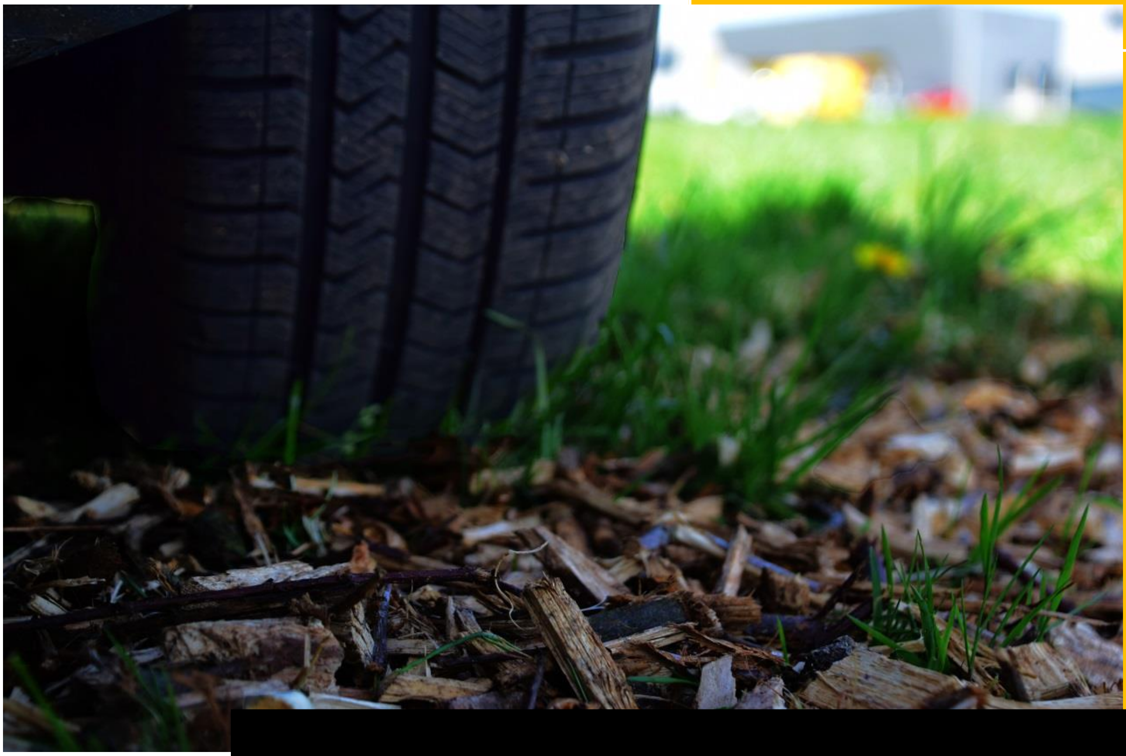
2020



Design of a Bio-Based Filler System for Tire Treads

Priyanka Sekar

University of Twente

6/18/2020

The design project was financially supported by SunCoal Industries GmbH.

Graduation committee:

Chairman and Program Director of PDEng	Prof. dr. ir. G. Brem	University of Twente
Thesis Supervisor	Prof. dr. A. Blume	University of Twente
Daily Supervisor	Dr. R. Anyszka	University of Twente
External Member	Dr. ir. Joost Duvigneau	University of Twente
Company supervision member	Dr. J. Podschun	SunCoal Industries GmbH

Design of Bio-Based Filler System for Tire Tread Application

Written by Priyanka Sekar

PDEng Thesis, University of Twente, Enschede, The Netherlands, June 2020

Cover design and picture by Anand Poomuthu

Design of Bio-Based Filler System for Tire Tread Application

PDEng Thesis

to obtain the degree of

Professional Doctorate of Engineering (PDEng) at University of Twente,

on the authority of the rector magnificus

prof. dr. T. T.M. Palstra,

on the account of the decision of the graduation committee,

to be defended

on Thursday, 18th of June 2020 at 14.00hours

by

Priyanka Sekar

Born on the 14th November 1994

In Chennai, India

This thesis has been approved by:

Thesis supervisor: Prof. Dr. A. Blume (University of Twente)

Company supervisor: Dr. T. Wittmann (SunCoal Industries GmbH)

Dr. J. Podschun (SunCoal Industries GmbH)

Daily supervisors: Prof. Dr. A. Blume (University of Twente)

Dr. R. Anyszka (University of Twente)

ACKNOWLEDGEMENTS

The whole PDEng journey of this two year is one of the most memorable parts of my life. To describe this feeling in one line, I would say it is a struggle between my scientific challenges and emotions which has been incredible and precious experience for my own personal and professional development.

I hereby acknowledge with deep appreciation the excellent supervision of Prof. Dr. Anke Blume and Dr. Rafal Anyszka. Anke’s constant push to practicality has always invoked my passion for learning and helped me a lot during the time of my research and writing of this thesis. I truly appreciate her efforts and time that she has devoted for my work. Especially, during the last phase of my PDEng, her constant support and her valuable contributions are noteworthy. I really owe a big thanks for her advice and for giving me this opportunity to grow as a scientist and a critical researcher. I also remain indebted to Rafal for his cordial relationship and collaboration. The person who I admired the most in my life. His dedication and always being enthusiastic about science nature have been a strong motivation to complete this challenge.

My special gratitude is extended to Dr. Wilma Dierkes for always standing for me and providing a good hospitality during my miserable times. I sincerely thank and appreciate her caring attitude, patience, willingness to understand me and being a moral support during my PDEng.

I would also like to express my wholehearted thanks to Sir Dries and Ceciel (my angel) for their kind timely help. Also, I would like to extend my immense gratitude to the whole Elastomer Technology and Engineering group members for providing a good working atmosphere: Marzieh, Gina, Marcin, Zuza, Jin, Choi, Sun, Chai, Indira, Anmol, Dorota, Hans, Ayush, Amir, Carmela, Arqam, Neven (Jovana), Rounak, Masaki, Akansha, Chesidi, Xiazhon, Stefan, Chigusa, Marcel, Jan Willem, Eva, Marnick, Prof. Dr. Jacques, Dr. Kaewsakul, Dr. Sahakaro, Dr. Grunert, Dr. Bernal Ortega, Dr. Viol, Dr. Reuvekamp. They have been always like another family in Netherlands.

I would like to acknowledge the financial, material and technical support from Suncoal Industries GmbH, Berlin. A special thanks to Dr. Tobias Wittmann for believing in me and providing me this opportunity to work on this project. Also, I would like to thank Dr. Jacob Podschun, Dr. Gerd Schmaucks, Dominik and Alex for being supportive and friendly in this hardship.

Also, my indebtedness goes to my mother, brother, Amutha (aunt) and Anand for all their love, moral support and freedom they have given towards my choice of career and life style. I’m always grateful for their patience and sacrifice. This also was essential to keep me focused during this entire study period. Last but not least, a special thanks to all my close friends: Rajalakshmi, Ranjani, Iqbal, Keerthivasan, Ram Narayan, relatives and my well wishers.

Table of Contents

1 Introduction

1.1 Background & Motivation

Tire is a complex structure of the vehicle consisting of assembly of several components such as tread, sidewall, inner liner, etc., as shown in **Figure 1.1**. All these components are built either by a rubber compound designed with a specific chemical formulation or by constructive materials like reinforcing fabrics and steel cords to meet the vehicle's performance. Most of the raw materials (either the base raw material i.e., synthetic polymers or a supplementary material such as reinforcing fillers (carbon black), processing aids, anti-degradants, curatives etc.,) used for formulating a rubber compound are dependent on non-renewable fossil fuels. The dependency on these petroleum-based raw material is creating a global concern in relation to its deleterious impact on the environment such as global warming. Also, due to the fact that the market growth of the tire industry is increasing day by day with the growing vehicle sales and expanding automobile fleet, it can be clearly visualized that this expeditious development emerges at the expense of over-exploitation of non-renewable resources [1].

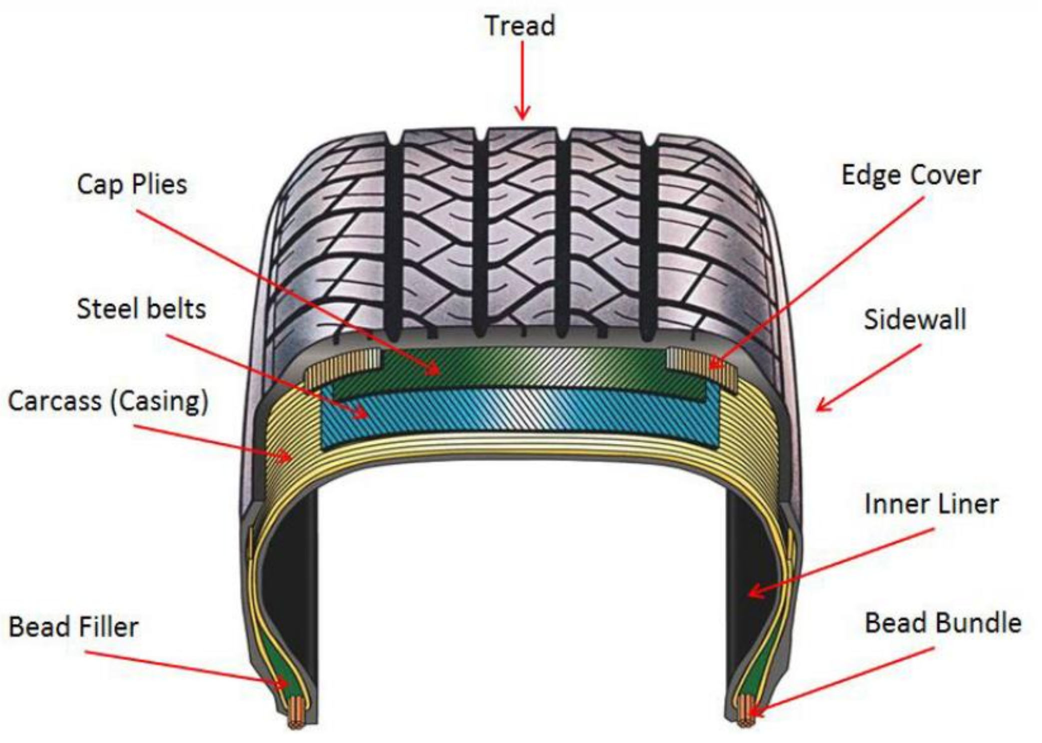


Figure 1.1 Construction of a passenger car tire [2]

More stringent rules and strict regulatory controls are being enforced by governing bodies in the view of neutralizing the global carbon footprint and sustaining the natural resources. One such regulation (No. 443/2009) is implemented by the European Union for reducing the CO_2 emission from passenger cars. The target was set to 130 g/km for 2015 which corresponds to a fuel consumption of around 5.6 l/100 km of petrol, whereas for 2021 the target to be achieved is 95 g/km (i.e., 4.1 l/100 km for petrol) [3]. Tires do contribute to the vehicle’s fuel consumption by influencing the rolling resistance. Any reduction in tire rolling loss would yield discernible fuel saving [4]. It is estimated that 10% reduction in tire rolling resistance can provide 1%-2% improvement in fuel economy for passenger vehicles [4]. Over past few decades, all these demands were addressed and fulfilled by the tire manufacturers through persistent development and advancement in tire tread compound, since it contributes to the large fraction of the total energy expended by the passenger car tire as shown in **Figure 1.2** without compromising the tire performance characteristics and balancing the “magic triangle” which features the relationship between rolling resistance, wet skid resistance and abrasion resistance. Especially, the revolution in filler technology through the replacement of traditional carbon black filler by mineral-based silica reduced rolling resistance roughly by 20%. Extended research gave a brief conclusion that filler parameters like morphology and surface characteristics, filler networking (both its architecture and strength), its loading and interaction with the polymer play a vital role in the viscoelastic behavior of the compound and affect the tire rolling resistance [5]. However, only with silica technology (for instance, with varied surface chemistries), it is not possible to meet the current EU demands of rolling resistance reduction of 20-30% resulting in 5%-6% decreased fuel consumption which would lead to lesser CO_2 emission from the present level [6].

