# **PREDICTION OF THERMAL CONDUCTIVITY OF NATURAL RUBBER COMPOUND FILLED WITH CARBON BLACK AND GRAPHITE**

E.A. Prabuddha Rangika Batuwatte

(158502C)

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Department of Chemical and Process Engineering

University of Moratuwa

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#### **DECLARATION**

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\_ \_

The above candidate has carried out research for the Master's thesis dissertation under my supervision

Name of the supervisor

Dr. Olga Gunapala

Signature of the supervisor: Date: 28/02/2020

## **DEDICATION**

<span id="page-2-0"></span>I would like to dedicate this thesis to my ever loving my family members, my father, mother, little sister, my wife, and my beloved son who lives among the stars right now.

Your loving kindness and unconditional support made me the best I can be! .

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#### **ABSTRACT**

<span id="page-4-0"></span>Rubbers and rubber composites are a vital materials category that has been used in multiple applications in the present day. Improving their characteristics, properties can make rubber material much more versatile in their performance at economically.

Improving the thermal conductivity (TC) of rubber composite is relevant to many aspects. Heat dissipation, heat build-up, curing, manufacturing, and product performance is directly and indirectly affected by the TC of a compound. In this research work, time – temperature data obtained by transient plane source (TPS) method was analysed to obtain TC of natural rubber (NR) and carbon black (CB) rubber compounds with added graphite. TCs were also obtained by two emphirical models Lewis – Nielson model and Hashin – Shtrikman model for the same samples.

Four rubber samples were used with varying graphite content from 0 phr (control), 5 phr, 10 phr and 15 phr. From the empirical modelling, modified Lewis-Nielson model (LN model) resulted thermal conductivities of  $(Wm^{-1}K^{-1})$  0.1618, 0.1736, 0.1858 and 0.1983 and Hashin-Shtrikman model (HS model) resulted 0.1619, 0.1655, 0.1688 and 0.1718 for 0 phr (control), 5 phr, 10 phr and 15 phr graphite added samples. For the same respective samples, TPS analysis TCs were obtained as  $(Wm^{-1}K^{-1})$  of 0.1462, 0.1495, 0.1545 and 0.1725. All graphite added rubber samples demonstrated an increase in TC over the control sample (0 phr Gr sample).

In order to further minimise the difference between the TPS results and the empirically model values, a mulplier correction factor was introduced to each model. Minimise the sum of the squared of the errors were set to zero and the multiplier correction factors were obtained for each model as  $\lambda_{\text{HS}} = 0.932$  and  $\lambda_{\text{LN}} = 0.864$  for HS model and LN model respectively. Predicted TC values from both optimised LN model and HS model reduced its percentage difference between TPS analysed values to less than 5% except the 15 phr Gr sample'sTC resulted from HS model which had a 7.10% difference after optimisation.

In order to increase the accuracy of the complex calculations and to improve the sensitivity it is recommended to use powerful mathematical software programs.

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Further improvement of the thermal conductivity can be potentially achieved by functionalisation of the graphite particles, decreasing the particle size and its distribution, which gives further future aspects for research. In depth, optimisation and detailed handling of parameters would be beneficial for the accuracy but at the same time this would compromise the time consumption and the simplicity of the computation method followed.

Using the optimised empirical models proposed in this study, TC can be reasonably estimated for NR and CB rubber compounds with added graphite. This understanding would definitely benefit the solid rubber industry

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## **LIST OF ABBREVIATIONS**

- <span id="page-10-0"></span>1. NR – Natural rubber
- 2. CB Carbon black
- 3. TC Thermal conductivity
- 4. Gr Graphite
- 5. phr Parts per 100 rubber parts
- 6. GRG General rubber goods
- 7. ETC Effective thermal conductivity
- 8. TPS Transient plane source

## **LIST OF APPENDICES**

<span id="page-11-0"></span>Appendix A: Calculation of the D  $(\tau)$  Dimensionless Specific Time Function

Appendix B: Values Obtained for D  $(\tau)$  Dimensionless Specific Time Function

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### **1 CHAPTER 1: REASEARCH INTRODUCTION**

#### <span id="page-12-1"></span><span id="page-12-0"></span>**1.1 Background**

Rubbers are one of the most widely used categories of materials in the world today, which have become an essential class of materials. We as consumers come across rubbers in many formats and versions in a daily basis.

Rubber is an engineering material due to its unique property including elasticity. Rubber molecules are long chain like and flexible, which allow them to perform fast molecular movements under applied force by deforming, and as soon as the applied forces is removed rubbers can return back to its original state. This important characteristic in rubbers has wide range of applications in industry, transportation, construction, aerospace etc.[1]



**World Rubber Production** 

*Figure 1-1: Global rubber production from 2002 to 2018*

*Source:[2]*

<span id="page-12-2"></span>World rubber production has been increasing steadily after 2009 as per [Figure 1-1a](#page-12-2)bove. Rubbers are classified as natural and synthetic rubber based on their source. Natural rubber (NR) is a product extracted from the sap of *Hevea Brasillensis,* which contains polyisoprene, which is the main polymer in NR. Synthetic rubbers are man-made rubbers that are byproducts from the petroleum sources which are then chemically treated and refined. SBR EPDM, BR, CR, NBR, etc. are some of the widely used synthetic rubbers in the industry with various properties and suitability for different applications.

#### <span id="page-13-0"></span>**1.2 Application of Rubber and Rubber Composites**

More than 50% of the global production of both natural and synthetic rubber is used in tire industry, which is by far the most dominant rubber consuming industrial segment [3]. Similarly, 65% of the NR produced is used in the tire industry as depicted in [Figure 1-2](#page-13-1) below.



*Figure 1-2: Distribution of the world natural rubber applications Source: [4]*

<span id="page-13-1"></span>Tire manufacturing is a very complex process, which consists of multiple steps. Final product needs to fulfil the needs of the application and requires to meet the market demands to survive the competition in the industry.

A considerable amount of attention has been attracted in the industry on alternative material compounding and combinations to further improve the performance of the tire or find materials that are more economical options, which are more economically viable. Also to reduce the energy consumption and increase the efficiency in the manufacturing process of tires.

#### <span id="page-14-0"></span>**1.3 Research Objectives**

Following are the objectives of the current study

- 1. Analyse time temperature transient plane source (TPS) data published Gunasekara, et al.(2018) which was conducted by Bogala Graphite Lanka PLC, Bogala Mines, Aruggammana Sri Lanka to obtain thermal conductivity values of the Natural Rubber /Carbon Black/Graphite (NR/CB/Gr) rubber composites with varying graphite content
- 2. Compare and check validity of thermal conductivity values of the rubber composites received by TPS analysis against the empirically modelled and predicted thermal conductivities.
- 3. Propose optimisations to the empirical models to predict NR/CB/Gr filler rubber composites thermal conductivity with high precision.

Developing a modified and optimised empirical model to predict and estimate the thermal conductivity (TC) of thick solid rubbers with optimum volume ratio of fillers reduce the moulding cycle of the solid rubber manufacturing process which reduces the energy consumption as well as the cost reduction.

#### <span id="page-14-1"></span>**1.4 Rationale of the Study**

Addition of graphite (Gr) to Natural rubber (NR) and Carbon black (CB) can potentially increase the TC of the rubber composite. The optimum volume ratio of the Gr with the CB and bulk rubber matrix depends on multiple factors such as the filler morphology, shape, particle size, concentration, interaction of the particles and matrix[5]. In addition, the processing method of the fillers utilised also affect the final anticipated TC.

By optimising, an existing empirical model for the specific work done on the subject considering the factors affecting and allows estimate the TC of the composite with high accuracy and reliability.

#### <span id="page-14-2"></span>**1.5 Significance of the Research**

Increasing the TC of the rubber composites will lead to a significant energy consumption reduction resulting a much more economical manufacturing process. Mainly a higher TC means the heating time, vulcanisation time and cooling time would be shorter which are significant energy consuming and time consuming steps in solid rubber manufacturing process. Efficient reduction of processing time and energy saving certainly increase the profitability of the solid rubber manufacturing process.

