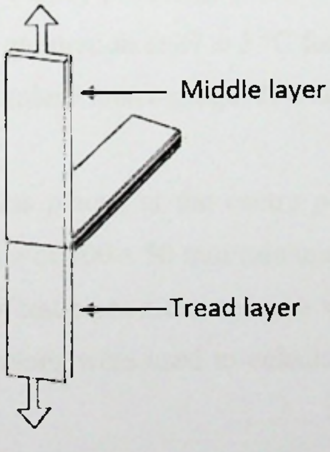

Figure 3.4 Adhesion test sample and forces

Samples for self-adhesion were prepared by keeping two layers of pre vulcanizate of the same compound, then secondary vulcanize at the desired temperature. The adhesion test was carried out as the same procedure as above.

All adhesion tests were conducted at 28± 2 °C to ensure data accuracy and preseseness [15].

3.4.3 Microscopic investigations

After completion of the adhesion test, failure surfaces (peeled surface) were observed with a binocular microscope in a magnification of 9.6. Failure location and failure surface nature were recorded.

3.4.4 Tensile properties

The tensile testing machine was used to determine the relationship between the applied force and the deformation produced. Compound sheets were pre vulcanized to different levels using a special mould with cavity dimension of 2.5 mm x 10 cm x 15 cm. Pre vulcanizates then introduced to another mould with cavity dimension of 2 mm x 10 cm x 15 cm for secondary vulcanization. Curing time was assumed as same as the rheometer t_{90} value due to the low thickness of the sample. Specific pressure of 4.5 bar was maintained for both primary and secondary vulcanization. After secondary vulcanization at 150 °C and 170 °C moulded sheets were cut in to dumb-bell shapes using standard dimension die cuts by punching. (ASTM D-412A)

The test pieces were kept for maturation at 27 ± 2 °C for 24 hours before testing. The thickness was measured by a micro meter gauge. Average of three test samples were used to get one test result.

The dumbbell test sample was placed at the centre position of the grip head and stretched at a rate of separation of 500 ± 50 mm/min until the test piece breaks. Force on test piece and elongation of test piece measurements were taken while the test piece was stretched. Below calculations were used to calculate tensile strength and 300% modulus.

- Tensile Strength = F/A

F- Breaking Force, A –Initial Cross-sectional area

- Modulus at 300% elongation = f / A

f- Force required at 300% elongation, A- Initial Cross-sectional area

3.4.5 Tear strength

Similar to tensile testing, primary and secondary vulcanization was carried out to get 2 mm moulded sheets. Crescent shaped specimen was prepared using a die cut. (ASTM D-624 die C).

A nick of depth 1 ± 0.2 mm was made at the centre of the concave edge of the test piece. Then the test piece was mounted in the testing machine and stretched at a rate of separation of 500 ± 50 mm/min until the test piece breaks. The maximum force at the break was recorded and 3 test results were taken to get an average result.

- Tear Strength = F/d

F- Maximum force, d – Median Thickness of each test piece

3.4.6 Hardness test

The hardness test piece cavity was incorporated into the tensile mould. Pre vulcanization and secondary vulcanization were carried out similar to the tensile test method. Resistance to the indentation of rubber samples was measured by using the Durometer rubber hardness tester. ASTM D 2240 test procedure followed to measure the hardness of test samples. 5 measurements were taken to get the average test result.

4. RESULTS AND DISCUSSION

In this chapter, the results obtained from the experiments, which were described in chapter 3, are presented and discussed in detail. Moreover, a detailed overview of results on interface adhesion between the middle and tread layer are discussed according to the primary vulcanization level and secondary vulcanization temperature.

4.1 Microscopic investigations of the bonded surface

Under different primary and secondary vulcanization variables, five distinct surface natures could be observed in failure surfaces. When the interface bonding strength was stronger than the compound self-adhesion, instead of tearing from the bonding interface the compound itself will tear (Figure 4.2). Therefore, the separation location was a vital observation. Generally, "tearing failure surfaces" with high surface roughness has exhibited great bonding strengths. The surfaces observed to be with good bonding strength were found to have a high surface roughness after separation. The bonding strength declined according to the changes of the surface nature. The highest bonding strength was observed in "rough" surface nature, which progressively decreased from "matt" to "glossy" surface natures.

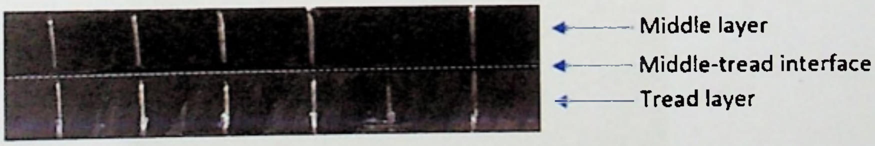

Figure 4.1 Middle-tread interface failure

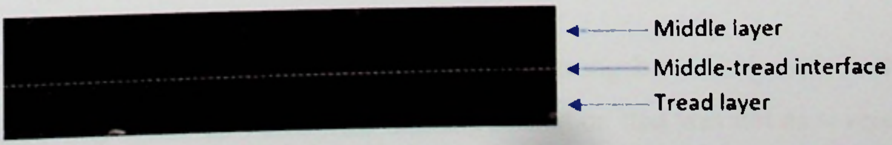

Figure 4.2 Middle tearing failure

4.1.1 Binocular microscopic images of failure surfaces

Binocular microscopic images for fracture surfaces are shown in Figure 4.3-Figure 4.7. The microscopic appearance was associated with the adhesion strength between two layers. A surface with "tearing" fracture has indicated that the rubber sample has failed form necking which intern signals high bonding strength. When the failure occurred by tearing the middle layer, it was identified as "middle tearing" (Figure 4.3), while the tearing propagated through the interface was named as "rough tearing" (Figure 4.4).

Figure 4.3 The surface finish of "middle teared" surface nature

Figure 4.4 The surface finish of "rough teared" surface nature

"Rough" nature of the facture has suggested fairly strong bonds between the two layers (Figure 4.5). It has also exhibited necking formation that was not as severe as in "tearing" surfaces.

Figure 4.5 The Surface finish of "rough" surface nature

Matt surfaces show smooth dull appearance; if the rubber failed without the formation of necking. “Matt” appearance is related to low adhesion strength between two layers (Figure 4.6).

Figure 4.6 The Surface finish of "matt" surface nature

The “glossy” appearance is associated with very low adhesion strength between two layers (Figure 4.7). In particular, these samples indicate almost no bonding between the layers.

Figure 4.7 The Surface finish of "glossy" surface nature

4.2 Rheometer results of primary vulcanizates

The cure curves were taken at 150 °C and 170 °C for different levels of primary vulcanizates of middle and tread compounds. Maximum torque (M_H), optimum cure time (t_{90}), minimum torque (M_L) and scorch time (ts_2) of different vulcanizates were taken with the aid of rubber process analyser (RPA).

4.2.1 Rheometer results at 150 °C and 170 °C for different primary vulcanization levels of the middle compound

Cure characteristics of middle compound pre vulcanizates tested at 150 °C and 170 °C are tabulated in Table 4.1 and Table 4.2.

Table 4.1 Cure characteristics of middle vulcanizates tested at 150 °C

	M0	M20	M40	M60	M80	M100
M_H (dNm)	20.58	20.68	20.60	20.62	20.77	20.78
M_L (dNm)	2.17	3.02	3.33	7.87	18.02	19.12
ts_2 (s)	195.60	159.60	88.20	51.60	28.40	1.20
t_{90} (s)	421.20	354.60	256.20	178.80	105.60	67.20

Table 4.2 Cure characteristics of middle vulcanizates tested at 170 °C

	M0	M20	M40	M60	M80	M100
M_H (dNm)	17.30	17.21	17.31	17.38	17.45	17.45
M_L (dNm)	1.51	1.79	2.27	5.88	16.05	16.87
ts_2 (s)	56.65	52.47	37.48	30.24	19.20	1.01
t_{90} (s)	108.39	104.47	81.32	64.02	62.41	43.10

As expected, for both temperatures, the scorch safety (time taken for 2 units to rise above the minimum torque) decreases with an increase in primary vulcanization level (Table 4.1, Table 4.2). The optimum cure time (time taken for attaining 90% of maximum torque) also decreases with increment in primary vulcanization level .These results indicate that when the primary vulcanization time increased, linkages that formed within the vulcanizates have increased. This reduces the ability to make further linkages with another layer during secondary vulcanization. M_L increments also obey this phenomenon.