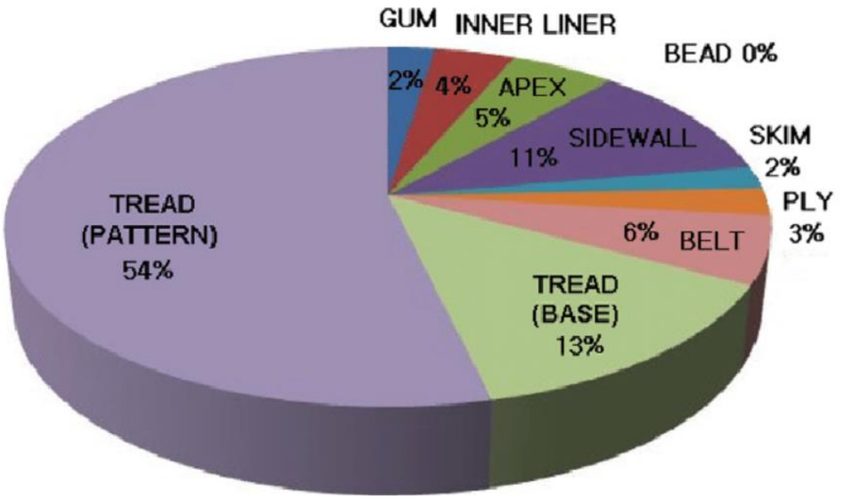


Figure 1.2 Contribution of passenger car tire components on vehicle rolling loss [7]

On the whole, to overcome the issues of non-renewable raw material debilitation and its environmental impact, tire manufacturers are driven towards the development of more green technologies and introduction of new alternative sustainable materials, which are able to provide a decline in tire hysteresis loss without affecting other tire performance criteria.

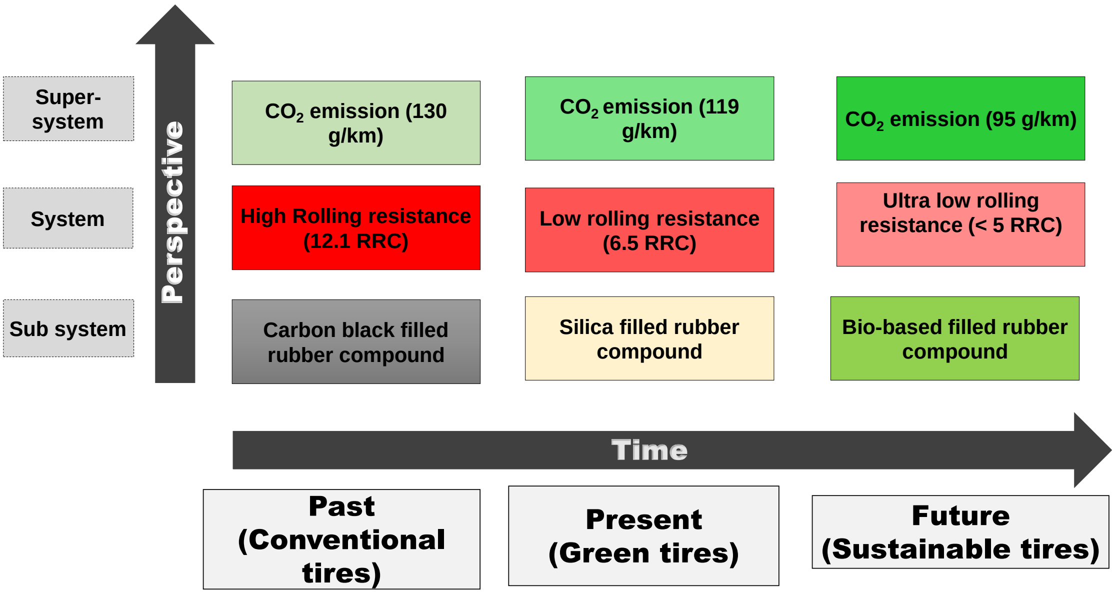


Figure 1.3 Schematic structure of the project motivation

The introduction of bio-based fillers in tires would be one of the economically viable solutions to boost sustainability and fuel economy targets as represented in **Figure 1.3**. However, the main challenge is to produce a sustainable counterpart for the products that have been evolving over decades with high technological standards. Thus, this project focusses on enhancing the reinforcing characteristics of one such sustainable bio-based material – lignin for tire tread application.

1.2 Company information

The whole project is supported by Suncoal Industries GmbH, Germany. They have developed Hydrothermal Carbonization Technology (HTC) to process ligno-cellulosic biomass into more technical and functional bio-based fillers (technical carbon) which might be utilized in material applications such as tires. The design project was initiated to improve the bio-based filler system for rubber reinforcement and to envisage its practical application in tires.

Apart from the technical carbons, bio-based platform chemicals or biofuels are also their area of commercialization.

1.3 Thesis structure

The thesis is composed of the following chapters:

Chapter 1: ***Introduction*** provides a general overview, motivation of the design project.

Chapter 2: ***Objectives*** comprises the problem outline and desired outcome of the project.

Chapter 3: ***Program of requirements*** introduces the stakeholders of the project and requirements of this design project in more detail, thereby finalizing the more specific achievables.

Chapter 4: ***Literature review*** covers the overview of the key components relevant to this design project.

Chapter 5: ***Design methodology*** presents the ideology and approach for developing the project.

Chapter 6: ***Development phase*** provides guideline steps for the implementation of the project plans.

Chapter 7: ***Experimental results and discussion***

Chapter 8: ***Design deliverables*** details the final prototype compound

Chapter 9: ***Summary and Outlook*** encapsulates and provides further prospective for improvement of the design.

2 Objectives

2.1 Description of design topic

Sustainability and circular economy has become the need of the hour in tire industry, since consumption of non-renewable resources and one-time use of tires pose a huge environmental challenge [8]. The ultimate goal of these two key topics is to maintain the product and material value for a long run thereby minimizing the utilization of the resources and waste generation [9]. To strive towards the ongoing needs, it is necessary to focus on all aspects of the tire; from materials sourced, to the production process, fuel efficiency and ultimately, the end-of tire life.

The current design work concentrates on developing one of these aspects, in particular, use of alternative renewable source (biomass) for the production of passenger car tire. A closer look at the composition of passenger car/light truck tires infer that synthetic rubber and filler covers vast portion as represented in **Figure 2.1**. Thus, replacing them by renewable alternatives would contribute to many ecological benefits. Of these, replacement of non-renewable fillers with renewable biomass has gained much attention due to their additional positive impact on tire rolling resistance. It is anticipated that Ligno-cellulosic biomass could be a promising alternative to fossil resources because of its abundancy, renewability and versatility. This research mainly focuses on the use of Hydrothermally Carbonized lignin (HTC lignin) derived from Ligno-cellulosic biomass as a sustainable filler to replace the conventional fossil and mineral-based rubber fillers in tire application.

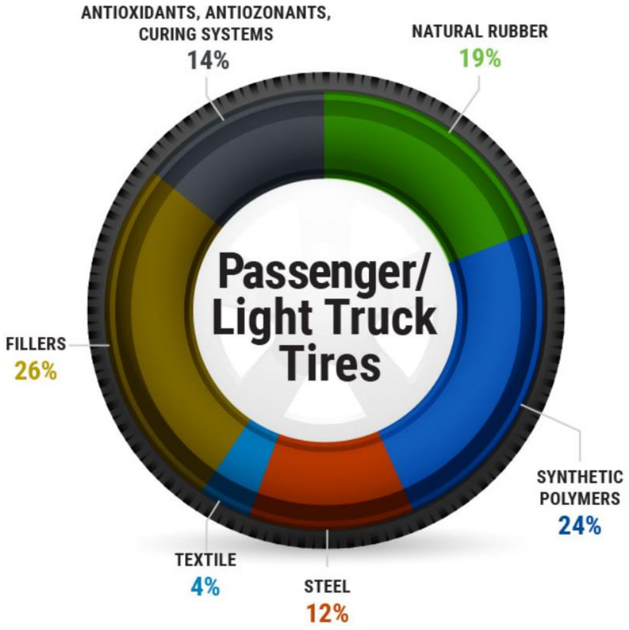


Figure 2.1 Raw materials composition of a tire [10]

2.2 Project Objectives

The focus of this PDEng project is to design a green sustainable tire tread compound using HTC lignin as a filler. The envisaged goal is to tailormade HTC lignin in such a way that it can reinforce and enhance both static and dynamic mechanical properties of the compound. The resulting properties also contribute to the improvement of tire specific properties such as wet traction, wear resistance, and rolling resistance. Under this context, the following objectives are to be accomplished:

- To understand the reinforcing potential of HTC lignin compared to conventional fillers.
- To comprehend the diverse structure and complex chemistry of HTC lignin in relation to rubber reinforcement.
- To anticipate if appropriate additives are needed to make HTC lignin compatible with hydrophobic rubber since bio-fillers in general are hydrophilic in nature.
- To understand the processing behavior to well disperse the modified HTC lignin in an elastomeric matrix
- To identify and define the crucial mixing parameters affecting the final compound properties.
- To investigate different compounding approaches to customize the HTC lignin filled compounds for use in tire tread application.

3 Program of requirements

The early phase of any design process is to define the requirements in terms of stakeholder needs which could ease the decision making process. Also, this could facilitate to work on committed goals without any uncertainties related to design [11]. Requirements could be either in the form of functional (technical/performance related) or non-functional (reliability, safety & environmental impact).

3.1 Functional requirements of the project

The first step in any requirement engineering process is to carry out a stakeholder analysis and to delineate the motivated requirements based on their needs [11].

3.1.1 Stakeholder analysis

The stakeholders and their goals for the current project can be viewed from different perspectives as shown in **Figure 3.1 & Table 1**. This also gives a hint of the considerations and constraints in developing the project.

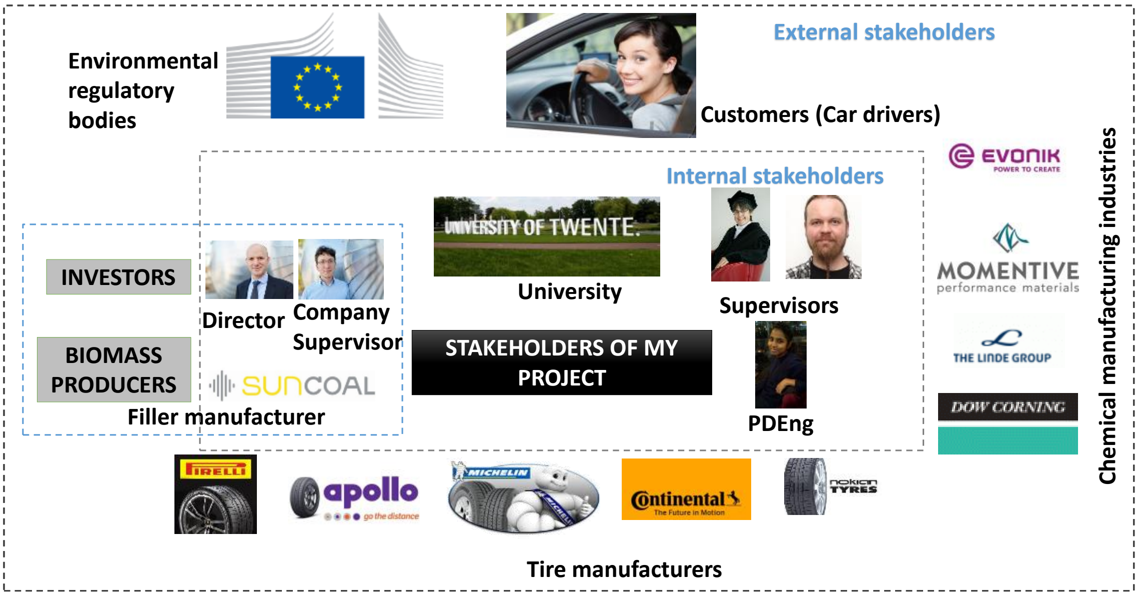


Figure 3.1 Stakeholder Analysis

Table 1 Anticipated goals of different stakeholders [12]