An optimised empirical model to predict the TC of rubber composites will lay a credible foundation to develop novel rubber composites for targeted applications as well as other branched research variants and derivations of the constituents. This will cut-down and simplify the experimental validation as well as contribute to the inherited knowledge on the subject. Also the modelling scheme can be integrated to present day research to establish novel effective compounding recipes and composites

#### <span id="page-15-0"></span>**1.6 Chapter Organisation**

#### **Chapter 1: Research Introduction**

This chapter provides a brief introduction and background on the rubber industry and applications of rubber in the present day. Objective of this research are then introduced. Rationale and significance of this research describes the contribution of this research to the current knowledge base on the subject and why this research is required.

#### **Chapter 2: Literature Review**

The present day relevant subject knowledge on the rubber composites and their respective TCs are discussed extensively in this chapter. Laying a foundation on the research is the prime objective of this chapter. Filler type, their characteristics and empirical models available to predict the TC of the rubber composites are discussed and the knowledge gap on the subject is clearly identified by this chapter.

#### **Chapter 3: Methodology**

Third chapter describes the method followed in this research to obtain results. There are mainly two components in this section which are the experimental analysis part and empirical modelling part.

#### **Chapter 4: Results and Discussion**

The results obtained are presented, analysed and critically commented compared with the similar work done on the matter. Explanations and justifications are discussed extensively.

#### **Chapter 5: Conclusion**

Based on the observations and discussion, comments have been presented on this chapter where conclusions are made and how well the research objectives are achieved. Also points and suggestion are included in the chapter for future related work to proceed.

#### **Chapter 6: Future Research**

Based on the knowledge gained, future research directions are which could enhance and reinforce the subject matter are proposed in this chapter.

### **2 CHAPTER 2: LITERATURE REVIEW**

#### <span id="page-17-1"></span><span id="page-17-0"></span>**2.1 Rubber Materials and Compounding**

Rubber compounds are made up of numerous different polymers, different types of fillers, chemicals, and minerals allowing and facilitating the vulcanisation. Depending on the application, other required materials are added to the rubber formulations.

Rubber can be either extracted from the rubber tree as natural rubber latex or otherwise chemically synthesised by using the raw materials received from the petroleum industry. These petroleum crude oil by-products undergo chemical refining processes to obtain different types of synthetic rubbers.

Rubbers have long molecular chains and these chains are made of the same repeating units known as a monomer. The selection of monomers, polymerisation technique and architecture of the backbone of the polymer are vital features which determine the properties of the final rubber product.

#### <span id="page-17-2"></span>**2.1.1 Typical Constituents of A Rubber Formulation**

Rubber formulation is the process of adding specific chemicals to raw rubber to achieve certain properties. The specific chemicals and type of chemicals depend on the specific type of rubber being used and the intended application of the final rubber product.

Typically, a rubber formulation can be divided into 5 main components as below.

- 1. Elastomer
- 2. Filler
- 3. Protectants
- 4. Processing aid
- 5. Curing system

Elastomer is the main rubber component which is suited for the intended application with the desired properties. Different type of rubbers will be best suited for certain applications. Fillers are added to the rubber compounding as a reinforcement or an economical aid for rubber. Carbon black, silica, clay etc. are widely used fillers in the rubber industry. Protectants can e antioxidants, anti-ozonants, waxes,etc. which assist to create a physical barrier to improve the performance. The fourth component is the processing aid which helps to support the processing and handling of the rubber manufacturing process Typical processing aids are oils which adds moisture and lubrication to the compound otherwise would have been dry and difficult to mix. The most important component of the rubber compounding is the curing system. The process involves of cross linkages between the polymer chains with each other and with fillers. Also the curing process reduce hysteresis by maintaining an acceptable level in terms of elongation at break.[6]. There are two main types of curing systems in the industry, which are sulphur curing and peroxide curing. Accelerators are also related to the curing system, which upon addition it shortens the curing time.

<span id="page-18-1"></span>Typical rubber formulation recipe is given below in [Table 2-1.](#page-18-1)

Ingredient	phr	
Elastomer	100	
Curing system	$\overline{5-15}$	
Anti-degradants	$0 - 7$	
Coupling agents	$0 - 2$	
Oils/Plasticizers	$0 - 250$	
<b>Fillers</b>	20-400	
<b>Special additives</b>		
Process aids	$0 - 20$	
Peptisers	$0 - 3$	
Mill release	$0 - 10$	
Flame retardants	$0 - 300$	
Smoke suppressants	$0 - 20$	
<b>Tacktifiers</b>	$0 - 30$	
Pigment and dyes	$0 - 6$	
Bonding agents	$0 - 20$	
Antistatic agents	$0 - 4$	
Odorants	$0 - 2$	
<b>Blowing agents</b>	$0 - 20$	

**Table 2-1: Common ingredients and concentration of rubber formulation**



#### <span id="page-18-0"></span>**2.1.2 Natural Rubber (NR)**

Due to its unique chemical and physical properties, NR is a very resourceful raw material used in solid rubber industry mainly and as latex in the lesser extent. As rubber a very poor

conductor of heat, heat build-up in the tire is a major concern in the tire industry. [3]. Low heat build-up, high mechanical strength, high elasticity, outstanding tack and green strength are some highly qualifying properties of NR for its high utilisation in tire manufacturing. [8]



*Figure 2-1: Natural rubber polymer structure (poly-cis-1,4-isoprene ) Source: [3]*

<span id="page-19-1"></span>Typical average molecular weight of the polyisoprene in NR ranges from 200,000 to 400,000 g.mol<sup>-1</sup> with a relatively wider molecular weight distribution. This accounts for about 3000 to 5000 isoprene units per polymer chain.[3]. As result high molar mass, molecular weight distribution and overlap density, NR has an outstanding processing behaviour with the following advantages over its synthetic counter parts.[6]

- High elasticity
- Strain-induced crystallisation
- Low heat build-up at high temperatures
- Higher tack and high green strength

#### <span id="page-19-0"></span>**2.2 Fillers**

Using of fillers in the rubber industry holds an utmost importance to achieve the desired properties of the vulcanised rubber after the vulcanisation of the rubber itself. Filler loading to the compound is typically 10-15 times higher than the other chemical additives used in rubber compounding. Fillers mainly contribute to the reinforcement characteristics, processing behaviour and final price of the material. [9]. However, fillers also tend to deliver specific effects on the final elastomer, which is the determining factor.

Reinforcing filler is a particulate material that is able to increase the tensile strength, tear resistance, hardness, and modulus and abrasion resistance of natural or synthetic rubber. Carbon black and silica fillers are widely used in the tire industry where its reinforcement function performed in the tire tread compounding is a crucial factor, which affects the performance of the tire.[10]. Reinforcing potential of the filler is affected by the particle size, surface area , structure and surface chemistry. [8]. Semi-reinforcing filler is a particulate

material that is able to moderately improve the tensile strength and tear strength, but does not improve the abrasion resistance. Non-reinforcing filler does not provide any increase on these properties and it only functions as a diluents to reduce the cost without affecting the reinforcing potential. Typical non-reinforcing fillers are soft clays, barites, and talc. [8].

Other typical classifications of fillers would be based on the colour, source and shape.



<span id="page-20-3"></span>*Figure 2-2: Classification of fillers considering the function and typical particle reference Source: [10]*

#### <span id="page-20-0"></span>**2.2.1 Important Filler Properties**

Several filler characteristics influence the filler performance. They are particle size, surface area, structure, and surface activity.[11]

#### **2.2.1.1 Particle Size**

<span id="page-20-1"></span>Depending on the particle size of the filler the effective surface area available to make a contact differ. [12] In order to avoid areas of localised stress leading to rupture of polymer chains the filler particle size should be within the distance between the polymer inter-chains and therefore the particle sizes above  $10^4$ nm must be avoided to effectively harness the full contribution from the filler particles.[11]

#### **2.2.1.2 Surface Area**

<span id="page-20-2"></span>Fillers with higher surface area probabilistically have a higher chance to have a higher contact area to bond with the polymer matrix, which increases the reinforcement function of the fillers. In addition, the shape of the filler influences the surface area available to bond. [11]

#### **2.2.1.3 Surface Activity**

<span id="page-21-0"></span>Filler –filler interaction and filler – elastomer interaction is largely influence by the surface activity of the filler particles. Filler – elastomer interface depends on the chemical and physical nature and the compatibility of the two components. Chemical compatibility is the driving force that induces the reaction between the elastomer and the active sites on the filler surface.<sup>[11]</sup>

### <span id="page-21-1"></span>**2.2.2 Carbon Black (CB) as a Filler**

This is one of the most widely used fillers in the industry due to its low cost and abundant supply.[13]. Known as the commercial powder form of the carbon, it possesses extreme fineness, chemical stability, and high surface area. About 90% of the all CB is used as reinforcement and only 10% used for pigments.