As expected, for each primary vulcanizates, at higher secondary vulcanization temperature, an increment in crosslinking reaction rate was evident with the corresponding decrease in scorch time and optimum cure time. Generally, the reaction rate of vulcanization could be increased by around 50% for every 10 °C increments in curing temperature.

Maximum torque, a measure of the state of crosslinking density; decreases when secondary vulcanization temperature is increasing. This behaviour could be explained as follows. The crosslinks formed at any initial temperature are mostly polysulphidic which are thermally unstable [7]. On prolonged heating, they converted into the shorter forms of linkages like disulphidic and monosulphidic links; the chain shortening increases the overall crosslinking density. This phenomenon is more relevant at low temperature curing due to longer curing times. But for high temperature curing, due to shorter curing (optimum) time, the compound is subjected to thermal action for a short period which makes polysulphidic linkages remain the same. This might be the reason for the decrease in M_H due to low crosslink density for higher secondary vulcanization temperatures. Another reason for the decrease in the maximum torque might be the viscosity changes of the sample that resulted from the molecular changes. Low-temperature secondary vulcanizate samples exhibit high M_H values, suggest provisions for chain shortening and additional crosslinking in longer curing times.

M_H- M_L (delta-cure) is a measure of crosslink density [28]. The decline in M_H - M_L is suggested that crosslink formation during secondary vulcanization drop with the rise of primary vulcanization level. Even though samples are fully cured, M100 samples show a very small increment from M_L value. This behaviour has been confirmed by repeating the test. This response could be due to the crosslink shortening or additional crosslinks that reduces the mobility of the molecules.

4.2.2 Rheometer results at 150 °C and 170 °C for different primary vulcanization levels of the tread compound

The cure curves of the tread pre vulcanizates were taken at 150 °C and 170 °C. Respective M_H, M_L, ts_2, and t_{90} are presented in Table 4.3 and Table 4.4.

Table 4.3 Cure characteristics of tread vulcanizates tested at 150 °C

	T0	T20	T40	T60	T80	T100
M_H (dNm)	16.28	16.36	16.33	16.44	16.32	16.53
M_L (dNm)	3.41	3.97	4.70	11.19	14.09	15.66
ts_2 (s)	322.20	265.20	128.40	52.20	31.60	4.80
t_{90} (s)	565.80	511.80	386.80	262.20	132.60	98.20

Table 4.4 Cure characteristics of tread vulcanizates tested at 170 °C

	T0	T20	T40	T60	T80	T100
M_H (dNm)	13.30	13.35	13.26	13.52	13.57	13.71
M_L (dNm)	2.51	2.69	3.24	9.41	12.08	13.02
ts_2 (s)	88.40	80.03	60.52	34.44	22.20	3.60
t_{90} (s)	151.70	148.42	121.54	89.32	86.64	82.96

As expected, scorch safety and the difference between M_H and M_L have reduced with an increment in primary vulcanization level at both high and low temperatures. In this case, it is also evident, at a higher level of primary vulcanizates, further crosslinking ability with another substance has reduced due to linkages within the vulcanizates.

The factors determine the maximum toque, scorch time and optimum cure time on of secondary vulcanization temperature of tread seem to be similar to those of middle vulcanizates. As expected, scorch time and the optimum cure time have deceased by increasing the secondary vulcanization temperature. Also, similar to tread vulcanizates, M_H found to be decreased with high secondary vulcanization temperatures than corresponding low temperature value. T100 also showed M_H and M_L difference during the test time, which was reconfirmed by a repeat test and thought to be due to viscosity changes during chain shortening. The tread compound has also exhibited a plateau rheometer curve for both temperatures. This is obviously supported by the strong antioxidant action of both middle and tread compounds.

4.3 Influence of middle and tread layer primary vulcanization level on their interlayer adhesion

The effect on interlayer adhesion between the middle and tread layer after secondary vulcanization at 150 °C and 170 °C could be discussed in terms of primary vulcanization levels. To assess the interlayer adhesion, both qualitative results like adhesion strength and quantitative observations like failure surface nature and separation location were attentively concerned for the discussion. Further experiments were carried out to examine the self-adhesion strength of middle and tread pre vulcanizates to explain the results obtained.

Particular for a solid tire, adhesion between middle and tread compounds is vital to ensure its performance over the service life. The industrial norm is set to ensure product integrity: any kind of layer configuration should be maintained at a minimum of 16 kg/cm adhesion level. This minimum acceptable level is also appraised during the discussion.

Dimensions of the samples are critical for accurate results [15]. Since the thickness and width of samples were well maintained, the energy required for peeling was not influenced due to dimension differences. It can state that the uniformity of the sample dimension has increased the accuracy of comparable results.

Chemical nature and ingredients of two compounds cannot be neglected for interfacial adhesion results [18]. For this study, all samples were prepared by using one compound batch of middle and tread. Therefore, the influence due to the compound variation of middle or tread is minimum. Hence, Influence on comparable results should be minimum.

4.3.1 Influence of middle and tread layer primary vulcanization level on their interlayer adhesion at low secondary vulcanization temperature

In Table 4.5 adhesion results are presented at the secondary vulcanized temperature of 150 °C. The primary vulcanization level of the middle and tread layer, failure surface nature and failure location are also summarized.

Table 4.5 Adhesion results of samples that secondary vulcanized at 150 °C

Sample name	Primary vulcanization time as a percentage of cure time (%)		Adhesion strength (kg/cm)	Separation location	Failure surface nature
	Middle	Tread			
L0/0	0	0	23.6	M	middle tearing
L0/20	0	20	23.4	M	middle tearing
L0/40	0	40	23.3	M	middle tearing
L0/60	0	60	23.3	M	middle tearing
L0/80	0	80	17.1	MTI	rough tearing
L0/100	0	100	14.3	MTI	rough-glossy
L20/0	20	0	23.2	M	middle tearing
L20/20	20	20	23.0	M	middle tearing
L20/40	20	40	22.9	M	middle tearing
L20/60	20	60	17.3	MTI	rough tearing
L20/80	20	80	7.0	MTI	rough-matt
L20/100	20	100	6.5	MTI	matt-glossy
L40/0	40	0	22.3	M	middle tearing
L40/20	40	20	21.8	M	middle tearing
L40/40	40	40	16.4	MTI	rough tearing
L40/60	40	60	9.2	MTI	rough-matt
L40/80	40	80	6.9	MTI	matt-glossy
L40/100	40	100	6.1	MTI	matt-glossy
L60/0	60	0	18.7	M	middle tearing
L60/20	60	20	15.3	MTI	rough-rough
L60/40	60	40	8.8	MTI	rough-matt
L60/60	60	60	1.1	MTI	glossy-glossy
L60/80	60	80	1.1	MTI	glossy-glossy
L60/100	60	100	1.0	MTI	glossy-glossy
L80/0	80	0	7.6	MTI	rough -matt
L80/20	80	20	4.5	MTI	matt-matt
L80/40	80	40	2.2	MTI	matt-matt
L80/60	80	60	0.3	MTI	glossy-glossy
L80/80	80	80	0.4	MTI	glossy-glossy
L80/100	80	100	0.2	MTI	glossy-glossy
L100/0	100	0	2.5	MTI	matt-matt
L100/20	100	20	2.1	MTI	matt-matt
L100/40	100	40	1.7	MTI	matt-matt
L100/60	100	60	0.2	MTI	glossy-glossy
L100/80	100	80	0.2	MTI	glossy-glossy
L100/100	100	100	0.2	MTI	glossy-glossy