System Under Development (SUD)	
Normal operators (Bio-filler manufacturers)	To improve the HTC lignin fillers to meet the desired criteria for target applications
Maintenance operators (Supervisors)	To provide support to the intended work and to get a good scientific outcome
Operational support (Material specialist, Technician)	To develop skills in the field of fillers and implement them to obtain the desired rubber reinforcement
Immediate environment of the SUD	
Functional beneficiaries (Tire industry & consumers, University of Twente)	➢ To have durable and economic tires without compromising e.g. mileage or safety ➢ To provide businesses with access to their innovative ideas and technology through research or even work with businesses and other external organizations to actively introduce the technologies to market.
Interfacing systems (Chemical i.e., Coupling agent manufacturers)	To innovate new technologies and establish their market in the field of innovative solutions.
Wider environment of the SUD	
Financial beneficiaries (Bio-filler manufacturers)	➢ To gain profit ➢ To develop trust. i.e., investment worthy relationship among the customers and investors
Economical beneficiaries (Tire industries & Bio-filler manufacturers)	➢ To establish a sustainable market ➢ To establish market in the field of reinforcing fillers
Negative stakeholder (Conventional filler manufacturers)	➢ To sustain their filler market ➢ To enhance the filler properties further
Threat agent (Environmental Protection agency)	➢ To conserve the plants thereby preventing deforestation. ➢ To avoid microplastic pollution.

3.1.2 Project needs and requirements

Based on the stakeholder analysis and their anticipated goals, the following project **needs** & **requirements** motivated in terms of both internal & external stakeholder goals are summarized below:

3.1.2.1 Project needs

- To have an excellent reinforcement with HTC lignin filler in comparison with other conventional fillers
- To make the filler more compatible with rubber
- To provide a design guide (compounding and processing) for use in tires
- To achieve positive end-use properties (tire performance) with HTC lignin filled compound to be used in tire
- To consider the environmental implications of the technology to be developed

3.1.2.2 Design requirements

- To understand the surface properties of the HTC lignin filler which plays an important role in reinforcement
- To obtain model formulation for the desired tire component (e.g., tread) from journals or industries
- To review the range of coupling materials which are combined in an elastomeric formulation with HTC lignin filler to generate a defined set of mechanical properties (reinforcement)
- To define the key property guidelines, for example,

Hardness (Shore A)	55-65
Tensile strength (MPa)	>10
Reinforceability index (M300/M100)	3-4
Hysteresis properties (tan δ at 70 °C and 3% dynamic strain)	≤0.15
Hysteresis properties (tan δ at 0 °C and 1% dynamic strain)	>0.15
Mooney viscosity (MU)	50-60

- Accuracy in the measurement (i.e., it should be reproducible and reliable) under the standard conditions

- Economically feasible and scalable to industrial scale

3.2 Non-Functional requirements of the project

Only most important and sensible non-functional requirements desired for this design are being defined in this section. Also, not all the set requirements are standardized by a SMART (Specific, Measureable, Achievable, Relevant, Time-based) approach [13].

3.2.1 Safety/Risks

Safety is the prime concern of any industries. Since this design might deal with tailoring the surface of filler, it involves chemical modification reactions using surface modifier. During this surface modification (either by pre-modification in a reaction vessel or in-situ modification in the mixer), by-products may be evolved which could be toxic and hazardous to the environment. The following safety requirements are taken into consideration during the design phase:

- In the screening phase of different surface modifiers, minimal risk chemicals have to be selected based on the H-statement [14]. For example, H-statement stating fatal, unstable explosives, toxic if inhaled need to be strictly avoided.
- At the end of the design project, the potential hazards of the tailor-made filler during modification/mixing, if any, has to be reported in the form of a Safety Data Sheet (SDS) to protect the occupational workers.

Apart from the occupational safety requirement, the prototype design (i.e., tire) should meet required technical safety criteria demanded by the tire industry. High traction/grip between the wheel and road surface is desirable for safe driving. The grip (snow/wet/dry) characteristics of the compound can be determined in laboratory by dynamic mechanical analysis (DMA) or by laboratory abrasion tester 100 (LAT 100). The DMA parameters tan delta/E’/E* can be used as an indicator for grip characteristics. The following requirements has to be fulfilled by compound in comparison to reference compounds (prepared using conventional fillers) to ensure vehicle safety:

- low/comparable E’ at -20 °C (MPa) (snow indicator) [15]
- high/comparable tanδ at 0 °C (wet grip indicator) [16]
- high /comparable E*at 50 °C (MPa) (dry handling indicator) [17]

In case of LAT100, a high rating should be obtained in comparison to the reference compounds. This gives an indication that the achieved properties are better.

3.2.2 Reliability

Reliability of any system can be related to technological feasibility of that system for long service. Reliability of the design depends on the unaltered surface properties (durability of the formed bond between filler-surface modifier) during cyclic deformation and harsh environmental conditions. Also, wear resistance of the prototype tread in a real tire test should be similar or better than conventional tire treads. This was predicted by Laboratory Abrasion test (LAT 100).

3.2.3 Finances/Costs

The cost of technical lignin ranges from 50-750 USD/MT depending on the level of purity and isolation process [19]. In comparison to the conventional fillers, the price of the HTC lignin is lower. Thus, the newly designed system shouldn't exceed the existing costs of conventional fillers, meaning the selected surface modifier should be affordable making the whole system easier for implementation. Even, if the newly developed design increases the production cost, it can be compromised by the achieved performance and environmental benefits provided by the filler.

3.2.4 Environmental/Sustainability

This project is strongly connected to environmental issues and sustainability. The requirement of this system in terms of sustainability is to achieve low rolling resistance (tan delta at 60 °C < 0.15 at 3% dynamic strain) which in turn reduces vehicle's fuel consumption. Also, the filler as such is synthesized from ligno-cellulosic biomass, a non-edible plant residue which is a renewable resource and doesn't have any negative impact on the environment as well as doesn't compete with food supply as the first generation feedstocks e.g. starch based materials [18]. It is reported that around $5\text{-}36 \times 10^8$ tons of natural lignin are produced annually. Apart, from that more than 70 million tons of technical lignin are generated as waste by-products from paper and pulp industries and biorefineries [19], which itself could be a serious concern in the near future. The usage of this surplus carbonaceous waste as an alternative filler in tire application could conserve the exquisite non-renewable resources and is potentially sustainable.

3.2.5 Recyclability/Disposability

Recycling of end-of-use tires (closing the loop) is another major issue in the tire industry. Although, the design in particular doesn't focus on this issue, further implementation of the design in industrial scale should take into account this hot topic.

4 Literature review

This chapter consists of two subsections describing the background, context, and topics of this thesis. The first subsection deals with a general introduction to fillers, their characteristics influencing the rubber properties, and dynamic mechanical properties. The second subsection focusses more on lignin, some terminologies, and definitions followed by chemistry, isolation of lignin from biomass, their characterization techniques, and finally, the application of technical lignins and their limits in the rubber industry. The hydrothermal carbonization process will be shortly covered at the end of this chapter.

4.1 Fillers

Elastomers are the class of polymeric materials with a low glass transition temperature. These elastomers can be of either natural (NR) or synthetic origin (SBR, BR, EPDM, IIR, etc.). Due to their relatively low mechanical properties, reinforcing fillers are added to improve elastomer performance.

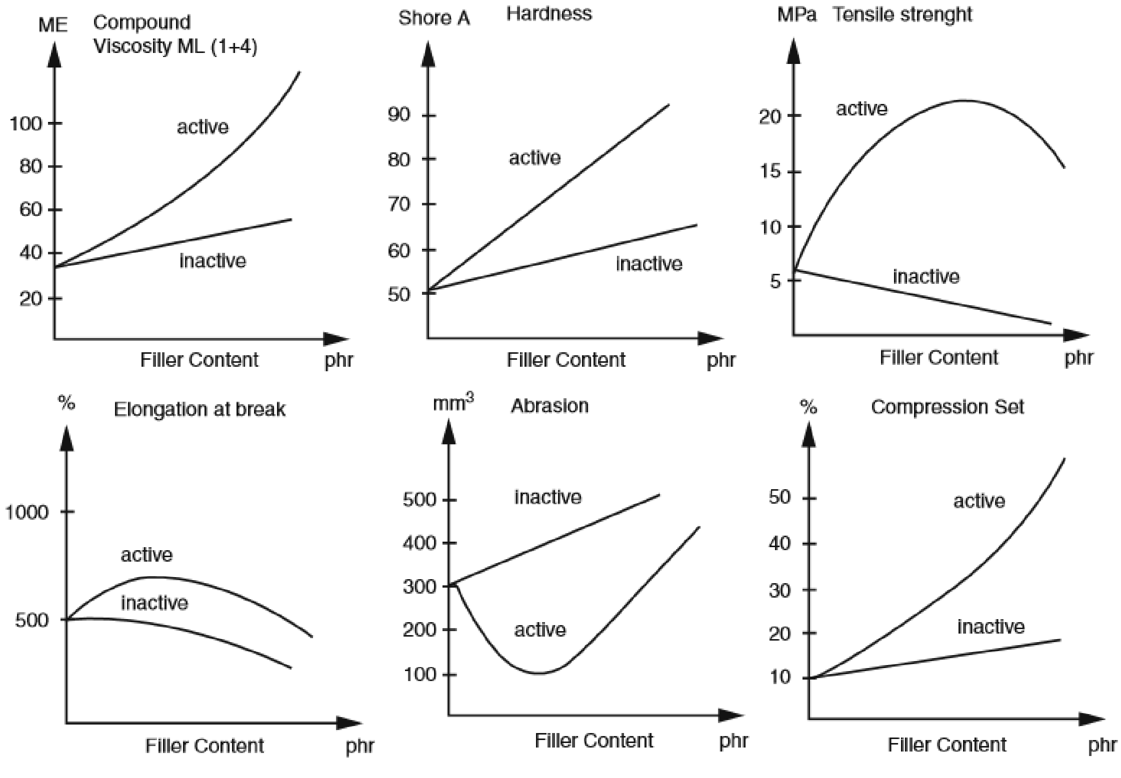


Figure 4.1 Influence of fillers on rubber properties [20-21]

Originally, particulate fillers were used for dilution to reduce cost, and for increasing the rigidity and hardness, but soon it was realized that a certain filler improved rubber properties like modulus, tensile strength, tear strength, abrasion resistance and dynamic properties such as hysteresis and fatigue resistance [20, 22]. Particulate fillers can be classified into two groups: (1) active/reinforcing filler (2) inactive/non-reinforcing filler based on the reinforcement exhibited by them, which can be well understood using **Figure 4.1**. Moreover, rubbers are always vulcanized, i.e., chemically cross-linked to have a highly elastic product capable of reversing back to its original shape (resilient properties) following very large deformations from a formable, viscoelastic nature. This can be imagined as a three-dimensional network, and the size of this will vary based on the crosslink density [23]. Besides the reinforcing filler, the formed crosslinks (crosslink density and their distribution) also influence the physical, mechanical, and viscoelastic properties of a vulcanizate. The general dependence of crosslink density on the properties of the rubber can be explained in **Figure 4.2** [24].