CB is superior to other materials such as graphite, diamond and nickel particles, and carbon filaments in providing thermal pastes of high performance. [14]. Among the other fillers, CB has various advantages due to its low density, high surface areas, good electrical conductivity, and high chemical stability.[15].

It was understood that CB varieties had great effects on physical and chemical interaction of filler and rubber matrix dues to the different structure.[16]. Li, et al., [17] discusses that minds of CB and they showed the surface area of CB playing a major role in making physical cross-linking in the monomer as the surface area increases the number of rubber chains entangling with CB aggregates as well as that of the cross-linking increases.

<span id="page-22-1"></span>

#### **Table 2-2: Classification of CB**

#### *Thermal decomposition*



#### <span id="page-22-0"></span>**2.3 Thermal Conductivity(TC)**

Thermal conductivity (TC) is defined as the rate at which heat is transferred by conduction through a unit cross section area. Due to the comprehensive applications, thermally conductive polymer composites have attracted significant attention in the industry. High TC is desirable in order for heat to be efficiently dissipated in which the operating temperature can be kept low, avoiding dielectric failures due to overheating and heat accumulation in the polymer composite.[19]. Polymers exhibit a low TC because of their relatively low atomic density, weak interactions, chemical bonding, and complex crystal structure in their molecular vibrations.[20]

#### <span id="page-23-0"></span>**2.3.1 Heat Conduction Mechanism in Polymers and Polymer Composites**

Phonon transport is the main mechanism of heat conduction in most polymers where they transfer heat energy through interactions with each other and with subatomic particles.[21]. Over the past two decades, with a better understanding of the fundamental heat transfer process at the micro, nano and even molecular scales, there have been significant efforts devoting to enhancing the thermal conductivity of polymers and polymer composites which expected to enable a broader range of applications.<sup>[22]</sup>

TC of bulk polymers are usually very low and in the order of 0.1-0.5  $Wm^{-1}K^{-1}$  which is due to the complex morphology of polymer chains.[23]. A crystalline structure in a polymer where the polymer chains are aligned and arranged systematically and amorphous structure where the polymer chains are entangled are given in [Figure 2-3](#page-23-2) below. Polymer chain alignment, structure of the chains including the backbone bonds and side chains and interchange coupling also affects the TC of a polymer.[24]



<span id="page-23-2"></span>*Figure 2-3: Schematic diagram of a polymer (a) crystalline and amorphous structure of a polymer (b) structure of a polymer chain Source: [22]*

#### <span id="page-23-1"></span>**2.3.2 Thermal Conductivity of Polymer Composites**

It has been identified that the most effective way to increase the TC is to include additional high thermally conductive fillers into the polymer composite matrix [25, 13, 19, 24]. Traditionally the TC in polymer composite is enhanced by the addition of thermally conductive fillers including graphite, CB, carbon fibres, ceramic or metal particles.[26]

TC of fillers is primarily determined be the way how the heat transfer occurs through the filler particles [27]. Typical thermal conductivity of the fillers are given below in [Table 2-3](#page-24-1) and it can be seen that the carbon based fillers tend to present in the high thermal conductivity range.

<b>Filler</b>	Category	<b>Thermal conductivity</b> (W/(m.K))
Aluminium	Metal	234
Copper	Metal	386
Carbon nanotube (CNT)	Carbon	1000-4000
Carbon fibre	Carbon	300-1000
Graphene	Carbon	2000-6000
Graphite	Carbon	100-400
Beta-Silicone Nitride	Ceramics	103-200
Aluminium Nitride	Ceramics	100-300

<span id="page-24-1"></span>**Table 2-3: Thermal conductivities of typical thermally conductive fillers Source: [28]**

Samsudin, et al. [27]concluded that the higher filler loadings ( Upto 70%) are normally required to attain suitable values of TC in thermally conductive polymer composites which leads to a significant processing challenge. Polymer processing operating such as extrusion and injectioin moulding is most of the time limited by the quantity of fillers in the formulation and thus efficiency of TC is a significant factor. [29]. Propeties like the maximum packing fraction of a filler imposes considerable concerns to materials ability to dissipate heat rapidly and successfully.

### <span id="page-24-0"></span>**2.3.3 Thermal Conductivity and Hybrid Fillers**

Samsudin, et al. [27]provides a summary of results found in the literature with references of hybrid fillers used in polymer composites which increased TC.King, et al. (2008) also reported a positive synergistic effect on the TC of composite when different fillers are combined in the same composite. Samsudin, et al.[27]credited hybrid filler systems for their ability to increa the packing density , lowering the system viscosity as well as with increasing TC. Also the advantage of tailoring the adding different types of fillers with different sizes,

shapes, types and dimensions as 1D, 2D and 3D into the polymer based composites Samsudin, et al. [27]recognises as added advantages.

It can be seen that the inclusion of different types fillers such as CNT, graphene , inorganic fillers in epoxy materials mainly and filler fraction varies upto 50%. The final hybrid composite thermal conductivity is has been improved compared to the polymer composite.

#### <span id="page-25-0"></span>**2.3.4 Factors Affecting Thermal Conductivity in Polymer Composites**

TC of polymer composites significantly depends on the properties and characteristics of the fillers.

- Filler volume fraction
- TC of the filler
- Filler size, shape and spatial arrangement
- Interfacial thermal resistance (ITR)
- Agglomerated state of filler into the matrix

### <span id="page-25-1"></span>**2.4 Empirical Prediction of Thermal Conductivity of Polymer Composites**

Tsekemes, et al., [19]discusses the difficulty in comparison of TC of different polymer composites due to their different manufacturing processes followed by the reseachers. Even a comparison between the same materials and fillers would not be meaningful as properties like crystal structure, size and shape are different.

In polymers debye kinetic equation is usually used for theoritical prediction of TC.

$$
k = \frac{C_P v \lambda}{3}
$$
 Equation 2-1

Where

 $C_P$  = Specifi heat capacity per unit volume

 $v =$  Average velocity of a phonon

 $\lambda$  = Phonon mean fresss path

(Average distance that a phonon travels between two collisions)

Furthermore there are widely studied many theoritical and emphirical models predicting TC of polymer composites. Ngo & Byon C [30]provides a concise collection on well-known models which are given in [Table 2-4](#page-26-0) below.

<span id="page-26-0"></span>

## **Table 2-4: Well-known models for predicting TC**

**Source: [30]**

The following common nomenclature has been used in the models.

 $k<sub>eff</sub>$  = Effective thermal conductivity (ETC) of the composite material

 $k_m$  = TC of the matrix material ( Continous phase)

 $k_p = TC$  of the filler material (Dispersed phase)

 $\phi$  = Volume fraction of the filler

Selected models of the TC predictive models are discussed in brief below.

#### <span id="page-27-0"></span>**2.4.1 Maxwell model**

This model provides an analytical solution to the effective conductivity of a heterogenic medium. The model assumes that spherical particles are embedded in a continuous matrix in small enough volume fractions that the spheres are significantly far apart from each other in respect to their size.[31]

$$
k_{eff}=k_m\,\tfrac{k_f+2k_m+2\varphi(k_f-k_m)}{k_f+2k_m-\varphi(k_f-k_m)}\quad \text{Equation 2-2}
$$



*Figure 2-4: Maxwell model for dilute concentration of spherical filler particles in a matrix Source: [32]*

<span id="page-27-2"></span>There have been multiple modifications to the basic model including effect of filler particle size, shape, interfacial thermal resistance and more than one type of filler the host material.[33]. Almost all the models carry a common aspect that models are accurate only at lower level volume fractions up to about 25%.[32]

#### <span id="page-27-1"></span>**2.4.2 Rayleigh Model**

Rayleigh model considered the spherical particles to be arranged in a simple cubic array in the polymer matrix where the thermal interaction between the particles had been taken into consideration opposed to the Maxwell model. Pietrak & Wisniewski [32]suggests that results from both models are the same and significantly deviates from reality for higher volume factors.