M- Failure happened by middle layer tearing

MTI- Failure happened at the middle-tread interface

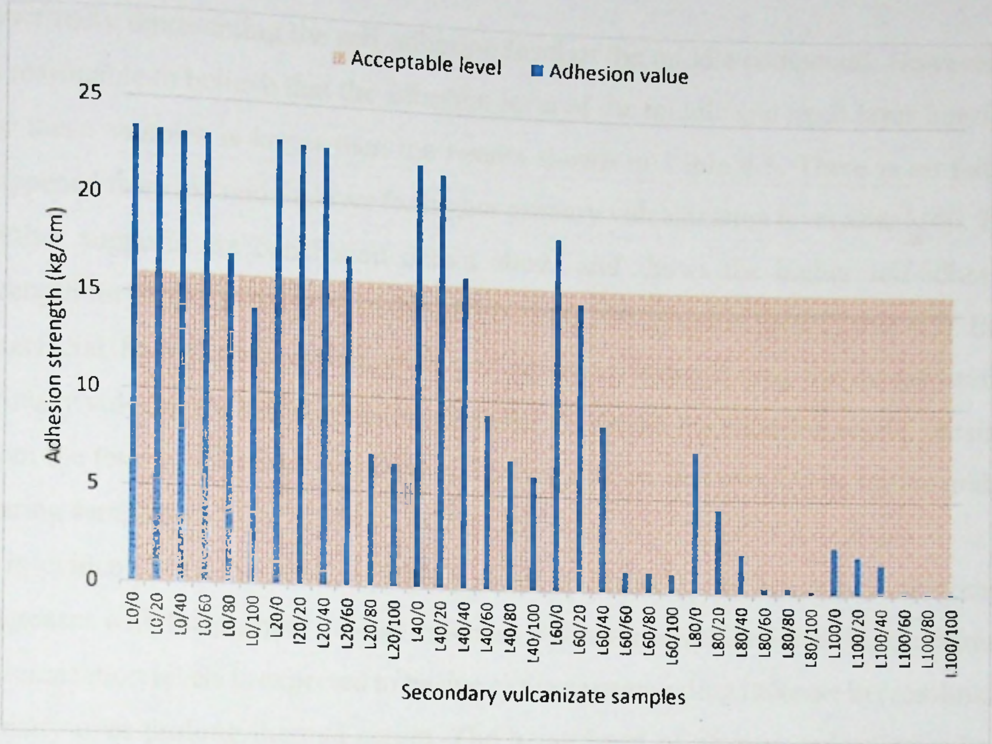

Figure 4.8 Adhesion results and acceptable level for samples that secondary vulcanized at 150 °C

Figure 4.8 illustrates the adhesion strengths of samples against the accepted level for all secondary vulcanizates at 150 °C. Few failures have occurred from the middle compound while the majority were failed at the interface of the middle and tread layer (Table 4.5). It's clear from the adhesion test (peeling test), the failures occur from the weakest point of the sample. During the failure, the energy associated with the work on separation is greater than the bonding energy between failed surfaces [19]. Samples L0/0, L0/20, L0/40, L0/60, L20/0, L20/20, L20/40, L40/0, L40/20, and L60/0 samples failed from the middle layer, indicating the middle layer as the weakest point of the system. This behaviour has proven by repeated experiments. During the test, stress acting point can lead to failure through the middle layer, tread layer or between middle and tread layer interface. Further testing was carried out to evaluate the self-adhesion of middle and tread pre vulcanizates, which were secondarily vulcanized at 150 °C (Table 4.6 and Table 4.7). Each sample failed at the middle layer has shown similar adhesion strength corresponding to the pre vulcanizate self-adhesion strength as expected, while tread pre vulcanizates have shown a significantly high self-adhesion level. These results suggested that the outcome of the adhesion test of those samples is virtually representing the self-adhesion level of the middle compound. However, it is reasonable to believe that the adhesion level of the middle and tread layer interface for those samples is larger than the results shown in Table 4.5. There is no failure happened from the middle layer for higher primary vulcanization level after M60. This further supports the conclusion drawn above and shows the higher self-adhesion strength for M80 and M100 than the L80/0-L100/100 adhesion level (Table 4.5). Each interfacial failure samples exhibit lower adhesion strength than the corresponding primary vulcanizate's self-adhesion strength. Therefore, the adhesion results obtained from the test represent the actual bonding strength between two layers, unlike middle tearing samples.

It is evident from the results (Table 4.6 and Table 4.7), the self-adhesion strength decreases with the primary vulcanization level. Lower self-adhesion at higher primary vulcanization levels is expected to be due to the corresponding increase in crosslinking density over prolong thermal action. The lower level of primary vulcanizates has a larger share of polysulphidic crosslinking which improves tear strength [13]- [14].

Table 4.6 Middle vulcanizate self-adhesion results, secondary vulcanized at 150 °C

Sample	Adhesion strength (kg/cm)
M0	23.4
M20	23.2
M40	22.0
M60	18.6
M80	17.4
M100	16.5

Table 4.7 Tread vulcanizate self-adhesion results, secondary vulcanized at 150 °C

Sample	Adhesion strength (kg/cm)
T0	35.2
T20	34.4
T40	32.4
T60	31.6
T80	31.2
T100	30.4

Sample L0/0 to L0/100 comprises M0 configuration with T0 to T100. Up to T60, the strength of adhesion is very high. Further, at T80, adhesion level exceeds the acceptable level. Thus, a clear advantage is gained by the high crosslinking ability of M0 due to zero primary vulcanization. Rough tearing surface finish at L0/80 also indicates good bonding between two layers. A significant adhesion level is shown at the L0/100 sample even though the tread layer is fully vulcanized. This behaviour has been established by recurrent results in repeat experiments. It can be attributed to the greater crosslinking ability of the M0 sample which would contribute to interlayer linkages. Glossy failure surface finish of the tread layer with a rough finish of the middle layer suggested a higher contribution of the middle layer for inter-linkages.

Sample L20/0 to L20/100 are M20 configuration with T0 to T100. The number of samples with middle tearing was limited to 3, along with a reduction of interface failure strength. Increment of primary vulcanization level seems to be contributed to an overall drop in interfacial bonding strength. It could be further explained by the reduction in the crosslinking ability of the middle compound during primary vulcanization, as a result of the allocation of some linkages to form bonds within the middle layer. It can attribute to the decline in interlayer bonding strength. This is evident with the T60 bonding strength, M0 showed over 23.3 kg/cm while M20 17.3 kg/cm adhesion strength. However, L20/60 still showing an acceptable adhesion level. The surface nature of L20/60 was also acceptable as rough tearing is an indication of good bonding between two layers. L20/80, L20/100 samples have shown a drastic drop in adhesion strength, as a high degree of pre vulcanization of the tread layer diminishes its ability to make interfacial crosslinking, which was further confirmed by the interface nature of matt and glossy finish.

For L40/0 to L40/100 samples, M40 configured with T0-T100. With M40 middle tearing has happened only up to T20. This is obviously due to the increase of primary vulcanization that reduces the interlayer crosslinking ability. T40 is the highest acceptable tread primary vulcanization level which conformed by both adhesion strength and the failure surface nature. The bonding strength with M40 has drastically dropped after T60 and matt and glossy surfaces are indicated bad bonding.