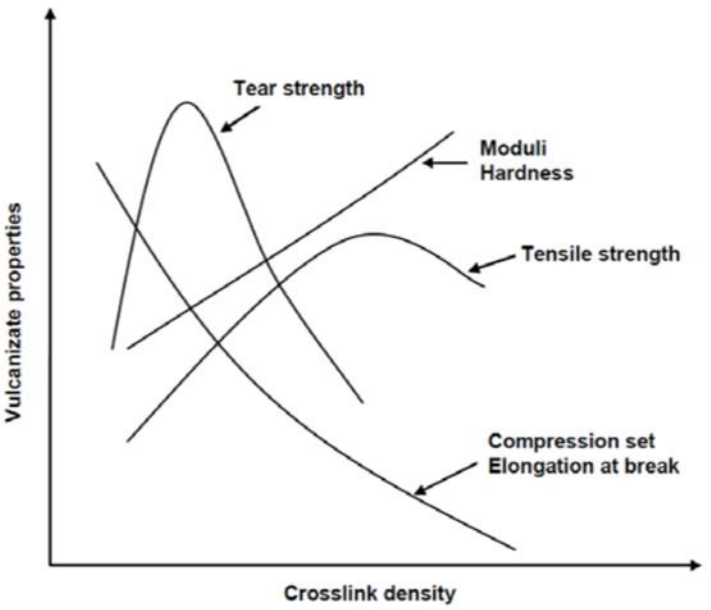


Figure 4.2 Influence of crosslink density on vulcanizates properties [24]

Thus, the use of fillers, together with accelerated sulfur vulcanization (or other crosslinking types), has remained the fundamental technique for achieving the broad range of mechanical properties required for the great variety of modern rubber products [25]. Furthermore, their addition could also enhance other exciting features to the final product (e.g., tire) such as rolling resistance, wear resistance, and abrasion resistance. The reinforcement of the elastomers by the particulate fillers to a large extent depends on the polymer properties, filler characteristics, and processing methods. Carbon black and silica are the reinforcing fillers most commonly used in rubber industries.

4.1.1 Filler characteristics influencing rubber reinforcement

Several filler properties are affecting the reinforcing characteristics of each type of filler used (for instance, carbon black, silica), namely particle size/surface area, structure, surface chemical characteristics/surface activity.

i. ***Primary particle size or specific surface area***: determines the effective contact area between the filler and polymer matrix [26].
ii. The ***structure*** plays an essential role in the restrictive motion of elastomer chains under strain [26]. Fillers are made of primary particles at the smallest size-scale (Angstrom to nanometer), which are strongly bonded to other primary particles to form a three dimensional aggregated structure (primary structure). These aggregates range from nanometer to micron in size, and they can interact with other aggregates, especially at higher loadings through weaker secondary bonding to form chain-like filler structures (carbon black) or clusters (silica), generally termed as 'secondary structure/agglomerates/filler network' as shown in **Figure 4.3**.

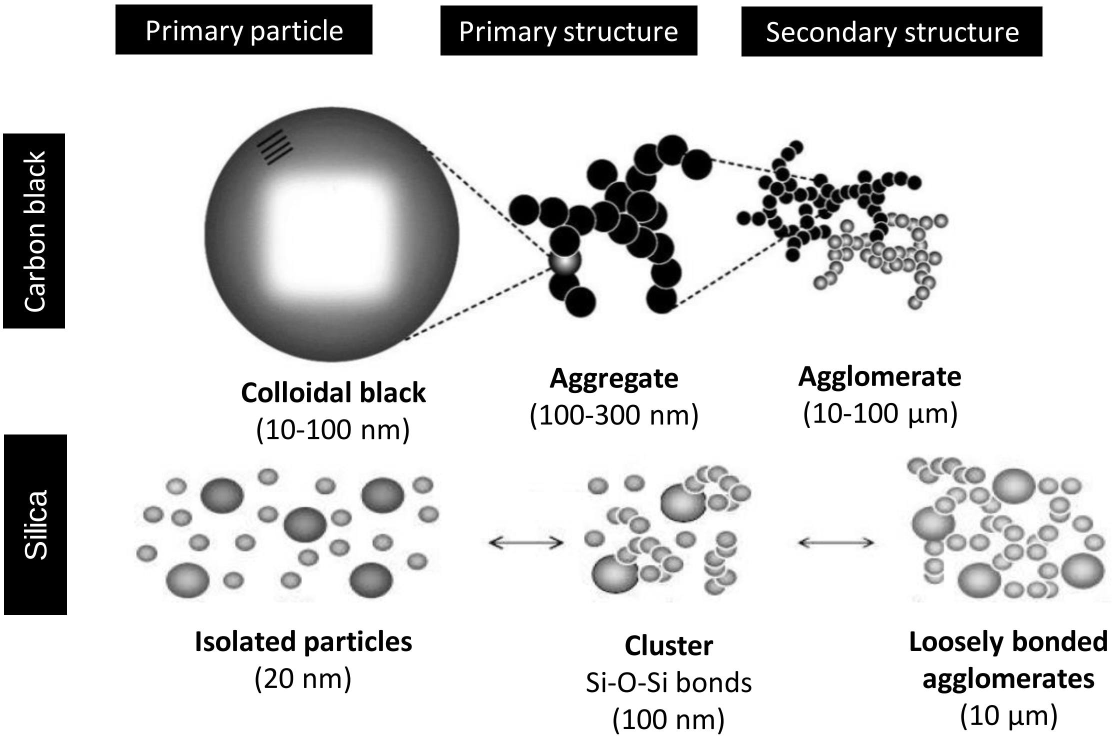
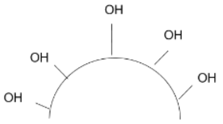
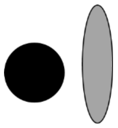
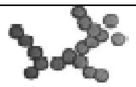
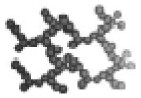


Figure 4.3 Basic structure of carbon black and silica filler [27-28]

iii. The ***surface activity***, which is the predominant factor concerning filler-filler and filler-polymer interaction [26].

For instance, the effect of silica characteristics influencing the polymer can be seen in **Table 2** [29].

Table 2 Silica filler characteristics [28-29]

	Morphology	Filler effect
	Surface chemistry (~10 Å)	Filler-Filler Filler-polymer
	Primary particle volume, shape (5-45 nm)	Hydrodynamic/mechanical reinforcement
	Aggregate (100-500 nm)	Hydrodynamic reinforcement Occluded rubber
	Agglomerate (>500 nm)	Filler networking Trapped rubber

Along with the characteristics mentioned above, the amount of filler added to the rubber also influences the reinforcement properties. There is an optimum loading for reinforcement properties such as tensile strength, tear, and abrasion resistance, whereas stiffness increases steadily, and elongation decreases at higher loadings. These properties also vary with the type of filler used. The optimum occurs because the reinforcing effect (surface effect) is counteracted and finally dominated by a dilution effect (volume effect).

4.1.2 Mechanism of rubber reinforcement

The reinforcement of rubber by colloidal fillers like carbon black or silica is a fascinating phenomenon. Since it is well known that the presence of small amounts of impurities in rubber such as sand will generally act as local stress concentration sites, which in turn initiate failure. However, it is surprising that the addition of similar rigid particulate fillers like carbon black and silica to rubber compounds imparts additional strength to the rubber [30]. This reinforcing potential is mainly due to two effects:

- the formation of a physically bonded flexible filler network (filler-filler interactions),
- strong polymer-filler interactions that arise from a high surface activity, and specific surface of the filler particles.

Thus, there is a strong impact on the rubber’s static and dynamic behavior upon the addition of fillers [30]. The modulus of filled rubbers decreases with increasing applied dynamic strain up to intermediate amplitudes. This typical behavior is shown in **Figure 4.4** using silica and carbon black compounds**.** This strain-dependent modulus is known as the Payne effect. Similar to this, it can also be noticed that some part of the modulus is strain-independent. This strain-independent shear modulus is a contribution from polymer network, hydrodynamic effect, and in-rubber structures [20, 26].

Hydrodynamic effect

The addition of rigid spherical particles results in a strain amplification effect, which cannot be deformed. As a consequence, the intrinsic strain of the polymer matrix is higher than the external strain yielding a strain-independent contribution to the modulus.

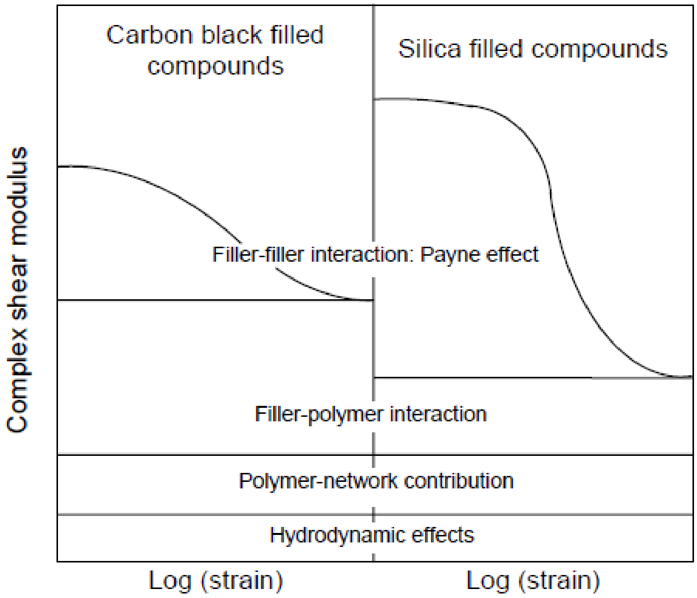


Figure 4.4 Different strain-dependent and -independent contributors to reinforcement: comparison of carbon black and silica [20]

Polymer network

The polymer network contribution depends on the crosslink density of the matrix and the nature of the polymer.

In-rubber structure (polymer-filler interaction)

The in-rubber structure can be understood as a combination of the structure of the filler in the in-rubber state (filler aggregates or agglomerates) and the extent of filler-polymer interaction (bound rubber and occluded rubber/rubber shell). Occluded rubber is a geometrical concept introduced by Medalia where rubber fills the internal voids of the filler aggregates, making it unable to participate in the macro-deformation. This portion of rubber behaves more like the rigid filler particle rather than the polymer matrix, which results in the increased effective volume of filler with regard to the stress-strain behavior of the filled rubber [31]. Filler-polymer interactions, detected as bound rubber, significantly increase the storage modulus G’ with increasing filler load. These are elastomer chains immobilized on the filler surface, which cannot be extracted from uncured filled rubber, not even by extraction with a good solvent. This can be attributed to physical (van der Waals) as well as chemical linkages or a mixture of both. In the case of the silica-silane system, this interaction is formed by chemical linkages [20, 26].

Filler-Filler interaction (Payne effect)

The elastic modulus of filled rubber is strongly dependent on deformation and decreases substantially at higher strains ('Payne effect'). This is attributed to the presence and breakdown of the filler network during dynamic deformation. The sigmoidal decline of the storage modulus at zero amplitude (G_0') to a high amplitude plateau G_i' was interpreted by Payne as the breakage of physical (London and van der Waals) bonds between carbon black filler particles. At low deformations, the energetic elastic contribution of the rigid filler network is dominant, in contrast, at high deformations, the filler has only a limited effect, which is hydrodynamic and caused by the rubber-filler interaction. It was also noted that the value G_0' is mostly recoverable upon return to smaller amplitudes, and it is shown that the phenomenon is independent of the polymer, provided enough time is allowed for recovery. However, it is dependent on the type of filler used. This phenomenon can be seen clearly in **Figure 4.4**, when silica is used as reinforcing filler, a high level of elastic modulus at low strains and a drop of elastic modulus at higher strain amplitudes prove the existence of a stable filler network formed by silica.[20, 27] The breakdown and reformation of the network linkages during dynamic deformation consumes energy (hysteresis loss), which reflects in the variation of the tangent delta with increasing dynamic strain.