<span id="page-28-1"></span>*Figure 2-5: Rayleigh model for cubic (a) and cylindrical (b) filler arrangement in a matrix Source: [32]*

Pietrak & Wisniewski [32] credits Rayleigh's contribution considering continuous matrix parallel cylindrical fibres, which acts as reinforcing fillers arranged, in a uniaxial simple cubic array.

$$
\frac{k_{\text{eff,ZZ}}}{k_m} = 1 + \frac{(k_f - k_m)}{k_m} \phi \quad \text{Equation 2-3}
$$

$$
\frac{k_{\text{eff,xx}}}{k_m} = \frac{k_{\text{eff,yy}}}{k_m} = 1 + \frac{2\phi}{C_1 - \phi + C_2(0.31\phi^4 + 0.01\phi^8 + ...)}
$$
 Equation 2-4  
Where  $C_1 = \frac{k_1 + k_m}{k_1 - k_m}$  and  $C_2 = \frac{k_1 - k_m}{k_1 + k_m}$ 

#### <span id="page-28-0"></span>**2.4.3 The Lewis-Nielson Model**

This empirical model is one of the most widely used models in the literature on the subject and provides credible results even though it does not include the interfacial thermal resistance (ITR) for filler volume fractions up to 40%. [32].

The simplicity and the coverage of the model make it convenient to be utilised for a wide range of particle shapes and composite matrix geometries. The following equations are developed from this model.

$$
k_{eff} = \frac{1 + AB \phi}{1 - B \psi \phi}
$$
 Equation 2-5

Where

$$
B = \begin{pmatrix} k_{1}/_{k_{m}} - 1 \\ \overline{k_{1}}/_{k_{m}} + A \end{pmatrix}
$$
 Equation 2-6

"A" is the shape factor for common filler types which is given as below [Table 2-5](#page-29-0)

<span id="page-29-0"></span>



$$
\psi = 1 + \left(\frac{1 - \varphi_m}{\varphi_m^2}\right) \phi \qquad \text{Equation 2-7}
$$

<span id="page-29-1"></span> $\varphi_m$  = Maximum filler volume fraction (As per [Table 2-6](#page-29-1) below)

## **Table 2-6: Maximum packing fractions for different arrangements Source:[34]**



#### <span id="page-30-0"></span>**2.5 Transient Plain Source Method**

Transient plane source method (TPS) which is also known as hot disc method relies on a plane element, which acts as both a temperature sensor as well as a heat source. This element consists of an electrically conductive plate of thin nickel foil  $(10\mu m)$  in spiral shaped, embedded in an insulating layer usually made of Kapton<sup>®</sup> which is about 60  $\mu$ m thick.[35] The TPS element is located between two disc shape samples with both sensor faces in contact with two of the same sample faces, which the thermal conductivity is to be measured. A load can be applied from both sides of the samples to have a better contact with the TPS element.[36]



*Figure 2-6: Schematic of the TPS Source: [36]*

<span id="page-30-1"></span>This TPS method is a transient state approach invented by Gustafsson [37] and there is already an international standard based on this method ISO 22007-2:2017.

This is relatively a newly developed transient approach for thermal conductivity measurement. In comparison to steady state methods, it is fast and applicable to range of materials[38].

Furthermore,Ahadi et al.[39]discussed the following capabilities and limitations of the TPS method.

- Capable of measuring thermal conductivity , thermal diffusivity and specific heat capacity
- Suitable for solids, liquid and powders
- Suitable for both isotropic and anisotropic materials
- Compact sensors and consequently small samples required.

Solorzano, et al. [35]also credit the TPS method advantages such as having a wide range of TC accessible (from 0.02 to 400  $Wm^{-1}K^{-1}$ ), marginal effor needed for sample preparation, flexibility in sample size and also possibility ot perform local or bulk measurements with only changing the sesnro diameter. As the same time he remarks that since this is a contact method special care is required in the experimental procedure.

After reaching the thermal equilibrium, a known constant amount of electrical power is applied to the sensor. Due to the temperature rise, the resistance of the sensor will increase and cause the corresponding increase in the voltage drover over the sensor. By recording, the voltage and current variation over a measured time period, accurate information on the heat flow between the sensor and the test material can be acquired which is then converted to a corresponding time - temperature data.

When the probe is heated, different thermal transport properties of the samples determines the temperature response of the probe. Probe temperature rises slower if the TC of the sample is larger whereas the temperature rises faster if TC of the sample is smaller.[38]

#### <span id="page-31-0"></span>**2.5.1 TPS Theory and Modelling.**

Based on the time-temperature variation of the samples obtained, results were numerically modelled. TC calculating procedure has been followed as below.

Transient plane heat sources (TPS hot disc) method is discussed below following standard of ISO 22007-2:2017

The total temperature variation  $\Delta T$  (t) can be written as,

 $\Delta T(t) = \Delta T_i(t) + \Delta T_s(t)$  Equation 2-8

Where

 $\Delta T_i(t)$  = Temperature increase in the insulation layers of the probe

 $\Delta T_s(t)$  = Temperature increase in the specimen surface.

Here the bifilar probe thermal conduction has been is approximated as function of the concentric and equispaced circular lined heat sources. Therefore the thermal conductivity of the rubber composite ( $k_{\text{eff}}$ ) can be obtained by the following relationship.

$$
\Delta T_s(\tau) = \frac{P_0}{\pi^{3/2} \cdot r \cdot k_t} D(\tau) \quad \text{Equation 2-9}
$$

Where

 $P_0$  = Power output of the probe (W)

 $r =$ Radius of the outermost ring source  $(m)$ 

 $k_t$  = Thermal conductivity of the rubber composite specimen and insulation layer  $(Wm^{-1}K^{-1})$ 

Also,

 $\tau$  = Dimensionless time parameter [40]

$$
\tau = \sqrt{(t/\theta)} \quad \text{Equation 2-10}
$$

and

 $\theta$  = Characteristic time defined as below [40]

$$
\theta = \frac{r^2}{\alpha}
$$
 Equation 2-11

Where

 $t = time(s)$ 

 $\alpha$  = Thermal diffusivity of the rubber specimen.(m<sup>2</sup>s<sup>-1</sup>)

 $D(\tau)$  is the dimensionless specific time function defined as below.[37, 41]

$$
D(\tau) = [m(m+1)]^{-2} \int_0^{\tau} \sigma^{-2} \left[ \sum_{l=1}^{m} l \sum_{k=1}^{m} k \exp \left\{ - \left( \frac{l^2 + k^2}{4m^2 \sigma^2} \right) I_0 \left( \frac{l k}{2m^2 \sigma^2} \right) \right\} \right] d\sigma
$$

Equation 2-12

Where

 $m =$ Number of concentric ring sources

 $I_0(x,0)$ = First kind zeroth order modified Bessel function

 $\sigma$  = Integration variable [38]

Which is defined as,

$$
\sigma^2 = \frac{\alpha_s(t - t_c)}{r^2}
$$
 Equation 2-13

In addition, a time correction values  $(t<sub>c</sub>)$  is also incorporated to compensate for the delay and lags in the electronics, hardware and measuring devices involved. This value only reaches a maximum of 0.5% of the measured time step value, which leads to a value of 0.05s. The measured time (t) should be corrected including  $t_c$  and also should be used in the optimisation procedures. The sensitivity of this  $t_c$  parameter is very minimum due to its very small magnitude and also considering the complexity of the calculations this  $t_c$  is neglected as it was assumed it has minimum effect on the calculations.

Substituting the values and parameters defined, Equation 3-1 can be written as below in terms of  $\tau$  and the relationship between  $\Delta T$  ( $\tau$ ) and D ( $\tau$ ) as follows.

$$
\Delta T(\tau) = \Delta T_i(\tau) + \frac{P_0}{\pi^{3/2} \cdot r \cdot k_t} D(\tau) \quad \text{Equation 2-14}
$$

This defines a linear relationship between the two parameters, which has  $\Delta T_i$  ( $\tau$ ) as the intercept and  $\mathsf{P}$  $\pi$ as the slope respectively.

After obtaining the temperature in the heating probe (Temperature variation in the insulation layer and the sample specimen), an  $\alpha_s$ (thermal diffusivity of the sample) value is guessed and D ( $\tau$ ) is calculated which is then used to plot a graph of  $\Delta T$  ( $\tau$ ) vs and D ( $\tau$ ).