As evident from the results of Table 4.5, L60/0 to L60/100 samples represent M60 vs T0 to T100 configurations. M60 makes acceptable level bonding only with T0; L60/0 shows an adhesion level of 18.7 kg/cm. Further, the failure mode is middle tearing that implies the adhesion level between the two layers is higher than the test results as explained earlier. L60/20 failure happened at the middle-tread interface while showing fairly acceptable surface nature. But the bonding strength has not achieved an acceptable level. Repeat tests were conducted to conform the findings and the same results were obtained. The higher degree of primary vulcanization of the middle compound and tread compound of pre vulcanization might reach an up to a critical level in bond formation level to make a strong bond between two layers. The tread primary vulcanization level below T20 could make a strong bonding between two layers that could be investigated by a future study. L60/40 is the last point where makes a significant bonding. After T60, there was almost no crosslinking between the middle and tread layers; surface finishes were glossy implying absent interlayer bonding. Very small adhesion level indicated in the testing may be due to Van der waals bonding among two surfaces at high pressure during secondary vulcanization.

Samples L80/0 to L80/100 are a combination of M80 with T0 toT100, the strength of adhesion between two layers was very low with an increase in primary vulcanization level of two compounds, which of cause follows the pattern of the previous sample. Even with T0, the adhesion level was low due to a higher level of primary vulcanization of the middle compound. Even though, M0 made acceptable adhesion level with T80, in this case, at T0 could not make acceptable bonding with the middle layer suggesting that middle primary vulcanization is critical to creating an acceptable bonding. After T20, both adhesion strength and surface finish were diminished drastically with an increase of tread primary vulcanization level.

Samples L100/0 to L100/100 were made with M100 vs. T0 to T100. The middle was fully pre-cured. Adhesion results obtained with the configuration of M100 with different primary vulcanization of the tread layer has exhibited a very low adhesion level between two layers. The surface nature was also not at an acceptable level that was worsened with a higher degree of primary vulcanization of the tread layer. Even though M0 exhibits significant adhesion level with T100, T0 could not make considerable adhesions with M100. This also confirms the fact that the middle primary vulcanization is more critical for two-layer interface bonding.

4.3.2 The influence of middle and tread layer primary vulcanization level on their interlayer adhesion at high secondary vulcanization temperature

Table 4.8 depicts the adhesion results obtained after the secondary vulcanization at 170 °C; the summary of the primary vulcanization level of middle and tread layers and failure surface information. In Figure 4.9, Adhesion strengths of samples presented against the accepted level for all secondary vulcanizates at 170 °C.

Table 4.8 Adhesion results of samples that secondary vulcanized at 150 °C

Sample name	Primary vulcanization time as a percentage of cure time (%)		Adhesion strength (kg/cm)	Separation location	Failure surface nature
	Middle	Tread			
H0/0	0	0	24.0	M	middle tearing
H0/20	0	20	23.7	M	middle tearing
H0/40	0	40	14.7	MTI	rough-glossy
H0/60	0	60	13.6	MTI	rough-glossy
H0/80	0	80	13.5	MTI	rough-glossy
H0/100	0	100	12.9	MTI	rough-glossy
H20/0	20	0	23.6	M	middle tearing
H20/20	20	20	16.8	MTI	rough tearing
H20/40	20	40	13.1	MTI	rough-rough
H20/60	20	60	9.0	MTI	rough-matt
H20/80	20	80	2.7	MTI	matt-matt
H20/100	20	100	2.0	MTI	matt-matt
H40/0	40	0	16.3	MTI	rough tearing
H40/20	40	20	6.2	MTI	matt-matt
H40/40	40	40	6.1	MTI	matt-matt
H40/60	40	60	2.3	MTI	glossy-glossy
H40/80	40	80	2.1	MTI	glossy-glossy
H40/100	40	100	1.7	MTI	glossy-glossy
H60/0	60	0	6.2	MTI	matt-matt
H60/20	60	20	6.0	MTI	matt-matt
H60/40	60	40	5.3	MTI	matt-matt
H60/60	60	60	1.3	MTI	glossy-glossy
H60/80	60	80	0.6	MTI	glossy-glossy
H60/100	60	100	0.4	MTI	glossy-glossy
H80/0	80	0	5.4	MTI	matt-matt
H80/20	80	20	2.0	MTI	matt-matt
H80/40	80	40	1.7	MTI	matt-matt
H80/60	80	60	0.2	MTI	glossy-glossy
H80/80	80	80	0.2	MTI	glossy-glossy
H80/100	80	100	0.2	MTI	glossy-glossy
H100/0	100	0	2.1	MTI	matt-matt
H100/20	100	20	1.7	MTI	matt-matt
H100/40	100	40	0.4	MTI	glossy-glossy
H100/60	100	60	0.2	MTI	glossy-glossy
H100/80	100	80	0.2	MTI	glossy-glossy
H100/100	100	100	0.2	MTI	glossy-glossy

M- Failure happened by middle layer tearing

MTI- Failure happened at the middle-tread interface

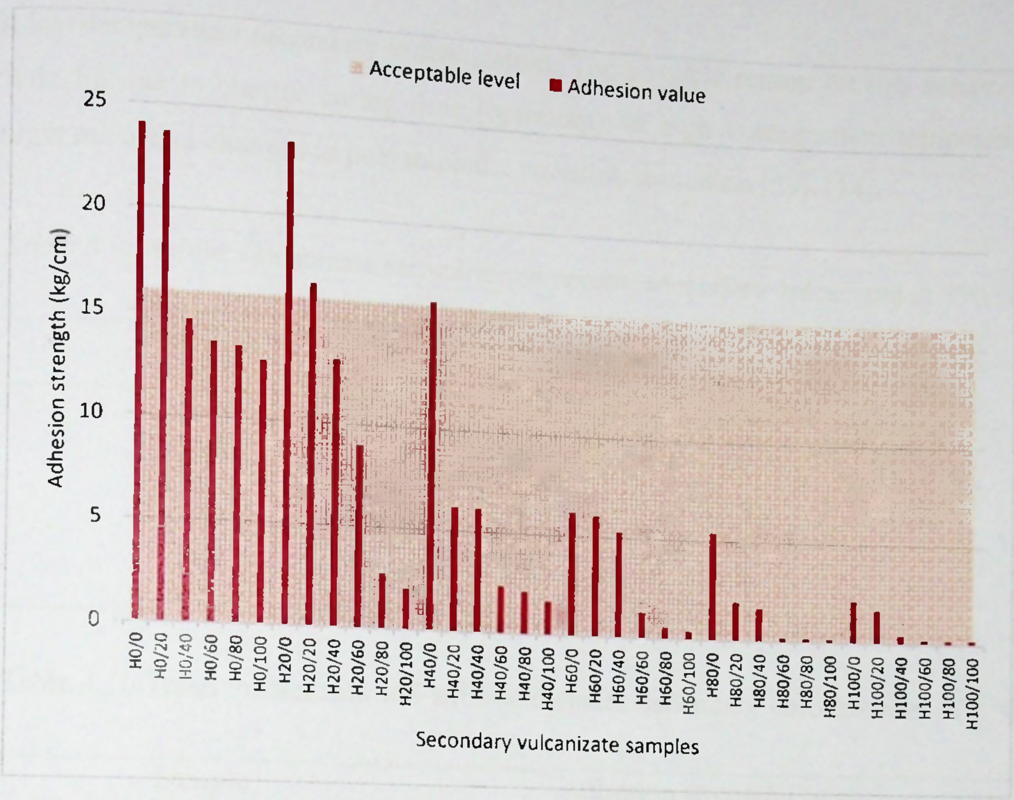

Figure 4.9 Adhesion results and acceptable level for samples that secondary vulcanized at 170 °C

Except in H0/0, H0/20, and H20/0, failure occurred in the rest of the samples at the middle-tread interface. Samples that failed from middle tearing exhibits significantly higher adhesion strength than the others. After secondary vulcanization at 170 °C, extended tests were carried out to evaluate the self-adhesion of middle and tread primary vulcanizates. Results of Table 4.9 and Table 4.10 indicate that the adhesion results obtained for H0/0, H0/20, and H0/40 samples comply with corresponding pre vulcanizate self-adhesion strengths as expected. Tread pre vulcanizates exhibit significantly high self-adhesion strength that indicates tread is the strongest component in the system. These results also suggested that interfacial adhesion levels of H0/0, H0/20, and H0/40 samples were greater than the values shown in Table 4.8. The rest of the sample failed at the middle-tread interface representing the genuine adhesion strength at the interface from the test result. As expected, those adhesion strengths were significantly lower than relevant pre vulcanizates of middle and tread self-adhesion strengths. The results presented in Table 4.9 and Table 4.10 shows that the self-adhesion is not decreased with an increase in primary vulcanization level as seen in low-temperature secondary vulcanization. The possible reason for this behaviour could be due to shorter curing time (optimum); at high vulcanization temperature might not affect changes in polysulphidic crosslink formation [29], [14].