4.1.3 Dynamic mechanical properties of rubber compound and tire performance

Incorporation of a filler system into the rubber influences its dynamic properties, especially the dynamic modulus and hysteresis during dynamic strain. It is well known that the dynamic properties of compounds can be influenced by filler parameters like morphology and surface characteristics (interaction between filler and polymer), filler networking (both its architecture and strength), and filler loading [32-33]. These dynamic properties, in turn, affect the tire’s final performance. The major functions of the tire in automobiles are as follows: moving load, providing isolation from road irregularities, transferring forces in driving, braking, and steering under all types of weather conditions on dry, wet, and ice/snow road surfaces. Furthermore, tires are expected to perform these functions with the following criteria, and all these are linked to the tread compound of the tire since it is the only part which is in contact with the road surfaces:

(a) The first and foremost thing is that it should generate the highest possible traction force on the road surface, thereby avoiding slippage by creating a good grip, which is an indication of safety. This traction is determined by the friction properties of the tread compound.

(b) For a good comfortability, the steering properties should be precise and highly predictable under all handling situations, which depends on the stiffness of the tread compound, and especially on its dynamic modulus and thereby improving the durability of the tire. This is related to the damping behavior of the compound.

(c) It should possess a low rolling resistance, which largely depends on the loss modulus, which is related to the dynamic hysteresis of the tread compound. This is required for improved fuel efficiency.

Tire performance criteria (rolling resistance, wet traction, and abrasion resistance) are significantly affected by the viscoelasticity of rubber compounds. Therefore, understanding the theory of viscoelasticity is extremely important in the tire industry to reach the most favorable final properties of rubber compounds. Rubber is a viscoelastic material: when it is deformed, a part of the energy is stored elastically (related to storage modulus G'), and the remaining part is dissipated as heat (relating to loss modulus G") into the material. This hysteretic loss is not recoverable and contributes to the total drag force of a moving vehicle. Both G' and G", have a strong dependence on frequency and temperature. Since time (frequency) -temperature superposition principle can be applied for the viscoelasticity of rubber compounds, several indications enabling to predict tire performances can be obtained by performing viscoelasticity measurements at different temperatures. The deformation frequency of a tire during the normal rotation is known to be at ca. 10 Hz and for sliding over the unevenness surface of the road between 10^3-10^6 Hz, respectively. 10 Hz corresponds to ca. 60 °C, and 10^3-10^6 Hz corresponds to the range of -10 to +10 °C under the normal conditions of the viscoelasticity measurement. Therefore, the values of the tangent delta at these temperatures can be used as indicators for the rolling resistance and wet grip performance of the tire. Herein, tan delta at 60 °C can precisely predict the rolling resistance, while tan delta at 0 °C has a certain limitation due to the complexity of the friction mechanism. The relationship between the viscoelastic properties of rubbers at different temperatures and tire performance is shown in **Figure 4.5** [34].

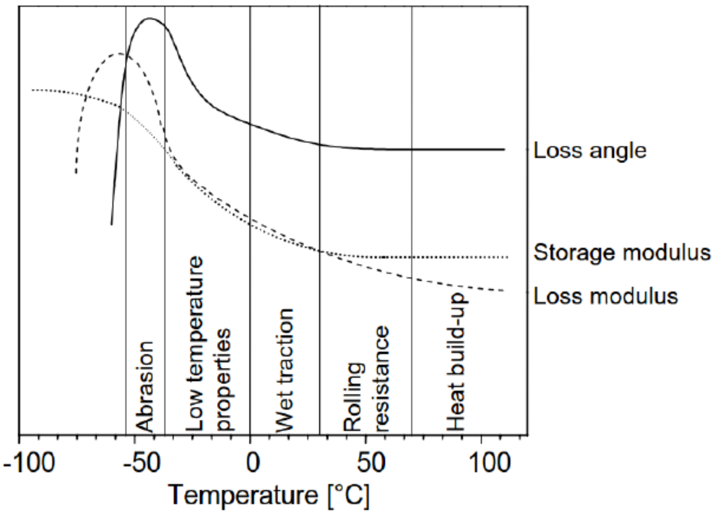


Figure 4.5 Temperature dependence of dynamic properties of polymers and tire performance at different temperatures [20, 27]

Different fillers influence dynamic properties differently. **Figure 4.5** presents the variation of tan *δ* values with different temperatures for carbon black and silica filled compounds.

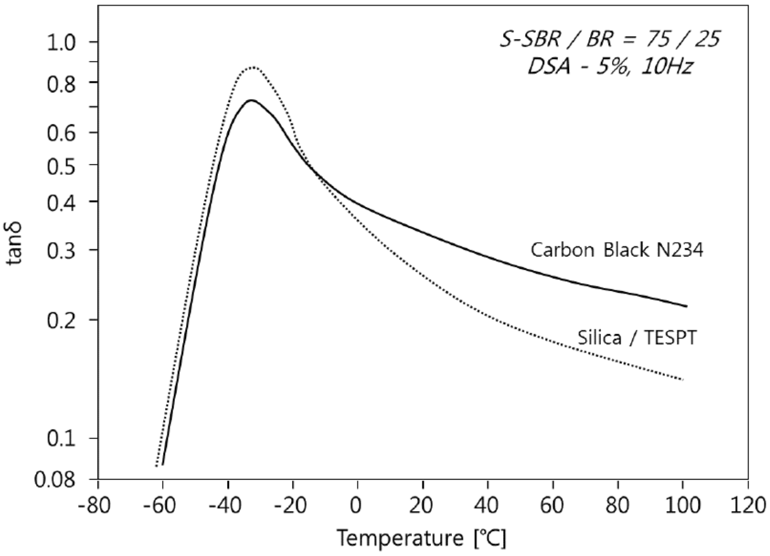


Figure 4.6 Variation of tan δ with temperature on carbon black and silica filled compounds [116]

sThis indicated that silica filled rubber has advantages in terms of rolling resistance and wet traction performance compared to carbon black filled rubber. The main reason for these differences between silica and carbon black reinforced compounds is the difference in surface properties of the two fillers. The silanization reaction occurring in silica filled compounds leads to increased filler-polymer interactions through chemical bonds, which improves the rolling resistance properties [20, 27]. The improvement in wet grip properties is attributed to the polar and hydrophilic silica surface, which can interact with the water film on the surface and can break it easier compared to a carbon black containing surface [34].

4.2 Lignin as an alternative filler for rubber compounds

Recently, sustainability, renewability, commercial viability, and environmental impact have become the major focus of the tire industry. The focus on the development of green tire formulated from renewable resources holds a promising outcome. Recent trends in technology innovation for green tires incorporate a bio-filler to substitute non-renewable fillers. The prominent concern in this area is their quantitative production to meet the demands of the tire industry and also ethical concerns such as restriction for the use of edible food sources as bio-filler. Lignin offers many possibilities as reinforcing filler since it doesn’t compete with edible food sources, and also it has a chemical composition that represents 30% of all non-fossil organic carbon [35]. Apart from this, it is abundantly available and relatively low cost when the conversion to products can be carried out economically and sustainably. It is important to recognize that the annual production of inedible native lignin on earth is in the range of 5-36*10^8 tons, and it is estimated that over 50 million tons of lignin is extracted by paper and pulp industries alone as technical lignin. Of these, around 95% of produced lignin is burnt for energy, and the remaining 5% is used for low-end commercial applications, including additives, dispersants, binders or surfactants, etc. [36]. This justifies the need to use this economical, potentially sustainable and versatile material in a more efficient, high engineering applications such as tires. Some of the challenging aspects of lignin (biomass source, structure, functional groups, isolation techniques) and characterization techniques will be covered under this section.

4.2.1 Chemistry of lignin

Lignin is the second most abundant renewable natural resource next to cellulose. It is a complex aromatic polymer consisting of basic phenylpropane units such as guaiacyl (G-unit), syringyl (S-unit), and p-hydroxyphenyl (H-unit) formed by polymerization of hydroxycinnamyl alcohols such as coniferyl, sinapyl and p-coumaryl alcohol respectively [37-38]. These key building blocks are usually known as monolignols, differing only in their degree of methoxylation, as represented in **Figure 4.7**.

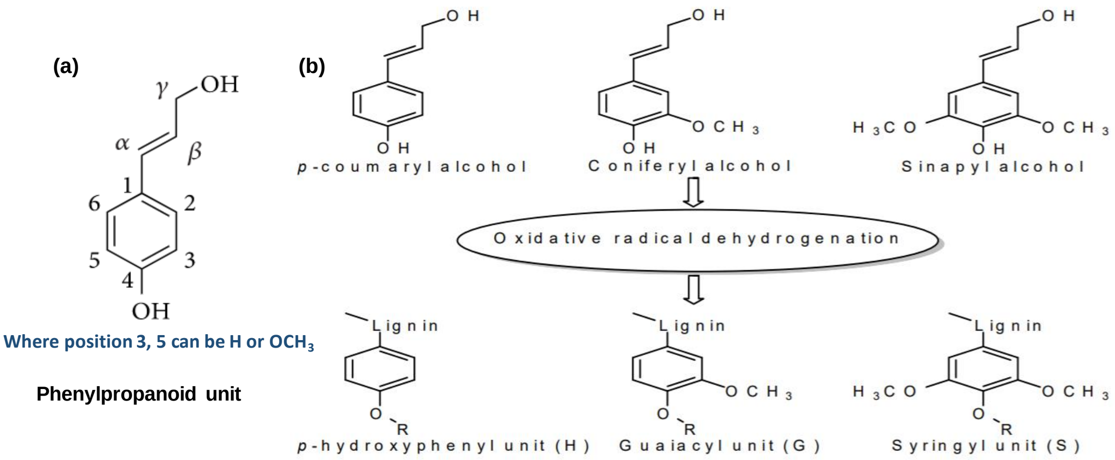


Figure 4.7 (a) General structure of monolignol (b) Structure of major monomers of lignin and their polymerization products [39]

The relative proportion of these units depends on the biomass source (hardwood, softwood, annual plants like grass). In softwoods, guaiacyl propanol, G-unit (coniferyl alcohol) is the main unit (90%) with other propanols such as p-coumaryl (H-unit) and sinapyl (S-unit). The lignin of hardwood is composed of a mixture of G- and S- units. Grass lignins are primarily derived from G- and S- units with 10-20% H- units [40]. Thus, based on the wood type (soft and hard), the structure and content of lignin in the lignocellulosic composition also vary. This is mainly due to the variation in the degree of methoxylation, which plays an important role in the type of bonds formed and also in the extent of cross-linking. Since the chemical structure of lignin is complex and changes according to the biomass source, it is not possible to define the precise structure of lignin as a chemical molecule. However, Freudenberg proposed a hypothetic structural formula of a lignin fragment, as shown in **Figure 4.8**.