According to Ahadi, et al., [39]and ISO 22007-2:2017, once the  $\alpha_s$  value us guessed correctly the curve would be a line after a short dimensionless time  $\Delta \tau_i$ , which is associated with  $\Delta t_i$ . This initial non-linear portion is disregarded as it represent the transient heat conduction through the insulation layer and after the curve reaches the steady state representation. Since **T**depends on $\alpha$ <sub>s</sub> regression analysis is performed to the data points iteratively for  $\alpha$ <sub>s</sub>.

 $\Delta t_i$  is defined as below.

$$
\Delta t_i = \frac{\beta_i^2}{\alpha_i}
$$
 Equation 2-15

Where

 $\Delta t_i$  = Relaxation time parameter (s)

 $\beta$ <sub>I</sub> = Thickness of the Kapton insulating layer.(m)

 $\alpha_1$  = Thermal diffusivity of the Kapton insulating layer. (m<sup>2</sup>s<sup>-1</sup>)

Summary of the TC calculation procedure by TPS method is given in below in [Figure 2-7](#page-34-0)



## *Figure 2-7: Iterative process of the TPS model Source: [39]*

<span id="page-34-0"></span>According to the TPS procedure specified in the ISO 22007-2:2017, D  $(\tau)$  and  $\Delta T$  plot was generated for the all samples. Based on the theory, after  $\Delta\tau$  associated with  $\Delta t$  the graph should become linear as the temperature increase in the insulating layer  $(\Delta T_i)$  becomes a constant. The initially guessed thermal diffusivity  $(\alpha_s)$  value then iteratively changed until the

linearity is established by a linear regression analysis. From this linear equation slope and the intercept is obtained to evaluate the thermal conductivity  $(k<sub>t</sub>)$  of the total specimen sample and the insulation.

It is then used to calculate the thermal conductivity of the sample specimen taking the sum of the thermal resistances as below.

$$
\frac{h_t}{Ak_t} = \frac{h_s}{A_s k_s} + \frac{h_i}{A_i k_i}
$$
 Equation 2-16

Where

 $h_t, h_s$  and  $h_i$  = Thickness of each layers total, specimen and insulation layers respectively (m)

A,  $A_s$ ,  $A_i$  = Heat conduction area of total, specimen and insulation respectively (m<sup>2</sup>)

 $k_t, k_s$  and  $k_i$  = Thermal conductivity of total, specimen and insulation layer respectively (Wm<sup>-</sup>  ${}^{1}K^{-1}$ )

ks.value can be calculated as all other parameters are known. Reference values are used for the Kapton insulating layer.
# **3 CHAPTER 3: METHODOLOGY**

#### **3.1 Research Plan**

In this research, thermal conductivity of the NR/CB with Gr added rubber composites were calculated in both empirically and using data obtained by TPS experiment. Selected predictive thermal conductivity models (Lewis Nielson model and Hashin-Shtrikman's model) are discussed and thermal conductivity of the hybrid rubber composite is obtained. Also the experimental results obtained and published by Gunasekara, et al., [42]. These experimental results were analysed numerically to obtain the effective thermal conductivity of the hybrid rubber composites. Both emphirical and numerical thermal conductivities are then compared.



*Figure 3-1: Summary representation of the research plan*

### **3.2 TPS Analysed Route**

Transient plane source (TPS) data published in Gunasekara, et al., [42]was used to obtain time temperature profiles of the natural rubber/carbon black with varying grpahite PHRare given in [Table 4-1](#page-42-0) for reference.

Temperature readings of the samples had been taken every 10 seconds until the temperature profiles reach to a constant value close to 150°C. All samples had reached approximately a constant temperature by 250s.

#### **3.3 Empirical Route**

Thermal conductivity models available for commonly discussed two phase systems are further extended and modified for three phase systems, which are composites with hybrid fillers. Modified Lewis – Nielson model and Hashin – Shtrikman model are discussed below.

The following common assumptions are made when modelling the TC and any specific assumptions relevant only to the particular model are mentioned in the discussion of the model.

- 1. Assumed that the filler particles are spherical in shape which have different particle size.
- 2. The spherical filler particles are randomly dispersed in the continuous phase of rubber matrix resulting a homogeneous composite.

Also the below property parameters are used in the mathematical modelling.

<b>Property</b>	<b>Material</b>	<b>Value</b>
Bulk thermal conductivity	Natural rubber (NR)	0.15
(W/m.K)	Carbon black N330 (CB)	0.3
	Graphite (Gr)	300
	Natural rubber (NR)	1.5
	Carbon black N330 (CB)	1.86
Density	Graphite (Gr)	2.1
$(g/cm^3)$	ZnO	5.61
	Stearic acid	0.54
	<b>MBTS</b>	1.54
	Sulphur	$\overline{2}$

**Table 3-1: Material properties**

Both models were considered for graphite phr range of 0 to 50 was based for the other components of the compounding. The corresponding volume fractions were calculated and the a graphical result of effective thermal conductivity of composite (  $k_{\text{eff}}$ ) vs volume fraction of graphite  $(\boldsymbol{\phi}_2)$  was obtained.

Graphite (Gr) $g$ -phr	<b>Natural</b> <b>Rubber</b> (NR)	ZnO	<b>Stearic</b> <b>Acid</b>	Carbon <b>Black</b> $(CB -$ N330)	<b>MBTS</b>	<b>Sulphur</b>	<b>Total</b>
$\theta$							121.9
5							126.9
10							131.9
15							136.9
20							141.9
25	100	$\overline{2}$	1.4	15	1.5	$\overline{2}$	146.9
30							151.9
35							156.9
40							161.9
45							166.9
50							171.9

**Table 3-2: Weights (g) in of the rubber-compounding recipe for the experiment**

**Table 3-3: Volume and volume fractions of fillers**

Graphite phr	<b>Volume</b> <b>NR</b>	<b>Volume</b> CB(1)	<b>Volume</b> Gr(2)	<b>Total</b> volume	<b>Volume</b> <b>Fraction CB</b> $(\boldsymbol{\phi}_1)$	<b>Volume</b> <b>Fraction</b> Gr $(\boldsymbol{\phi}_2)$
$\boldsymbol{0}$			$\boldsymbol{0}$	78.55	0.10	$\overline{0}$
5			2.38	80.93	0.10	0.03
10			4.76	83.31	0.10	0.06
15			7.14	85.69	0.09	0.08
20			9.52	88.07	0.09	0.11
25	66.67	8.06	11.90	90.46	0.09	0.13
30			14.29	92.84	0.09	0.15
35			16.67	95.22	0.08	0.18
40			19.05	97.60	0.08	0.19
45			21.43	99.98	0.08	0.21
50			23.81	102.36	0.08	0.23

#### **3.3.1 Modified Lewis – Nielson model**

The two component Lewis – Nielson model has been modified for a hybrid system to predict the TC of NR composite. Model formula and relevant parameters are calculated as below.

$$
k_{eff}^* = \, \tfrac{k_{eff}}{k_m} = \, \tfrac{1 + \sum_{i=1}^n A_i B_i \varphi_i}{1 - \sum_{i=1}^n B_i C_i \varphi_i} \quad \text{Equation 3-1}
$$

Where

$$
B_i = \frac{k_{i/}_{k_m} - 1}{k_{i/}_{k_m} - A_i}
$$
 Equation 3-2

$$
C_i = 1 + \frac{1 - \phi_{\text{max}}}{\phi_{\text{max}}^2} \phi_i
$$
 Equation 3-3

 $A_i$ = Depends on the filler shape: For randomly distributed spherical particle,  $A_i$  = 1.5

 $\phi_{\text{max}}$  = Maximum packing factor for a randomly close spherical particle, $_{\text{max}}$  = 0.637

 $n =$  Number of types of fillers. For a hybrid composite  $n = 2$ 

 $i = 1$  represents carbon black (CB) and  $i = 2$  represents graphite (Gr)

Numerical results are given in appendix [0](#page-70-0) and results of volume fraction of graphite vs TC is given below in [Table 3-4.](#page-39-0)

phr Gr	Volume fraction Gr $(\phi_2)$	$k_{\text{eff}}$ LN
0	0.000	0.1618
5	0.029	0.1736
10	0.057	0.1858
15	0.083	0.1983
20	0.108	0.2112
25	0.132	0.2245
30	0.154	0.2382
35	0.175	0.2524
40	0.195	0.2671
45	0.214	0.2824
50	0.233	0.2982

<span id="page-39-0"></span>**Table 3-4: Volume fraction of Grand ETC from modified Lewis – Nielson model**

## **3.3.2 Hashin-Shtrikman's Model (HS model)**

$$
k_{\text{eff}}^* = \frac{k_i}{k_m} = \frac{1+2\sum_{i=1}^n E_i \varphi_i}{1-\sum_{i=1}^n E_i \varphi_i}
$$
 Equation 3-4

Where

$$
E_{i} = \frac{{\binom{k_{i}}{k_m}}-1}{{\binom{k_{i}}{k_m}}+2}
$$
 Equation 3-5

#### **Table 3-5: Volume fraction of Gr and ETC from Hashin-Shtrikman's model**



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# **4 CHAPTER4: RESULTS AND DISCUSSION**

TPS analysed results and the empirical modelling results are presented in this section followed by the discussion.