Table 4.9 Middle vulcanizate self-adhesion results, secondary vulcanized at 170 °C

Sample	Adhesion strength (kg/cm)
M0	23.8
M20	23.5
M40	22.5
M60	22.9
M80	22.8
M100	22.8

Table 4.10 Tread vulcanizate self-adhesion results, secondary vulcanized at 170 °C

Sample	Adhesion strength (kg/cm)
T0	31.5
T20	30.4
T40	29.8
T60	29.2
T80	29.2
T100	29.1

The association of adhesion between two layers on the primary vulcanization level of the middle and tread compound was similar in this case also. As the primary vulcanization level increases on each vulcanizate, the bonding strength between two-layers decreases. This is also expected, explained by the reduction in crosslinking ability (to make interlayer linkages) of each vulcanizate as primary vulcanization already complete a portion of linkages.

Sample H0/0 to H0/100, M0 configured with T0 to T100. H0/0 and H0/20 samples were failed from the middle compound and show very high adhesion strengths. As explained earlier middle failure surface nature is exhibited middle teared surface finish that gives an indication of moderately high bonding between two layers. The high crosslinking ability of zero-degree primary vulcanizate took advantage of these results. After the T40 interface failure, the adhesion strengths were not reached the acceptable level. Even though T100, M0 showed significant bonding strength similar to low secondary vulcanization results. As the pre vulcanization level increases, the ability to make interlayer linkages also decreases.

Sample L20/0 to L20/100 has a configuration of M20 with T0 to T100. Only H20/0 showed middle tearing that indicates adhesion strength between two layers over 23.6 kg/cm as explained early. However, H20/20 still showed a significant adhesion level, exceeding the acceptable level. The surface nature of the H20/20 sample is rough tearing which indicates good bonding between two layers. From the series after T40 adhesion levels showing a drastic drop which is followed by the nature of the surface. Samples followed the decrease in interfacial bonding ability with the increase of pre vulcanization level.

H40/0 to H40/100 samples, M40 configured with T0 to T100. No middle tearing occurred in these samples. H40/0 is the only sample that shows an acceptable bonding level. Surface nature was also acceptable as it showed rough treating at the interface. Bonding strength drastically has dropped after T0; interface surface nature has exhibited glossy matt finish indicating poor bonding between two surfaces. Interfacial bonding strength decreases with an increase in pre vulcanization level.

The H60/0 to H80/20 samples have shown very low adhesion strengths with no bonding between two compounds; none of them have exhibited an acceptable level of bonding strength. Even with zero-degree pre vulcanization level of tread vulcanizate, adhesion levels were very poor. This has suggested that the contribution of the middle layer primary vulcanization level is critical than the primary vulcanization level of the tread layer that is similar to the conclusion driven for secondary vulcanization temperature of 150 °C. An increase in pre vulcanization level of middle and tread layers decreases the strength of interfacial bonding strength. This could be due to loss of ability to further crosslink during secondary vulcanization as some of the linkages already formed within the pre vulcanizates during the primary vulcanization step.

4.3.3 Effect of secondary vulcanization temperature on M0 with different primary vulcanization level of tread layer

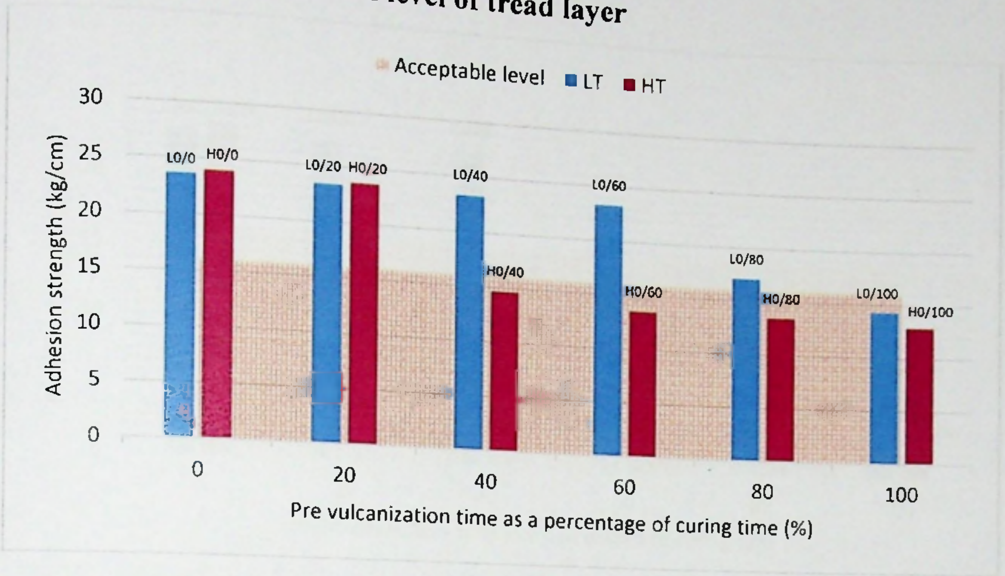

Figure 4.10 Adhesion results between M0 with different tread pre vulcanizates

The effect of secondary vulcanization temperature with different temperatures is presented above Figure 4.10. L0/0, H0/0 and L0/20, H0/20 shows similar adhesion levels in both temperatures. It was discussed previously that these failures occurred by middle tearing and it represents the low self-adhesion strengths of vulcanizates. Evaluation of self-adhesion has revealed that there is no influence of secondary vulcanization temperature on self-adhesion at a lower degree of primary vulcanization. (Table 4.6-Table 4.10). However, it was not possible to compare the adhesion strength of these samples because the failure occurred due to the middle layer tearing. The only possible comment made on this sample is that the adhesion strength of the two-layer interface is higher than the middle tear strength. After T40 it could be clearly stated that interfacial adhesion is always higher for lower primary vulcanization temperature than the secondary vulcanization temperature. Five acceptable samples were found in low-temperature samples whereas only 2 acceptable samples were found in high-temperature samples (Figure 4.10). This could be explained by the low crosslinking density at high-temperature curing [7]. Low linkages formed between two layers results in a reduction of interface bonding. [19]. At a low-temperature, the tread layer can be pre vulcanized up to 80%, while with high temperature it could go up to 20% maintaining the acceptable level of adhesion.