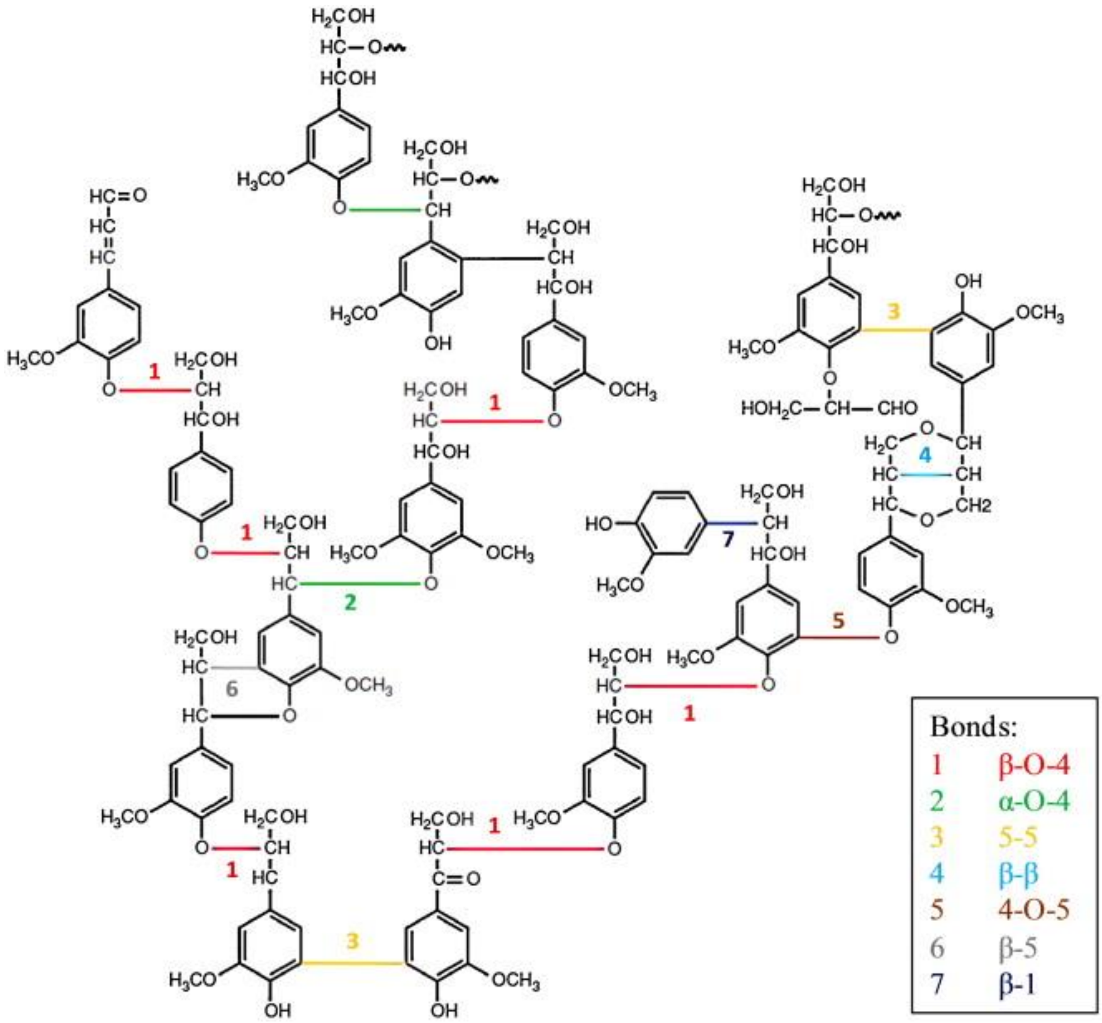


Figure 4.8 Hypothetical structural formula of Softwood lignin [35-36]

Based on Freudenberg's structural formula, it is obvious that during polymerization, most of the phenylpropane units or C_9(monolignols) are joined together either by alkyl-aryl ether units, i.e., C-O-C (α-O-4, β-O-4, 4-O-5), or C-C (β-5, 5-5, β-1, β-β) linkages to form complex three-dimensional molecular architectures [36]. It can be concluded that lignin is an amorphous (disordered), three-dimensional hetero-polymer without any overall defined chemical structure. Apart from this heterogeneity, the oxygen in the lignin can belong to a variety of functions and groups. It is well known from the monolignols that the attached oxygen is either in the form of methoxy groups or in phenolic hydroxyls, as represented in **Figure 4.7 & 4.8** [41]. However, during polymerization, several other functional groups can be formed, such as primary and secondary aliphatic hydroxyl, carbonyl groups such as ketone & aldehyde, carboxylic acid groups, as depicted in **Figure 4.9**. These functional groups confer unique functional properties to lignin depending upon their amount, nature, and isolation process.

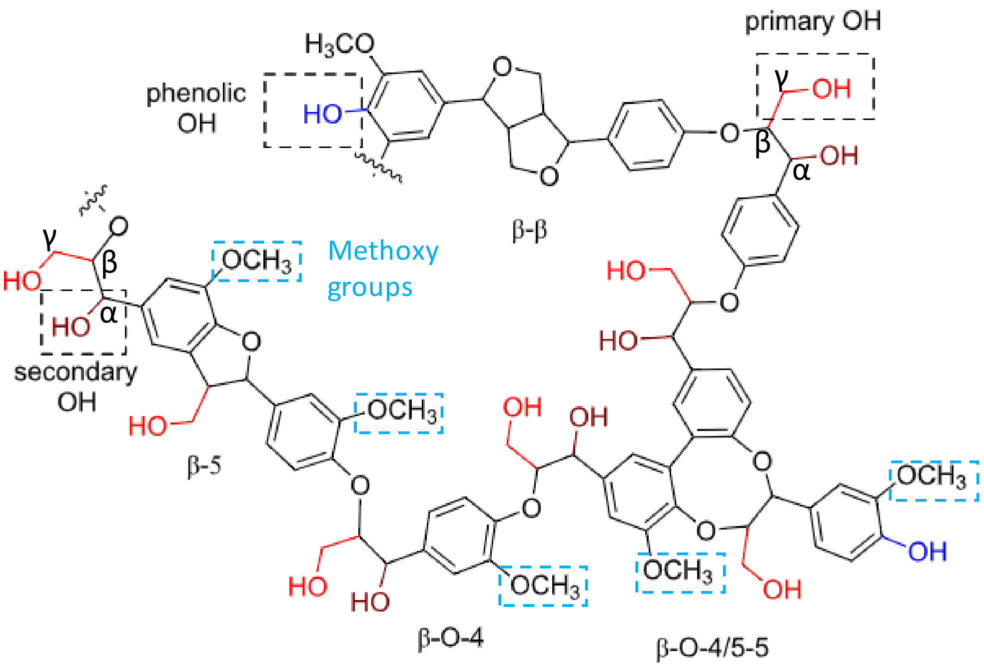


Figure 4.9 Molecular representation of lignin showing hydroxyl functional groups and methoxy groups [42]

Thus, the generic structure of native lignin can be described by basic units (phenylpropanoid units), inter-unit linkages (alkyl-aryl ether units or C-C units), and functionality (-OH, -OCH_3, etc.). Based on this, it can be concluded that the structure of lignin itself makes their isolation (which will be discussed in the upcoming **Section 4.2.2**) complicated as it involves depolymerization as well as cleavage of lignin-carbohydrate covalent bonds.

4.2.2 Isolation of lignin from wood

In bio-refineries and pulping industries, wood and other lignocellulosic resources are used to extract the cellulose and hemicellulose for ethanol or paper production. At the same time, lignin is considered a low-value residual/waste byproduct. This is mainly due to its complex structure, as discussed in **Section 4.2.1** and uncertain reactivity of lignin, which limits its wide-scale usage. This extraction process can involve different physical, chemical, and biochemical treatment methods and can be termed as delignification / isolation /cooking process. Depending on the isolation procedure, the native lignin undergoes profound structural changes and significant modifications of molecular weight distribution as well as the distribution of functional groups based on which different physical and chemical properties are obtained [36, 43]. These modified lignin samples are referred to as technical lignin. **Figure 4.10** shows the classification of the commercial isolation process [35-36, 43]. The acid sulfite and sulfate/Kraft processes are the common delignification processes, and the technical lignins produced by these techniques are named as sulfite (lignosulphonates) and alkali/Kraft lignins, respectively. There are also some known sulfur-free delignification processes such as solvent pulping and soda pulping process where alcohol-water mixtures and alkaline medium respectively used to extract the lignin.

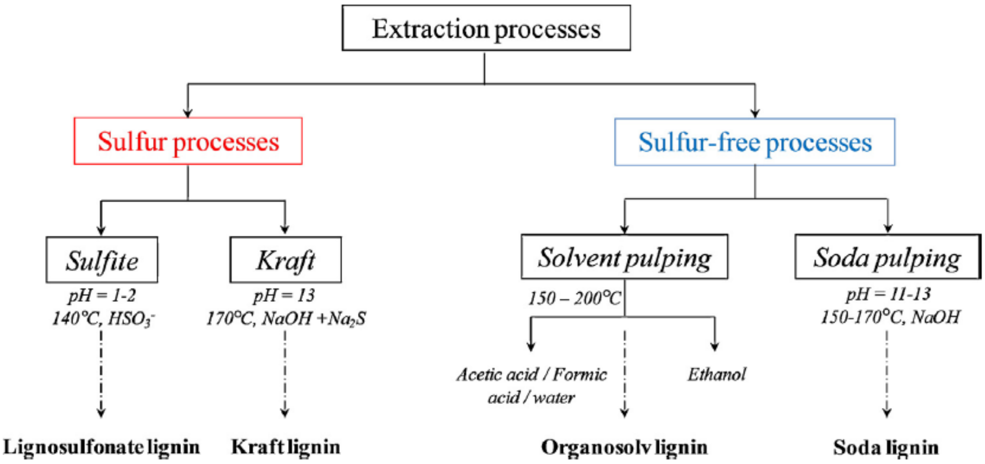


Figure 4.10 Industrial processes for the production of technical lignins [36]

4.2.3 Characterization of lignin

4.2.3.1 Structure of lignin

Since lignin is a heterogeneous polymer which is influenced by several factors (such as plant origin, isolation technique, post-treatment/purification), it is important to distinguish the structural differences and concentration of surface functional groups of the obtained lignins. Spectroscopic methods such as Ultraviolet-Visible (UV-Vis), Fourier Transform Infrared (FTIR) [44], Raman [45], both solid and liquid states of One-dimensional ^{1}H, ^{13}C, ^{31}P, and Two-Dimensional Heteronuclear Single Quantum Coherence (2D HSQC) NMR spectroscopies [44, 46-51] and other chemical degradative methods like pyrolysis GC-MS, permanganate oxidation, nitrobenzene oxidation, and thioacidolysis can reveal the H / G / S composition of the lignin [43, 52]. These methods are based on the cleavage of the lignin backbone and analysis of the fragments obtained. Based on the specificity of the treatments, the obtained data changes. In recent years, one and two dimensional NMR spectroscopies have become indispensable tools for the structural elucidation in comparison to other spectroscopic techniques due to their high resolution enabling a larger amount of information to be obtained [53]. These methods have confirmed the presence and distribution of the various functionalities present in lignin and have provided additional structural information regarding the H/G/S units. Despite the advances in these NMR approaches, both 1D (e.g., ^{1}H and ^{13}C NMR) and 2D correlation (e.g., HSQC) techniques have their limitations; 2D NMR is typically not fully quantitative, and 1D NMR usually suffers from the spectral overlap of functionality. An alternative approach to the abovementioned ^{13}C and ^{1}H NMR methodologies is to selectively label functional groups such as hydroxyl groups with a specific NMR-active nucleus and then analyze the derivatized substrate by NMR. These active nuclei normally have much broader chemical shift ranges with less signal overlap and less interference from the homonuclear coupling. Phosphitylation followed by ^{31}P NMR analysis is one of the first methodologies to use this approach to characterize the lignin structure. It uses the phosphorylating agent 2-chloro-4,4,5,5-tetramethyl 1,3,2-dioxaphospholane (TMDP). The reactions of TMDP with hydroxyl functional groups are illustrated in **Figure 4.11**. This leads to phosphite products which are resolvable by ^{31}P NMR into separate regions arising from aliphatic, phenolic and carboxylic groups. The peak assignment of these groups in the spectra is listed in **Table 3.**