Variation of time vs. temperature results of all the samples have been given below in [Table](#page-42-0)  [4-1](#page-42-0) and graphically represented in [Figure 4-1](#page-43-0) below. Data was obtained by Bogala Graphite Lanka PLC, Bogala Mines, Aruggammana Sri Lanka, which was published in [42]

	<b>Graphite amount added</b>					
Time (s)	Sample 01	Test 01	Test 02	Test 03		
	<b>Control</b>	5 phr	$10$ phr	$15$ phr		
10	51.8	46.8	54.6	44.9		
20	67.4	69.9	80.9	70.2		
30	82.5	88.7	97.7	89.2		
40	96.3	102.5	109.6	106.9		
50	109	115.3	119.5	118.1		
60	115.1	123.9	127.2	126.4		
70	124.1	131.8	133.2	133		
80	130.8	136.9	137.3	137.5		
90	135.3	140.6	141	141		
100	138.4	144	143.6	143.6		
110	142.7	146.2	145.5	145.8		
120	143.5	147.8	147	147.5		
130	145.1	149.5	148.3	148.7		
140	146.6	150.5	149.2	149.6		
150	147.3	151.3	149.8	150.4		
160	148.1	151.9	150.3	151		
170	147.9	152.4	150.6	151.4		
<b>180</b>	148.6	152.7	151	151.8		
190	148.1	153.1	151.2	152.1		
200	148.1	153.3	151.4	152.2		
210	149.3	153.5	151.6	152.4		
220	149.3	153.6	151.7	152.6		
230	149.4	153.7	151.8	152.6		
240	149.7	153.8	151.8	152.7		
250	149.9	153.8	151.9	152.8		

<span id="page-42-0"></span>**Table 4-1: Time - temperature variation of the samples measured**

**Source: [42]**



<span id="page-43-0"></span>*Figure 4-1: Temperature –time profile received from the TPS analysis of the rubber samples*

Based on the TPS analysed results obtained for different samples with different graphite percentage, it can be seen that the all the graphite included samples have a higher temperature relative to the control after 25s onwards. This observation proves that the graphite has increased the effective thermal conductivity of the rubber compounding. Also out of the graphite included samples 5PHR has the highest temperature increase and 10 PHR is the lowest. 15 PHR thermal conductivity is in between the 5 PHR and 15 PHR samples.

			$\Delta T$ (°C)			
Time (s)	T	$D(\tau)$	<b>Control</b>	5 phr	$10$ phr	$15$ phr
$\overline{0}$	0.0000	0.00000	$\overline{0}$	$\overline{0}$	$\overline{0}$	$\boldsymbol{0}$
10	0.0667	0.01754	21.8	16.8	24.6	14.9
20	0.0943	0.02435	37.4	39.9	50.9	40.2
30	0.1155	0.02937	52.5	58.7	67.7	59.2
40	0.1333	0.03346	66.3	72.5	79.6	76.9
50	0.1491	0.03694	79	85.3	89.5	88.1
60	0.1633	0.03998	85.1	93.9	97.2	96.4
70	0.1764	0.04269	94.1	101.8	103.2	103
80	0.1886	0.04512	100.8	106.9	107.3	107.5
90	0.2000	0.04733	105.3	110.6	111	111
100	0.2108	0.04935	108.4	114	113.6	113.6
110	0.2211	0.05121	112.7	116.2	115.5	115.8
120	0.2309	0.05291	113.5	117.8	117	117.5
130	0.2404	0.05448	115.1	119.5	118.3	118.7
140	0.2494	0.05594	116.6	120.5	119.2	119.6
150	0.2582	0.05729	117.3	121.3	119.8	120.4
160	0.2667	0.05854	118.1	121.9	120.3	121
170	0.2749	0.05970	117.9	122.4	120.6	121.4
180	0.2828	0.06078	118.6	122.7	121	121.8
190	0.2906	0.06178	118.1	123.1	121.2	122.1
200	0.2981	0.06272	118.1	123.3	121.4	122.2
210	0.3055	0.06359	119.3	123.5	121.6	122.4
220	0.3127	0.06440	119.3	123.6	121.7	122.6
230	0.3197	0.06516	119.4	123.7	121.8	122.6
240	0.3266	0.06586	119.7	123.8	121.8	122.7
250	0.3333	0.06652	119.9	123.8	121.9	122.8

**Table 4-2: Time dependent**  $\tau$  **and**  $D(\tau)$  **values calculated and the corresponding temperature difference for the test samples**

Measured time is then converted to a dimensionless time parameter of  $\tau$  from the given relationship. Time vs.  $\tau$  variation is given as below in [Figure 4-2](#page-45-0) where it can be seen there is an exponential growing relationship between the two variables.



*Figure 4-2: Time vs. dimensionless time parameter (* $\tau$ *) variation* 

<span id="page-45-0"></span>Using the  $\tau$  value obtained,  $D(\tau)$  is obtained which is the theoretical specific time function, a time dependent increase for the analysis, which is depicted in [Figure 4-3.](#page-46-0) This function describes the conducting pattern of the sensor, with the assumption of the sensor being a collection of concentric ring elements. This assumption was justified and validated by Bouguerra, et al., (2001) for a  $\tau$  values in the range of 0 to 3 that was satisfied in this research work, which is apparent in [Figure 4-3](#page-46-0) where the maximum  $\tau$  value is less than 0.8. First kind zeroth order modified Bessel function and an independently defined integral function were also used in the computation of  $D(\tau)$  for a 15 number of concentric rings in the probe element.



*Figure 4-3:*  $\mathbf{r}$  *vs D (* $\mathbf{r}$ *)variation* 

<span id="page-46-0"></span>The total temperature increase  $(AT)$  during the transient conduction of the probe is affected by two factors, which are as below.

- 1. The temperature difference across the insulating layer  $(\Delta T_i)$
- 2. Temperature difference across the specimen sample surface  $(\Delta T_s)$

As the power, output of the heating element considered to be constant and the insulation layer is sufficiently thin,  $(\Delta T_i)$  will become a constant after a short time. This time is called the relaxation time (( $\Delta t_i$ ) which is defined by  $\Delta t_i = \beta i 2\alpha i$  [Equation 2-15](#page-34-0) and associated  $\Delta \tau_i$ is as below.

$$
\Delta t_i = 3.6 \times 10^{-3} s = 3.6 \text{ms}
$$

This value is confirmed by ISO 22007-2:2017where it states a typical insulated probe will have a relaxation less than 10 ms.and time requred to reach a constant temperature difference is less than 100ms.

The  $\Delta \tau_i$  value associated with the  $\Delta t_i$  obtained above is calculated as

## $\Delta \tau_i = 0.0027$ .

Since the obtained  $\Delta \tau_i$  is extremely low and it does not signifies a clear differentiation value in the corresponding  $D(\tau)$  as it is very close and cluster around zero value. Therefore, iterative values of  $\alpha_s$  do not reflect any distinct point in the  $\Delta T$  vs. D ( $\tau$ )graph, which hinders the clarity of the linearity of the profile as discussed. The sum of the error function does not converge to a minimum value for iterative values of the specimen thermal diffusivity  $(\alpha_s)$ values.

This may be because the sensitivity of the parameters calculated and the complexity of the functions as there are integrals and complex mathematical functions within computations. A powerful computing programming is believed to be utilised to follow the exact ISO 22007- 2:2017.

Hence in order to continue the work, a simplification assumption was made in this context. As the typical  $\alpha_s$  values are in the order of 1 x 10<sup>-7</sup> m<sup>2</sup>s<sup>-1</sup> of rubbers which was also referenced in ISO 22007-2:2017. , it has been used as a fixed value for the calculations for all samples. This would be a reasonable assumption as any changes in thermal diffusivity of the for samples would not change by large orders of magnitude by the addition of graphite as per TPS analysis.