4.3.4 Effect of secondary vulcanization temperature on M20 with different primary vulcanization level of tread layer

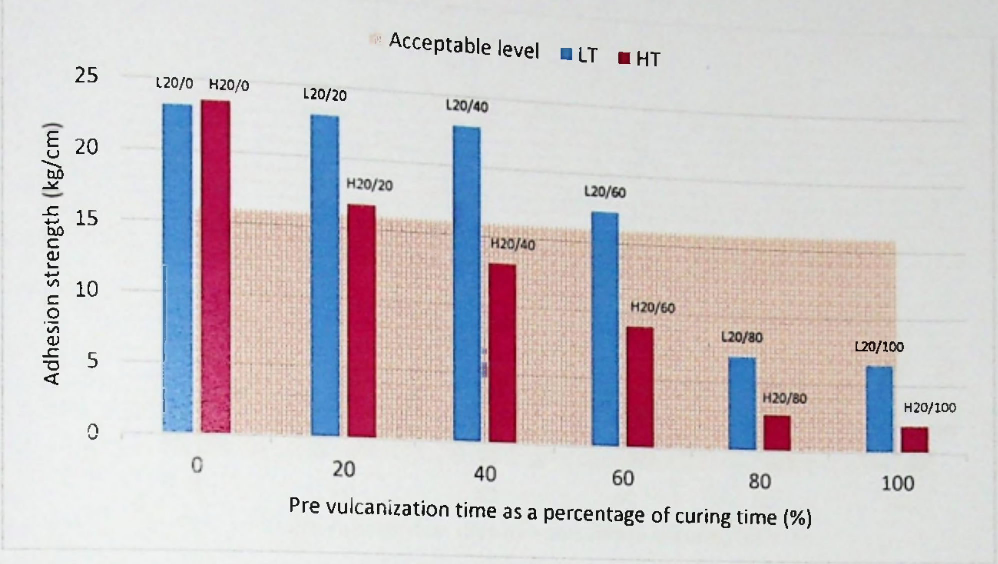

Figure 4.11 Adhesion results between M20 vs different tread pre vulcanizates

The effect of secondary vulcanization temperature on M20 and tread pre vulcanizates is presented in Figure 4.11. Similar to the M0 sample, when evaluated to identify the effect of secondary vulcanization temperature, the overall decrease in adhesion could be observed in high-temperature secondary vulcanization than in low temperature vulcanization. With an increment in secondary vulcanization temperatures, the samples reaching acceptable adhesion level was reduced from 4 to 2.

While maintaining the acceptable level of adhesion, low-temperature secondary vulcanization tread layer could be pre vulcanized up to 60% whereas at high temperature it could go up to 20% of pre vulcanization level. Drop in interfacial adhesion at high temperature could be explained by low crosslink density which reduces the bonding strength.

4.3.5 Effect of secondary vulcanization temperature on M40 with different primary vulcanization level of tread layer

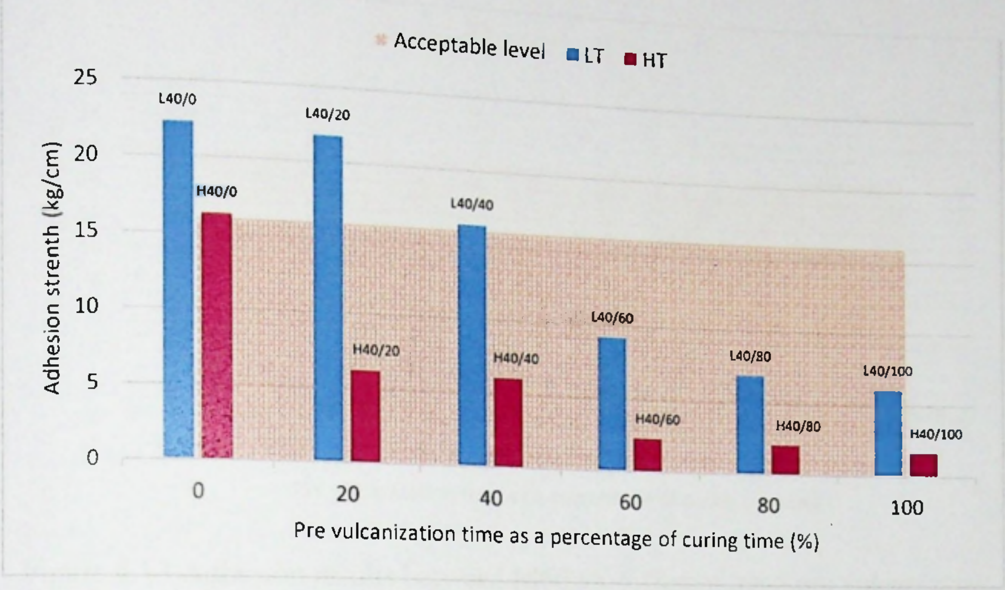

Figure 4.12 Adhesion results between M40 vs. different tread pre vulcanizates

Figure 4.12 shows adhesion results between M40 vs. different tread pre vulcanizates. The dependance of adhesion strength on vulcanization temperature is similar to the previous results. An acceptable level was reached by 3 and only one sample respectively at low and high secondary vulcanization levels. Two middle tearing has occurred at low temperature but no middle tearing was obsred at a high temperature. Low-temperature tread can pre-vulcanize up to 40% but at the high-temperature tread, the layer cannot exceed 0% in order to achieve an acceptable level of adhesion. Decrese in interlayer adhesion strength at high temperature was expected due to low crosslink density formed due to shorter curing time.

4.3.6 Effect of secondary vulcanization temperature on M60 with different primary vulcanization level of tread layer

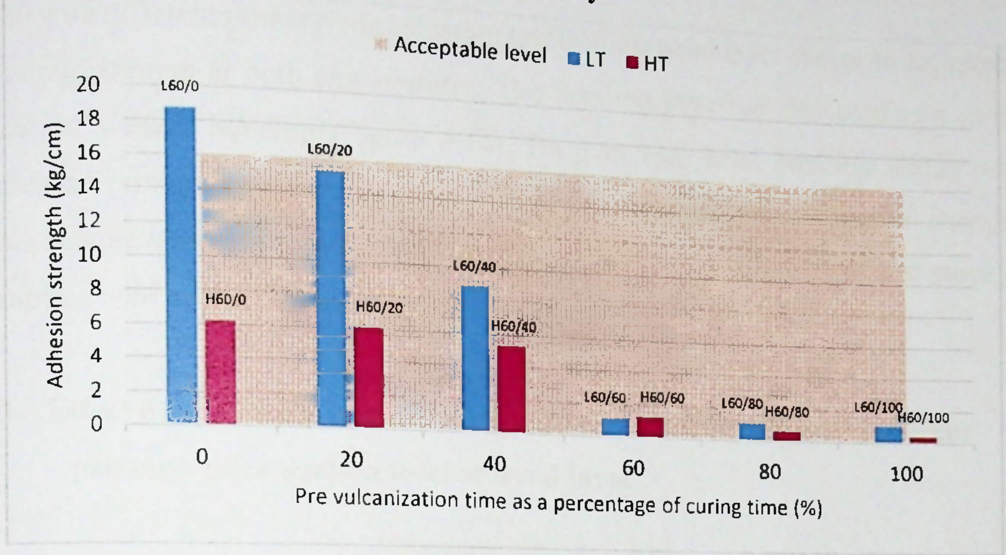

Figure 4.13 Adhesion results between M60 vs. different tread pre vulcanizates

Adhesion results between M60 vs. different tread pre vulcanizates presented in Figure 4.13. Only one sample at low temperature meets the acceptable adhesion level. For all samples, a lower adhesion strength was observed at a high temperature than at a low temperature. Low crosslink density could be affected by this behaviour.