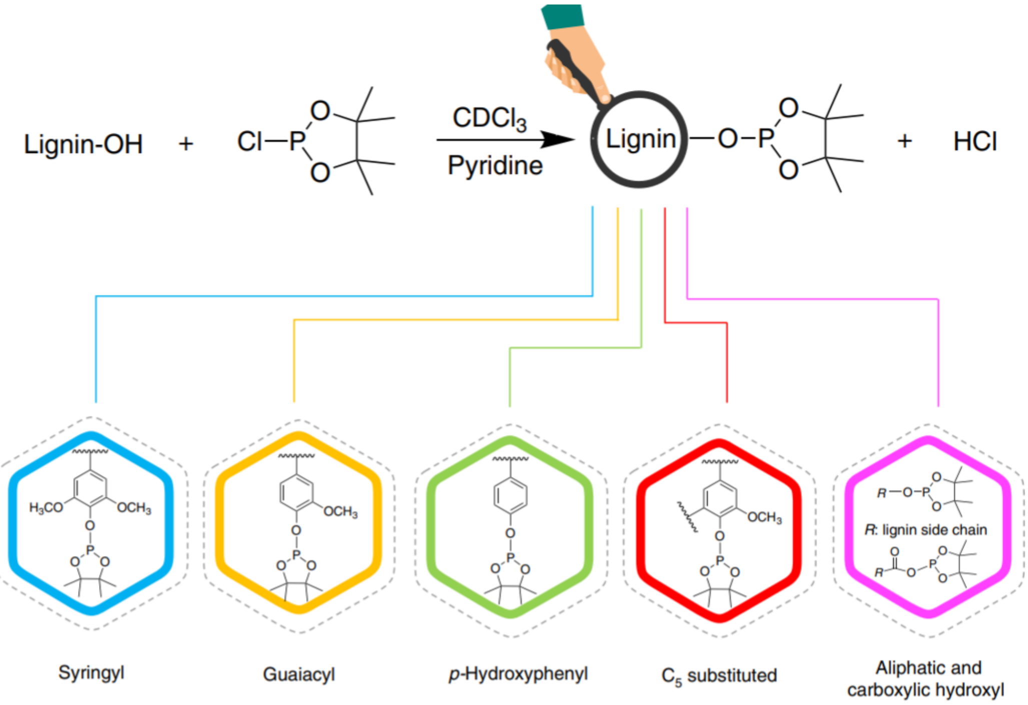


Figure 4.11 Derivatization of phenolic structures with 2-chloro-4,4,5,5-tetramethyl 1,3,2-dioxaphospholane (TMDP) in the presence of solvents [54]

Table 3 Typical integration regions for lignin in a ^{31}P NMR spectrum [54]

Chemical shift/ppm	Structural assignments
145.5-150.0	Aliphatic OH
137.6-144.0	Phenolic OH
140.0-144.5	C5 substituted
141.2	5-5
142.3	4-O-5
142.7	Syringyl
143.5	B-5
139.0-140.2	Guaiacyl
137.8	p-Hydroxyphenyl
133.6-136.0	Carboxylic acid OH

4.2.3.2 Functional group analysis

Much research has focused on functional groups, as discussed in **Section 4.2.1**, and all these different groups confer unique functional properties to lignin depending on their amount, nature, and isolation process. Wet chemical methods for the measurement of specific lignin functional groups can be found in the literature [52]. Among these groups, phenolic hydroxyl groups influence solubility and reactivity of isolated lignin. The phenolic hydroxyl group is one of the most important functionalities affecting the physical and chemical properties of the lignin during delignification. The chemical reactivity of lignin in various modification processes is also profoundly influenced by its phenolic hydroxyl content (e.g., in the reaction with formaldehyde for the production of lignin adhesives). Thus, quantitative measurements of phenolic hydroxyl groups provide pertinent information relating to the structure and reactivity of lignin.

Determination of phenolic hydroxyl groups

The quantitative analysis of phenolic hydroxyl groups can be performed by several methods, both physical and chemical, or combinations of both, as shown in **Table 4**. Each technique has its advantages and disadvantages [55].

Table 4 Techniques to determine phenolic OH groups [56]

Methods	Techniques
Wet-chemistry methods	➢ Diazomethane methylation [57] ➢ Aminolysis [55, 58] ➢ Periodate oxidation [59]
Analytical/physical methods	➢ Potentiometric or conductometric Titration [60-61] ➢ UV spectrophotometry [62-63] ➢ NMR spectroscopy [57]
Indirect degradation methods	➢ Permanganate reaction ➢ Thioacidolysis [64] ➢ Pyrolytic gas chromatography [65]

Wet chemical and indirect degradation methods can provide a precise understanding of specific functional groups and structural moieties. These studies also indirectly contribute to the analysis of lignin structure. In contrast, these methods are time-consuming, and often correction coefficients were needed for accurate and quantitative measurements of functional groups [53]. Ultraviolet (UV) spectrophotometry has been extensively employed in the study of the chemistry and molecular structure of lignins due to its ease of measurement [66]. In particular, modified UV spectrophotometry based on Δε (ionization difference) method of Aulin-Erdtman has been used widely to determine the phenolic –OH content of lignin. The method determines the phenolic content based on the difference in spectroscopic properties of ionized (i.e., alkaline media) and the non-ionized phenol (i.e., in neutral media) at 300 and 350 nm [56, 63]. The drawbacks of this technique are as follows:

- suitable only for soluble lignin
- it is not absolute since the measurement must be calibrated by using appropriate lignin model compounds or lignin of known phenolic hydroxyl content [63]

Due to this drawback of the Δε method, UV/VIS spectrophotometry based on colorimetric reactions was developed, which is a relatively simple, fast, reliable, and inexpensive method for determining the phenolic hydroxyls in lignin. De Sousa developed, e.g., a procedure for the determination of phenolic –OH groups using UV. This method is based on a phosphotungstic-phosphomolybdenum reagent to produce a blue color, which is proportional to the total amount of phenolic hydroxyl groups and which is easy to detect by visible light spectrophotometry [67].

4.2.4 Use of technical lignin as a natural alternative filler

Several studies exist on lignin-based rubber compounds which focus on reinforcement, dynamic mechanical properties, and rolling resistance [68-72]. Some papers from the literature about the use of lignin in the rubber industry are highlighted in **Table 5**.

The use of lignin as reinforcing filler was studied as early as 1947 by Keilen, and it is reported that when Kraft lignin was co-precipitated with synthetic or natural rubber latex, it exhibits a high degree of dispersion resulting in 5-10 times shorter milling time than the gum rubber. It was also concluded that the obtained tensile strength values are similar to those obtained using channel blacks at low loadings and higher tensile strengths and tear resistances at high loadings [70, 77]. The observed good results of the latex co-precipitation method are related to the formation of fine particle size during coprecipitation resulting in their homogeneous distribution in the rubber compound [40]. Several studies were carried out to investigate the influence of co-precipitation conditions (temperature, pH, the concentration of lignin and surfactant) on rubber properties and how to overcome the problem of the slow rate of cure of co-precipitated lignin natural rubber compounds. All these studies of co-precipitation of rubber latex and alkaline solutions of lignin illustrate that in this way lignin can reach the reinforcing level of carbon black or silica of equivalent particle characteristics [40]. In contrast to these findings, co-precipitation methods cause a major issue limiting lignin’s application. During this process, acid is employed as flocculant. The pH of the used acid plays an important role in governing the particle size of lignin. If the pH value ranges below 4, it result in an irreversible aggregation of lignin particles, which further can deteriorate the performance of rubber [78]. Furthermore, the flocculation and filtration of lignin/rubber co-precipitates are extremely slow when the ratio of lignin to rubber is high, limiting further development of lignin-based rubber composites [79]. Hence, a direct mixing of lignin and rubber is pursued because of its industrial availability. But conventional mixing of Kraft lignin powder into the rubber matrix shows almost very little to no reinforcement of mechanical properties, and the conclusions from these studies considered lignin as an inert filler [40, 80,81]. The cause of this disparity in behavior is related to the large particle size of lignin (ranging from 10 µm to >100 µm) and the lack of interfacial interactions between the lignin and the rubber matrix [79, 81-82]. To improve the reinforcing efficiency of lignin, some researchers proposed surface chemical modification techniques and use of hybrid filler technology to address the issue of the dispersion and compatibility of lignin in the rubber matrix. For instance, chemical modifications of sulfur-free lignin with hexamethylenetetramine [76] or lignosulphonates with cyclohexylamine [83] show an improvement in compatibility with non-polar rubbers leading to enhanced properties. These studies also highlight the fact that even though surface chemical modification provides a finite reinforcing effect, the modified lignin still lacks strong interfacial adhesion with rubber limiting its dispersion behavior at nano-scale.

Table 5 Application of technical lignins as a rubber filler [40]

Type of Lignin	**Rubber Type**	**Application**	**Finding**
Co-precipitation of lignin with latex			
Alkali Lignin	NR latex	Reinforcing filler	The improved oil resistance of rubber latex film and enhanced strength at loading between 10 and 12 wt.% [73]
Sulfate Lignin	SBR	Cationic lignin modified with montmorillonite (CLM) as nanofiller	Higher co-coagulating rate of CLM as compared to unmodified lignin / Improved performance of composite with 10 phr of CLM [74]
Sulfur-free Lignin	NR	Reinforcing filler	Increased resistance of NR vulcanizates to thermooxidative degradation in air
Direct mixing of lignin in rubber			
Sulfate Lignin	ENR	Reinforcing filler	Lignin aggregated and immiscible with ENR matrix and improved performance of composite
Alkali Lignin	NR	Reinforcing filler-hybrid filler of silica/lignin	Weaken the Payne effect and improve processability, anti-aging resistance, and anti-flex cracking / Exhibited optimal overall mechanical properties at 20 phr of lignin and 30 phr of silica [75]
Sulfur-free Lignin (steam explosion process)	NR (STR20) and SBR	Reinforcing filler as partial replacements for carbon black	Low performance due to the high amount of impurities [ash and polysaccharide] and polarized hydroxyl groups in lignin, which interfered with lignin–rubber interactions [76]

The same is true for a hybrid filler approach where Kraft lignin combined either with montmorillonite [84] or with carbon black [85] shows an improvement in tensile strength, thermal stability, and low rolling resistance. This is because lignin, as a component of hybrid fillers, can suppress the formation of filler networks of other fillers, facilitating the overall dispersion. However, the interfacial interaction between lignin and rubber is still poor in the hybrid fillers/rubber composites [79]. The reason for poor interfacial adhesion of lignin with rubber is mainly due to the polarity difference between them. Lignin has a high content of hydroxy groups on its surface due to which lignin agglomerates are formed, resulting in incompatibility issues. Suncoal industries GmbH tries to address this issue by post-treating the technical lignin by a **H**ydro**t**hermal **C**arbonization process (HTC), which will be discussed in **Section 4.2.5** [86-87].

4.2.5 Hydrothermal Carbonization process

As discussed in Section 4.2.2, during the respective pulping process, different lignin types are recovered from different techniques. Furthermore, these lignin types can be chemically modified/post-treated to a greater or lesser extent depending on the isolation process by which they are derived. One such post-treatment method is the **H**ydro**T**hermal **C**arbonization technique (**HTC**). This post-treatment technique involves derivatization of carbonaceous materials from any technical lignin (Kraft/Organosolv/Lignosulphonate) with varying morphologies, physical (pore structures, such as nano, meso, and macropores), and chemical properties (varying composition, surface functionalities, thereby changing the chemical reactivity) [88]. In this technique, wet biomass is processed at moderate temperatures (~180-250 °C) under pressure (~20-30 bar), which leads to numerous chemical reactions on the used technical lignin such as hydrolysis, dehydration, decarboxylation, polymerization, aromatization, and condensation. This exothermal process lowers both the oxygen and hydrogen content of the material resulting in high carbon material, which can be used for high-end applications and improve surface compatibility [89].

5 Design Methodology

Design methodology provides a path to fulfil the context of stakeholders and goals of the design project. In this case, the design project which is considered as an artifact (the object under study) flows through a circular loop of an iteration process called a design cycle as shown in **Figure 5.1**. This cycle iterates over the activities of the design by performing the following tasks: problem investigation (problem identification and motivation), treatment design (requirement specification, design and development), treatment validation (prototype development and its effect which will be discussed in detail in this chapter) [12].