Consequently, the linearity between the entire analysed time ranges were assumed and the plotted graph was fitted with a trend line.  $R^2$  value was computed for all samples and their corresponding graphs of  $\Delta T$  vs D ( $\tau$ ) are shown in [Figure 4-4](#page-48-0) to [Figure 4-7](#page-50-0) below.

The summary of linear regression trend line specifying the gradient and the intercept as well as the corresponding  $R^2$  values are shown below in [Table 4-3.](#page-48-1)

<span id="page-48-1"></span>

<b>Sample Name</b>	<b>Trend line equation</b>	$\mathbf{R}^2$ value
Control	$y = 2669.3x - 23.744$	0.99
5 phr	$y = 3018.5 - 31.196$	0.98
$10$ phr	$y = 2769.1x - 16.929$	0.98
$15$ phr	$y = 3033.x - 30.834$	0.97

**Table 4-3: Linear regression line equation and corresponding R<sup>2</sup> values**

 $R<sup>2</sup>$  values obtained are reasonable close to 1 and therefore it can be concluded that the line fit is a good representation of the analysed data.



 $D(\tau)$  vs  $\Delta T$  of Control sample (0 phr Gr)

<span id="page-48-0"></span>*Figure 4-4: D(* $\tau$ *) vs*  $\Delta T$  *of Control (0 phr Gr) sample* 



*Figure 4-5:*  $D(\tau)$  *vs.* $\Delta T$  *of5 phr Gr sample* 



*Figure 4-6: D(* $\tau$ *) vs.*  $\Delta T$  *of10 phr Gr sample* 



*Figure 4-7:*  $D(\tau)$  *vs.*  $\Delta T$  *of 15 phr Gr sample* 

<span id="page-50-0"></span>The following parameters have been used in obtaining the thermal conductivity for the sample specimens by the TPS analysed data.





Thermal conductivity values are given below with the values received from empirical models of the modified Lewis – Nielson (LN) model and Hashin – Shtrikman model (HS) below in [Table 4-5](#page-51-0)

# <span id="page-51-0"></span>Table 4-5: Summary of TC results found for both TPS analysis ( $k_{TPS}$ ) and empirical **models ( HS – Hashin – Shtrikman, LN – Modified Lewis Nielson)**





# **from TPS and empirically modelling**

**Thermal conductivities of the graphite included samples found** 

<span id="page-52-0"></span>*Figure 4-8: TC values obtained from TPS analysis and empirical modelling*

It can be seen that by all 3 methods ( 2 empirical models and TPS analysis method, all three graphite added samples display an increase in the thermal conductivity compared to the control sample. Also from the graphite added samples, thermal conductivity increases with the amount of graphite added as shown in [Figure 4-8.](#page-52-0)

From the addition of graphite, the following percentage improvements of thermal conductivity have been obtained over the control sample from the three methods as shown in [Figure 4-9.](#page-53-0) Relative increase in the thermal conductivities are always have been higher in the LN model compared the to the experiment value whereas the HS model displays a lower relative improvement. In addition, the two empirical models demonstrate a linear improvement in the thermal conductivity with the graphite content. Even though the relative improvement shows a significant improvement percentage in the absolute thermal conductivity, values only range from  $0.1460 \text{ Wm}^{-1}\text{K}^{-1}$  to  $0.1725 \text{ Wm}^{-1}\text{K}^{-1}$  in all three methods. Therefore, it can be concluded that models are in a considerable level of agreement.



<span id="page-53-0"></span>*Figure 4-9: Percentage improvement of TC relative to the control sample by each method*

Similar work done by Brahil *et al*[43]where they have measured the thermal conductivity of the natural rubber/graphite composites, they have observed the trend of thermal conductivity Suleiman[44]has also done similar research using the TPS method and commented that the effect of temperature change ( during measurement) on thermal properties of a composite is very complex and depends on several important factors which can be potentially counteractive. For example he points out that the size and number of micro voids created in the composite by the chain movements and also by increasing the chain alignment and arrangement within the matrix, are critical factors which can affect the TC. The former reduces the thermal conductance due to adding more thermally insulating gaps whereas the latter actually encourages the thermal conductance as more order inside the matrix. In the presence of two competing factors such as in this case, at times the consistency of the relationships can varyagain under the influence of multiple factors. Suleiman[44]also reiterates the fact that predicting the rubber composite thermal properties is not an easy task as properties may change from batch to batch , time to time , environment conditions etc. Therefore he also suggests a shorter measuring time steps as rubber degradation during measurement is reduced and gives a significant spread for the measurements. Also Suleiman<sup>[44]</sup>is infavour of emphirical modelling of rubber composites to capture such variations as a credible non-distructive and fast method to be used as quality assuarance measure to validate as well as to predict the intended outcomes.

[Table 4-6](#page-55-0) below summarises the percentage difference of the TCs received from each empirical model. Except HS model predicted value in the 15PHR sample all other values are over - estimated by the two models in comparison to the TPS analysed values. As the models estimated values contain a considerable amount of deviation, a correction factor has been introduced to further improve the estimations by the two models have been considered in this context.

TPS analysed values and empirical model values results can be further quantitatively compared by the sum of squares (SS). The  $R^2$  coefficient is not used here because these are empirically obtained values and  $R^2$ better suited for experiment values[39]. The sum of squares (SS) is calculated by summing the square of the TPS analysed value minus the empirical modelled value.

Optimisations of the modelled values were achieved using the Ms Excel solver function. Based on the results obtained correction factors are incorporated to the existing models, which are discussed below.



<span id="page-55-0"></span>**Table 4-6: Summary of percentage difference among the thermal conductivity results from the TPS analysis and empirical models (HS and LN model)**

Sum of the squares are calculates as below.

 $SS = \sum (k_{TPS} - k_{model})^2$  Equation 4-1

The below values are obtained for the values after optimisation. k <sub>model</sub> represents the empirically calculated values for TC

**Table 4-7: Summary of the sum of the squares values after optimisations**

	$k$ TPS	<b>HS</b> $(k_{TPS} - k_{HS})^2$	LN $(k_{TPS} - k_{LN})^2$
<b>Control</b>	0.1462	2.304E-05	4.029E-05
5 phr Gr	0.1495	2.446E-05	3.617E-07
10 phr Gr	0.1545	9.058E-06	3.739E-05
15 phr Gr	0.1725	1.500E-04	1.162E-06
		2.066E-04	7.921E-05
		$SS$ <sub>HS</sub>	$SS_{LN}$

For the HS model correction factor –  $\lambda_{\text{HS}} = 0.932$ 

For the LN model correction factor  $-\lambda_{LN} = 0.864$ 

The experimented and modelled thermal conductivities before and after optimisation is shown below in [Figure 4-10](#page-56-0) and [Figure 4-11.](#page-56-1)



*Figure 4-10: TC obtained before optimisation of modelled values.*

<span id="page-56-0"></span>

<span id="page-56-1"></span>*Figure 4-11: TC obtained after optimisation of modelled values.*

It can be seen that in [Figure 4-11](#page-56-1)*,* thermal conductivity values that have been calculated by the emphirical modelling are now have an improved fit for the experimeted values. Reducing the deviation between the TPS analysed values and emphirically model values can be viewed as an improvement of accuracy and the predictivity of the model estimations. Hencehereby propose the multiplication correction factor for the thermal conductivities received from the two models as below. Subscript "opt" represents the optimised TC value from the corresponding model

> **k HS** opt =  $\lambda$ **HS**<sup>\*</sup> **k HS** = 0.932 **k HS k LN** opt =  $\lambda_{LN}$ <sup>\*</sup> **k LN** = 0.864 **k LN**

Using the above optimised thermal conductivity values , final thermal conductivity values obtained from all three methods can be summerised as below.