4.3.7 Effect of secondary vulcanization temperature on M80 with different primary vulcanization level of tread layer

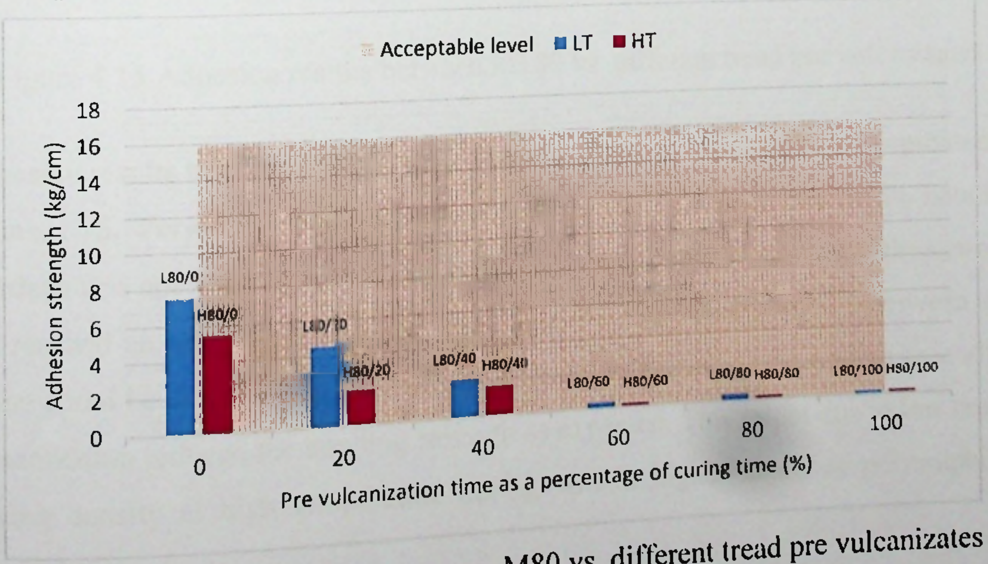

Figure 4.14 Adhesion results between M80 vs. different tread pre vulcanizates

M80 with different primary vulcanization levels of the tread layer shows no acceptable bonding strength at both temperatures. The bonding interface also conforms to the signs of weaker bonding (Figure 4.14). Drop in interfacial bonding ability with increased primary vulcanization levels could be affected for low adhesion strength. Each sample showed low adhesion strength at a high temperature similar to previous samples could be due to low crosslink density.

4.3.8 Effect of secondary vulcanization temperature on M100 with different primary vulcanization level of tread layer

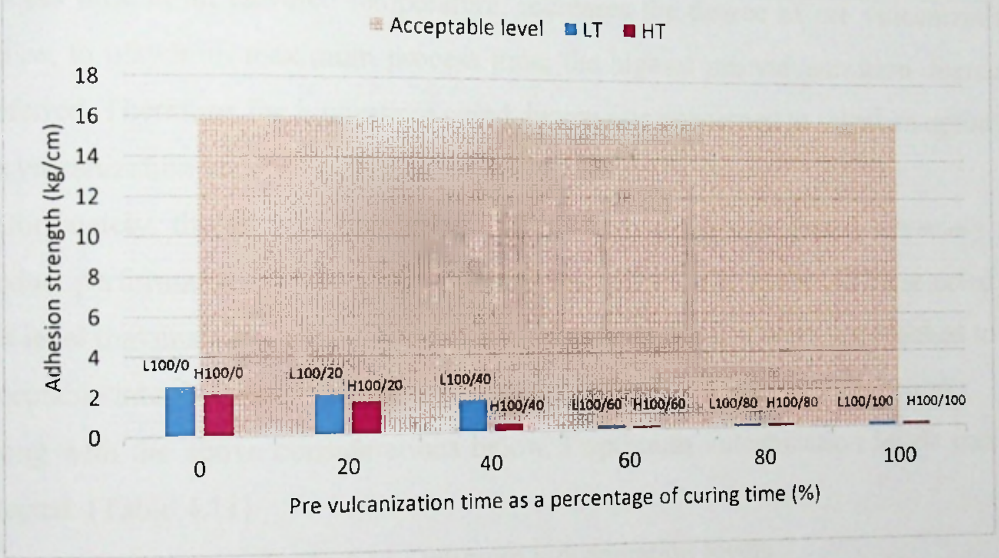

Figure 4.15 Adhesion results between M100 vs. different tread pre vulcanizates

Adhesion results between M100 vs. different tread pre vulcanizates were presented in Figure 4.15. Very weak bonding was observed. The surface nature of the bonding interface was not showing a chemical bond. In both temperatures, none of the samples has reached an acceptable adhesion level. The low interfacial adhesion between two layers could be due to a high pre vulcanization level. Elevated temperature secondary vulcanization reduced the bonding strength as expected. This might due to low cross-linking density at high temperature curing with a higher share of polysulphidic crosslink form.

4.4 Physical property evaluation of optimum vulcanizate samples

4.4.1 Selecting an optimum vulcanizate sample

The decision on selecting optimum primary vulcanization for tire manufacturing industry should follow a logical manner considering practical limitations associated with manufacturing conditions.

Typically, solid tire manufacturing engaged with high-temperature processing. Therefore, zero-degree primary vulcanizate candidates are inapplicable and excluded from the selection.

Extend of pre vulcanization at a given temperature is depend on processing time as explained in Section 3.3.2. In order to maintain high flexibility during green tire building, the longer process is desired. It was explained earlier that an increase in process time at an elevated temperature, increases the degree of pre vulcanization. Hence, to play with maximum process time, the highest pre vulcanization degree is preferred. Therefore, the highest pre cured degree was concerned to select an optimum pre vulcanization level.

Unfortunately, the state of pre-curing during tire building is affected adversely for product performances. Thus, a high primary vulcanization level should be selected up to a level that ensures acceptable adhesion level. Samples that were not reached to an acceptable interfacial bonding strength (16 kg/cm) excluded from the selection.

Along with the above considerations below 3 optimum vulcanization levels can be selected. (Table 4.11)

Table 4.11 Optimum vulcanization levels

Sample	Middle primary vulcanization %	Tread primary vulcanization %	Secondary vulcanization temperature (°C)	Adhesion strength (kg/cm)
L20/60	20	60	150	17.3
L40/40	40	40	150	16.4
H20/20	20	20	170	16.8

Three candidates were obtained that ensures adhesion strength and manufacturing expectations or limitations. These pre vulcanizates were further tested for selected physical properties.

4.4.2 Physical properties of optimum primary vulcanizate samples

The physical properties of optimum vulcanizates are presented in Table 4.12, Table 4.13 and Table 4.14. Reference for both middle and tread was selected as zero-degree primary vulcanizate for comparison of results. Secondary vulcanization temperature for reference samples was selected as 150 °C which is more similar to current production conditions.

Table 4.12 Physical properties of optimum primary vulcanizate configuration 1

	Ref(M)	M20(LT)	Ref(T)	T60(LT)
Tensile strength (MPa)	17.2	17.2	28.3	19.2
Tear strength (MPa)	5.7	5.8	6.4	5.1
300% Modulus (MPa)	8.6	8.5	13.2	14.8
Hardness (Shore A)	63	63	65	68

Table 4.13 Physical properties of optimum primary vulcanizate configuration 2

	Ref(M)	M40(LT)	Ref(T)	T40(LT)
Tensile strength (MPa)	17.2	15.4	28.3	20.7
Tear strength (MPa)	5.7	4.2	6.4	5.5
300% Modulus (MPa)	8.6	9.4	13.2	14.5
Hardness (Shore A)	63	65	65	67

Table 4.14 Physical properties of optimum primary vulcanizate configuration 3

	Ref(M)	M20(HT)	Ref(T)	T20(HT)
Tensile strength (MPa)	17.2	18.2	28.3	29.9
Tear strength (MPa)	5.7	6.3	6.4	6.6
300% Modulus (MPa)	8.6	7.4	13.2	12.0
Hardness (Shore A)	63	60.0	65	62.0

Due to the similarity of tensile and tear strengths of middle and tread vulcanizates, the results were discussed together. Tensile strength and tear strength of both middle and tread decreases with an increase in primary vulcanization level at 150 °C secondary vulcanization except M20. This is obviously due to an increase in crosslinking density with the conversion of polysulphidic form to monosulphidic form upon a longer curing time. Tensile and tear strength shows increment at secondary vulcanization of 170 °C. The higher tensile and tear strength at secondary vulcanization of 170 °C may be due to a larger concentration of polysulphidic crosslinks due to shorter curing time [13]. As expected, both hardness and modulus were increased with an increase in primary vulcanization level at secondary vulcanization of 150 °C, except at M20. These properties are directly related to crosslinking density [30]. Modulus and hardness were decreased at secondary vulcanization of 170 °C due to lower crosslink density. The influence of pre cure on M20 physical properties seems to be minimum, thought to be due to a lower level of primary vulcanization.