	Thermal Conductivity $(Wm^{-1}K^{-1})$				
	$k$ TPS	$\bf{k}$ HS opt	$\mathbf{k}$ LN opt		
Control	0.1462	0.1510	0.1399		
5 phr Gr	0.1495	0.1544	0.1501		
10 phr Gr	0.1545	0.1575	0.1606		
15 phr Gr	0.1725	0.1603	0.1714		

**Table 4-8: Summary of the final TC values after optimisation of the two empirical** models in comparison with the experimental values  $k_{TPS}$ 

[Table 4-9](#page-58-0) shows the differences in the values received after including the correction factors to each model. It is evident that deviations from the TPS analysed values have been significantly reduced except the HS model value for 15 phr Gr. Even though the error has been reduced overall for all other samples HS model predicted the 15 phr Gr TC extremely closeto the TPS analysed value prior to the optimisation. But overall the optimsation can be acknowledged as credible based on this results obtained.



# <span id="page-58-0"></span>Table 4-9: Summary of percentage difference between the TC results against the  $k_{TPS}$ **and empirical model values after optimisation**

After the optimisation of the parameters, the differences in the results can be assigned to the human error and the lack of specificity for each individual component level. Also all these models negelected the fact the thermal contact resistance in the interface of the fillers and in the matrix. This could be potentially a major concern which would have impacted but to maintain the simplicity of mathematical modelling this factor was neglected in this context.

## **5 CHAPTER5: CONCLUSION**

Following conclusions can be made out of this study:

- $\triangleright$  Temperature versus time data recorded during heating the natural rubber samples filled with carbon black and graphite were analysed by transient plane source (TPS) method and the thermal conductivity was calculated based on two of the empirical models considering the material property parameters and other specific geometrical properties.
- $\triangleright$  Effect of graphite on thermal conductivity of rubber compounds obtained from calculations offered by Lewis and Nielson model and Hashin – Shtrikman model agreed well with experimentally obtained results from which It can be concluded that the addition of graphite to the NR/CB rubber composites would contribute to increase the thermal conductivity compared to the control sample.
- $\triangleright$  From the empirical modelling, Lewis and Nielson model provided a thermal conductivity improvement of 22.57% over the control sample whereas Hashin – Shtrikman model provided a 7.13% improvement for the same sample consisting of highest amount of graphite corresponding to 15 parts per hundred (PHR) rubber and 17.99% improvement was obtained from the TPS analysis of the obtained data.
- $\triangleright$  In order to minimize deviation between empirically calculated thermal conductivity values and TPS analysed values, further statistical based optimizations were executed. Squared sums were calculated and incorporated to the Lewis and Nielson model with specific proposed correction factor $\lambda_{LN} = 0.864$ , which reduced the difference between the empirical values and TPS, analysed values. For the 15 PHR sample Lewis Nielson model estimates the TC value as  $0.1714 \text{ Wm}^{-1}\text{K}^{-1}$  after incorporating the correction factor.
- $\triangleright$  The optimized empirical model proposed in this study could predict thermal conductivity of NR/CB/Gr rubber composites, which could be very beneficial in solid rubber manufacturing such as tire industry as the product heating times, curing times etc. can be closely estimated with a less margin of error. This would in turn increase understanding the process parameters, which then can be utilized to proper process engineering decisions.

## **6 CHAPTER6: FUTURE RESEARCH**

Following recommendations are proposed for future further research.

The time temperature profile of the control,5 phr, 10PHR and 15PHR samples obtained from the TPS model requires with comprehensive and complex mathematical functions to be calculated in order to compute the TCs of the samples. For data analysis, more intricate programming software such as MATLAB<sup>®</sup>, Mathematica<sup>®</sup> or open source Python<sup>®</sup> can be considered to solve these complex functions. This would minimise the error and increase the sensitivity of the computations in contrast to the regression analysis based methods followed in this study.

Also, time step can be further reduced to a lesser value instead of 10 seconds. If temperature variations are available every 5 seconds rather than 10 seconds the accuracy could have been further improved and the temperature based property changes such as thermal conductivity, specific heat capacity, etc. would have been much more gradual and less impactful. This strategy is very common in integral calculus as smaller the step change clarity of the outcome would be high but this again would require powerful programming tools.

Furthermore, the effect of the particle size and particle size distribution can have a considerable influence on the thermal conductivity. Particle size of the graphite which have been used in this research is  $40\mu m$  and reducing the particle size would be a promising aspect explore on the same objective. One can also use functionalised groups to improve the mixing of the fillers in the continuous rubber phase, which reduces, or minimise the agglomeration of the particles in the composite. Such procedure would also mitigate the localisation of graphite (filler) particles and lead to an even distribution enhancing the homogeneousness of the rubber composite throughout. Functionalisation could be done in both physically and chemically which would be potentially the best combination of actions to improve the even dispersion of particles in the composite.

Overall, in order to further improve the modelling component accuracy wise and reliability wise more repeats would be highly required and recommended. The hypothesis that had been made here is that the TPS analysed results can be closely approximated by an empirical model would be the most efficient use of time and resources. In order to increase the accuracy of natural rubber/carbon black and graphite rubber composites more specific and inherent property parameters can be incorporated in the Lewis-Nielson model and Hashin – Shtrikman

Model which has been discussed. Such optimisations could potentially contribute to better outcomes as utilisation of a versatile, reliable and intricate model can closely predict thermal conductivity of the composites.

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## **APPENDICES**

**Appendix A: Calculation of the D () Dimensionless Specific Time Function**

$$
D(\tau) = [m(m+1)]^{-2} \int_0^{\tau} \sigma^{-2} \left[ \sum_{l=1}^m l \sum_{k=1}^m k \exp\left\{-\left(\frac{l^2 + k^2}{4m^2 \sigma^2}\right) I_0 \left(\frac{lk}{2m^2 \sigma^2}\right) \right\} \right] d\sigma
$$
  
\nP30  
\nP30  
\n2.12

Above function has to be solved in order to obtain the numerical results for the TPS analysis. As this includes complex integral functions and summations, the entire function was calculated by parts using excel.

Here as defined previously,

- $m -$  Number of rings in the heating element (m=15)
- 1 and  $k$  Counter variables (Going from 1 up to 15)
- $\bullet$   $\sigma$  Integration function

Where

$$
\sigma^2 = \frac{\alpha_s(t - t_c)}{r^2}
$$
 Equation 2-13

**Step 1**



# **Step 3**

Corresponding answers received in step 1 and 2 above are multiplied together to obtain the entire values within the summation.

# **Step 4**

Integrate the entire sum with respect to  $\sigma$  with the limits of 0 to  $\tau$ .

# **Step 5**

Multiply the integrated output by m function (P30)

Once this process is followed, each " t (time)" reading will provide a  $\tau$  value, where a corresponding  $D(\tau)$  is calculated.

Hence time-temperature relationship can be converted to a  $D(\tau)$  and temperature relationship which is the basic principal of the TPS model.

# Appendix B: Values Obtained for D ( $\tau$ ) Dimensionless Specific Time Function

# **Step 1 – P10**

<span id="page-70-0"></span>








## **Step 1 – P11**











## Step  $2 - P20$











## **Step 2-P21**











## Step  $3 - P30$



phr Gr	$\boldsymbol{\phi}_2$	$C_1$	C <sub>2</sub>	$B_1$	B <sub>2</sub>	$\mathbf{A}$	$\boldsymbol{\phi}_1$	$\boldsymbol{\phi}_2$	$k^*$ <sub>eff</sub>	$k_{\text{eff}}$ LN
$\boldsymbol{0}$	0.000	1.092	1.000	0.286	0.999	1.5	0.103	0.000	1.079	0.162
5	0.029	1.089	1.026	0.286	0.999	1.5	0.100	0.029	1.158	0.174
10	0.057	1.087	1.051	0.286	0.999	1.5	0.097	0.057	1.239	0.186
15	0.083	1.084	1.075	0.286	0.999	1.5	0.094	0.083	1.322	0.198
20	0.108	1.082	1.097	0.286	0.999	1.5	0.092	0.108	1.408	0.211
25	0.132	1.080	1.118	0.286	0.999	1.5	0.089	0.132	1.496	0.224
30	0.154	1.078	1.138	0.286	0.999	1.5	0.087	0.154	1.588	0.238
35	0.175	1.076	1.157	0.286	0.999	1.5	0.085	0.175	1.683	0.252
40	0.195	1.074	1.175	0.286	0.999	1.5	0.083	0.195	1.781	0.267
45	0.214	1.072	1.192	0.286	0.999	1.5	0.081	0.214	1.882	0.282
50	0.233	1.070	1.208	0.286	0.999	1.5	0.079	0.233	1.988	0.298

**Appendix C : Empirical Results from Lewis - Nielson Model**