4.4.3 Influence of optimum primary vulcanizates on solid tire performance

As presented in Table 4.12 vulcanizate configuration 1 (L20/60) shows no influence of pre vulcanization on the middle compound which is satisfactory. Tread vulcanizate shows a significant decline in tensile and tear properties reference to 0% pre vulcanization level. In the application of a solid tire tensile and tear properties are very essential for a tread portion. Drop-in these properties could lead to a reduction in the tire life cycle. An increase in hardness and modulus increase the rigidity of the tire. Unlike pneumatic tires, a solid tire's shock absorption component is supported by the rubber. Due to an increase in hardness and modulus, it can lead to vibration issues during the operation. However, this should be confirmed by vibration testing because present results are insufficient to make such a conclusion.

In Table 4.13, the physical properties of configuration 2 (L40/40) are presented. In this configuration, both middle and tread vulcanizates show a drop in tensile and tear strength than the refence, but higher than configuration 1. Further, it is showing an increase in hardness and modulus. As discussed, drop-in tensile and tear strength is not expected since they are critical properties for the tread compound. The reduction of tensile and tear strengths in the middle compound also cannot be compromised. Under high load, severe shearing actions could be led to failure from the middle layer. Therefore, for product integrity, the middle compound also should be maintained at an acceptable tensile and tear strength. It is obvious that the increase in modulus and hardness can lead to vibration issues as explained earlier. But these performances should be conformed from the product level before making a conclusion. Hence, To select optimum pre vulcanization levels at secondary vulcanization temperature of 150 °C, both L20/60 and L40/40 are could be considered as disputable candidates. Configuration 1 (L20/60) middle layer showed higher tensile strength and lower hardness and modulus results than configuration 2 (L40/40). It is obvious that better tensile and tear performances are favourable for product performance under high shearing actions and deformations. Low modulus and hardness also support to increase rubber elasticity that will benefit with high comfortability. Therefore, the L20/60 sample middle compound showed promising performances than the L40/40 sample middle compound. Tread layer physical properties of L20/60 and L40/40 samples also compared. The L40/40 sample tread layer exhibits higher tensile and tearing performances with slightly lower hardness and modulus than the L20/60 sample tread layer. Since the tread layer of a solid tire subjected to tearing and tensile actions severely during the application higher tensile and tearing performance is more critical for a thread layer than the middle layer. Hence criticality of tearing and tensile properties on the middle and tread layer suggested that candidate 2 (L40/40) is more favourable for solid tire application than candidate 1 (L20/60). Therefore, M40 and T40 could be considered as the optimum pre vulcanization level at secondary vulcanization temperature of 150 °C.

Table 4.14 presents the physical properties of configuration 3 (H20/20). This is the obvious optimum pre vulcanization level at secondary vulcanization of 170 °C temperature selected from previously explained criteria. In this case, both middle and tread compounds have shown a higher tensile and tear properties than the reference values and other two candidates. This is a preferred situation that the tread compound exhibits high tensile and tear performance while the middle compound also shows improved performance. Especially in the application during high shearing actions action on a solid tire these properties are essential to perform a longer life cycle. Further, the lower level of modulus and hardness than both the references and the rest of the two candidates also favourable. The shock-absorbing ability of the solid tire could be supported by this compound performance. Nevertheless, with very low modulus level can increase the deflection of the tire under load. That can lead to a reduction of ground clearance of the vehicle. As suggested previously also this should be confirmed from the product level.

Based on middle-tread adhesion results and physical properties it could be concluded that optimum primary vulcanizates combination is M20 vs. T20.

Table 4.15 Pre vulcanization time of optimum pre vulcanizates

Sample name	Primary vulcanization time (minutes)
M20	15.9
T20	17.7

Concluded optimum pre vulcanization at a temperature of 100 °C is proposed that the processing time of the middle and tread layer respectively 15.9 mins and 17.7 mins (Table 4.15). This time included compound warming time, green tire building time and all idle time until insert in to the mould. Even though it seems proposed process times are a challengeable target when compare with common solid tire manufacturing locations, this is an ideal proposal to an efficient production line. The proposed secondary vulcanization temperature (curing mould temperature) is 170 °C will benefit with shorter curing time that could increase production efficiency. Maintain the green tire temperature around 100 °C at mould inserting step also vital to shorten the curing cycle. In order to do that production line arrangement, time for different activities should be optimized. Therefore, for the efficient production line above mentioned (Table 4.15) process times are realistic.

It is obvious that the gap between green tire temperature and mould temperature is around 70 °C. This permits massive expansion of the green tire compound with absorbed temperature from the mould after moulding. Since a solid tire is a thick rubber profile and poor heat conductibility of rubber this expansion can continue for a significant time that can complete the vulcanization of tire surface. Breaking the vulcanized surface by expanded rubber flow is known as a backrinding defect in the tire industry. The possibility of backrinding on manufacturing set-up under the proposed condition would be an interesting study. But, backrinding could be avoided by controlling the flash level of the green tire, the number of bumping cycles, mould closing pressure or with mould design approaches.

In this study, the pre vulcanization temperature was assumed as constant over total process time. A similar study can be extended by investigating practical thermal history that compound subjected over the processing time. Further studies also could be carried out by changing the pre vulcanization temperatures and secondary vulcanization temperatures.

5. CONCLUSION AND RECOMMENDATION

Adhesion between two solid tire compounds were studied at various pre cure levels of each compound and temperatures of secondary vulcanization, using adhesion test (peeling test) to analyse the bonding strength of typical middle and tread compound layers.

It was found, an increase in secondary vulcanization temperature has decreased the adhesion between two layers. In conclusion, following relationships were observed between middle and tread layer pre vulcanization levels and secondary vulcanization temperatures: to develop an acceptable level of bonding;

(i). at 0% pre vulcanization of middle layer, the tread layer could pre vulcanized up to 80% at secondary vulcanizing temperature of 150 °C and up to 20% at 170 °C.

(ii). at 20% pre vulcanization of middle layer, the tread layer could pre vulcanized up to 60% and 20% at secondary vulcanization temperature of 150 °C and 170 °C respectively.

(iii). at 40% pre vulcanized middle layer, tread layer could pre vulcanized up to 40% at secondary vulcanization temperature of 150 °C. However, at secondary vulcanization temperature of 170 °C the tread layer did show acceptable bonding strength only at 0% degree of pre vulcanization.

(iv). At 60% pre vulcanized middle layer made acceptable bonding only with 0% pre vulcanized tread layer at secondary vulcanization temperature of 150 °C. However, acceptable bonding strength was not found at any pre vulcanization degree at 170 °C of secondary vulcanization temperature.

(v). Above 80% level of middle layer pre vulcanization, acceptable bonding was not found at neither 150 °C nor 170 °C of secondary vulcanization temperature.

Based on inter layer adhesion level, physical properties, manufacturing limitations and preferences it could define an optimum pre vulcanization level to each secondary vulcanization temperatures. Therefore, in conclusion, 40% of middle layer and tread layer pre vulcanization levels could be suggested as optimum pre vulcanization level at secondary vulcanization temperature of 150 °C.

If secondary vulcanization temperature is 170 °C, 20% of middle layer and tread layer pre vulcanization levels could be suggested as optimum pre vulcanization levels. Out of 150 °C and 170 °C secondary vulcanization temperatures, 170 °C, 20% of middle layer and tread layer pre vulcanization levels could suggested as the optimum pre vulcanization level.

Recommendations

- Investigate the influence of pre cure on other properties of middle and tread layer
  E.g. – abrasion resistance, heat build-up, fatigue performances, etc.
- Investigate production capability of maintaining concluded optimum pre cure levels
- Investigate optimum pre cure level of M0 to M40 middle pre cure range with a combination of T0 to T40 tread pre cure range that ensures the expected properties at secondary vulcanization temperature of 170 °C.
- Extend the study by subjecting the actual thermal history for the compound in production conditions.
- Build a tire with optimum pre vulcanization level to see the influence of product performance.

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