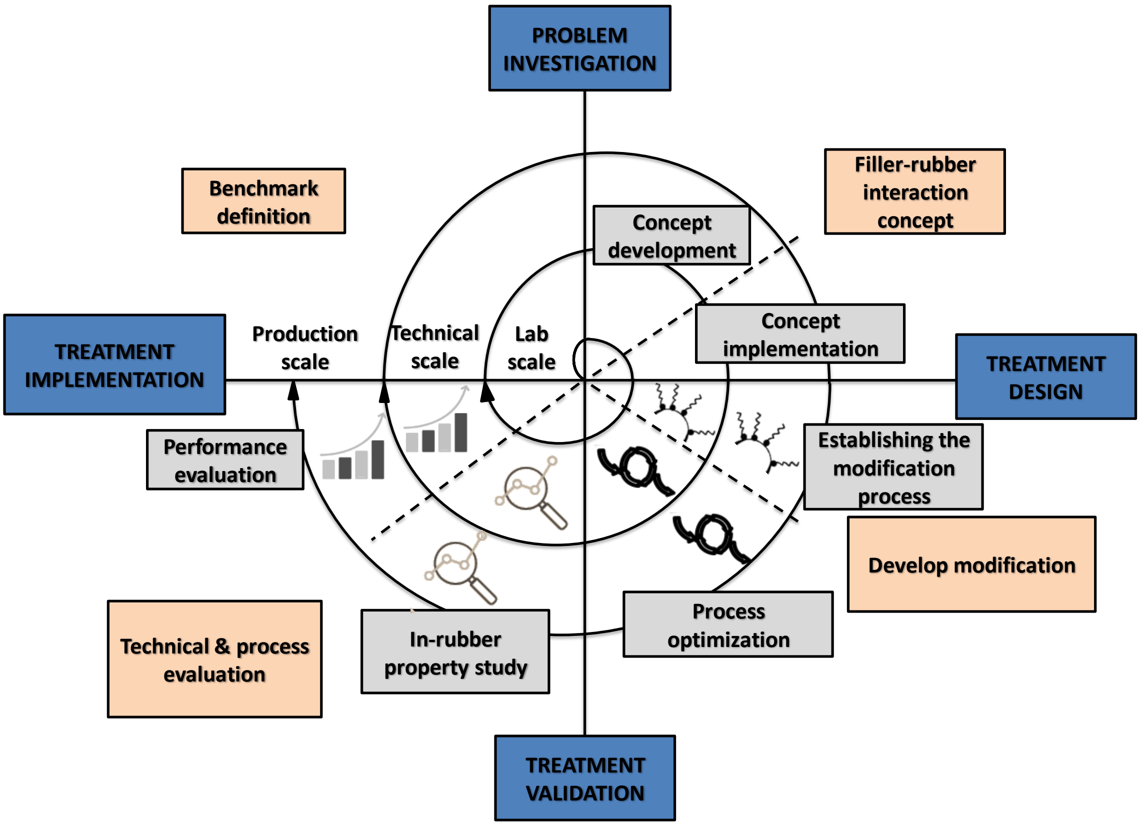


Figure 5.1 Design methodology for the current project

5.1 Problem investigation

The key learnings from **Chapter 4, Section 4.2** highlights that lignin is a polydisperse polymer with no extended sequences of regularly repeating units, its composition is generally characterized by the relative abundance of H / G / S units and by the distribution of inter-unit linkages in the polymer [43]. Besides, different variants of lignin with different composition (different monomeric units & their connective patterns, different surface chemistries) and properties can be obtained with different isolation and post-treatment procedures. This is summarized using a schematic represented in **Figure 5.2** [35].

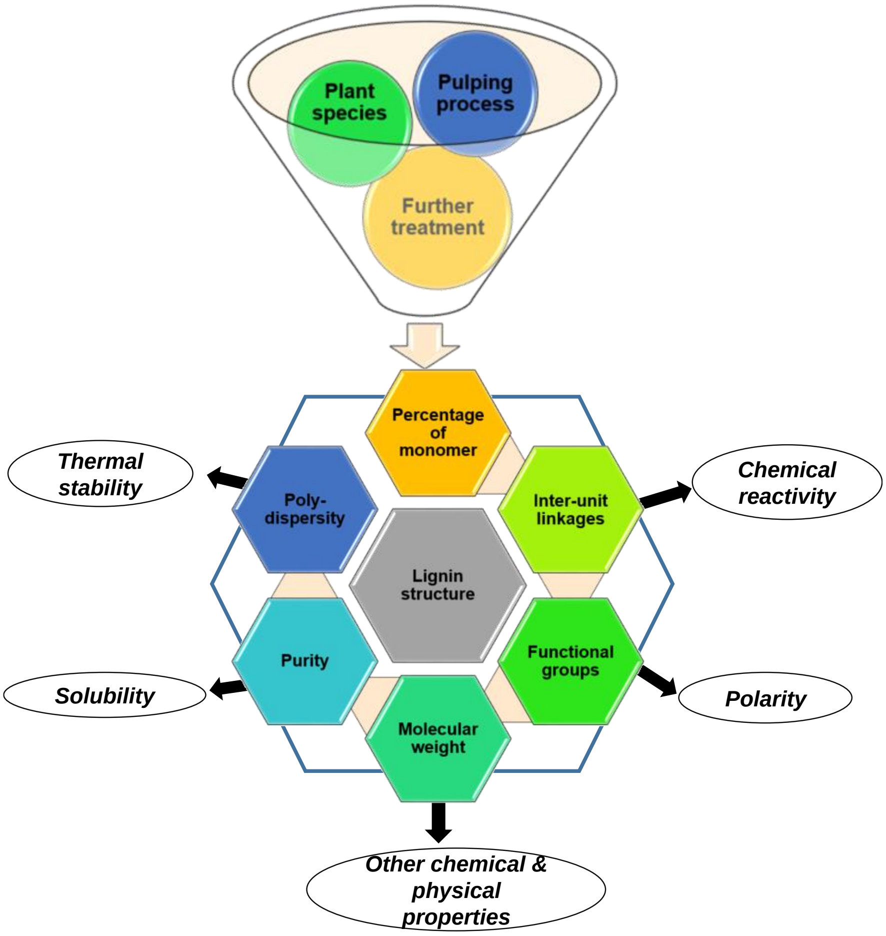


Figure 5.2 Relation between origin, structure and properties [35]

This complex structure and surface functional groups of lignin pose challenges in interacting with the hydrophobic polymer. This might also lead to weak filler-polymer interaction leading to poor reinforcing behavior of lignin.

5.2 Treatment design & validation

Tailoring the surface characteristics of the HTC lignin filler (while retaining the bulk properties of it) could make it compatible with rubber thereby enhancing the performance characteristics of the final compounds. Use of silane coupling agent as a surface modifier for hydrophilic filler is a common approach in rubber technology [90].

The first part of this design project involves selection of right reference tire tread formulation. With the selected formulation, a fundamental study is carried out to understand the interaction and reinforcement provided by HTC lignin in comparison to the conventional fillers. The second part focuses on pre-requisite studies for surface modification i.e., filler characterization followed by the selection of promising coupling agents for the surface modification, which can form a strong bond between the rubber and filler. Based on this study, it will be decided which type of modification technique (in-situ/ex-situ) will be applied to study the in-rubber properties. Finally, optimization of surface modification and its influence on properties will be investigated to deliver a final 'green' tread compound. This compound will be formulated by combining the most promising bio-based filler system (HTC lignin + surface modifier) concluded from each investigation.

1. Characterization of the filler:

The initial characterization of filler is done to quantitatively using a Phosphorus Nuclear Magnetic Resonance (^{31}P NMR). The information obtained from ^{31}P NMR gives an insight to understand the structure and different -OH compositions (e.g., syringyl, phenolic -OH, aliphatic -OH, carboxylic -OH etc).

2. Surface modification of filler and characterization:

Surface modification can be carried out in two ways: (i) In-situ modification i.e., modification of the filler surface by chosen coupling agents in the rubber mixing chamber along with other rubber additives. (ii) Ex-situ modification i.e., Pre-modification of the filler in a solvent (liquid phase modification), where the filler and coupling agent are reacted at specific conditions (temperature, time, concentration). For this design, In-situ modification is preferred as it is efficient and fast.

- **2.1 Selection of coupling agents:** One of the crucial steps of this design is the selection of promising coupling agents, which can form stable bonds with HTC lignin surface and also can couple to the elastomer matrix. The resulting filler-polymer interaction can enhance mechanical and viscoelastic properties of the final compounds. The screening of the most promising coupling agents will be done based on their chemical structure, reactivity with the filler and also bond stability, which are expected to make the HTC lignin surface hydrophobic and decrease the surface energy close to the polymer during mixing.
- **2.2 Optimization study:** For in-situ modification, it is important to tailor the mixing parameters (time and temperature) as well as adjust the compounding to improve the overall compound properties.

After each compounding and mixing trail, in-rubber properties such as mechanical, rheological and other tire related properties are measured using different techniques (tensile test, Rubber Processer Analyzer (RPA), Dynamic mechanical Analysis (DMA)). Apart from these measurements, the potential of the modified fillers was further evaluated by measuring the Payne effect (filler-filler interactions).

6 Development phase

Based on the summary of **Chapter 5**, the design development begins with the initial characterization of the filler and is followed by in-rubber analysis. The detailed description of the materials and equipment used in the experiments, characterization techniques, test method and procedure are briefly elaborated in this chapter.

6.1 Experimental setup for Filler characterization

6.1.1 Phosphorus-31 Nuclear Magnetic Resonance (^{31} P NMR)

6.1.1.1 Materials

All the chemicals and reagents described in **Table 6** were obtained from commercial sources and were used as received.

Table 6 Chemicals and reagents used for NMR study

Function	Chemical	Product specification/suppliers
Solvents	Anhydrous pyridine; 99%	CAS-110-86-1, ABCR
	N,N-Dimethylformamide-d7(DMF-d7); 99.5 atom %D; 10*0.75ml ampoules	CAS-4472-41-7, ABCR
	Deuterated chloroform	CAS-865-49-6, Sigma-Aldrich
Relaxation agent	Chromium (III) acetyl acetonate (97%) ($Cr(acac)_3$)	CAS-21679-31-2, Sigma-Aldrich
Phosphorylating agent	2-chloro-4,4,5,5–tetramethyl-1,3,2-dioxaphospholane; 95% (TMDP)	CAS-14812-59-0, Sigma Aldrich
Internal standard	N-hydroxy-5-norborene-2-3 dicarboximide (NHND)	CAS-21715-90-2, ABCR

6.1.1.2 Apparatus and equipment

NMR tubes 600 MHz (8 in. length), Wilmand; Hamilton gastight 1700 series syringes, Sigma-Aldrich; Glass vials (Sigma Aldrich); NMR spectrometer (Bruker AVANCE II 600 MHz, capable of ^{31}P detection); vacuum oven.

6.1.1.3 Preparation for NMR analysis

Preparation of solvent solution

For an accurate quantitative liquid-state NMR measurement, one of the essential prerequisites is complete solubilization of the used substrate in an appropriate solvent. Taking into consideration the limited solubility of HTC lignin in conventional deuterated chloroform and pyridine solvent mixture, a third solvent N,N-dimethylformide is introduced. 3000 µl of solvent solution of anhydrous pyridine, deuterated chloroform, deuterated DMF at a volume ratio of 1:1.2:1 (v/v/v) was prepared.

Preparation of mixture solution

Chromium (III) acetylacetonate solution was prepared by using an aliquot of solvent solution at a concentration of 3.6 mg/ml. To this solution, N-hydroxy-5-norborene-2-3-dicarboximide solution at a concentration of 4 mg/ml (~0.02 mmol) prepared using the solvent solution is added. The final resulting solution is referred as mixture solution.

Preparation of phosphitylated solution

20 mg of dried HTC lignin (i.e., dried under vacuum at 40 °C for 24 hrs) was accurately weighed into a 4 ml vial equipped with a PTFE-lined silicone septum and to this, 500 µl solvent solution was added and sealed with the Teflon cap. The mixture is shaken well for a few minutes at room temperature to dissolve the SCF (10-15 mins). An aliquot of the mixture solution of 150 µl was introduced into the vial containing HTC lignin solution using a Hamilton syringe. The mixture in the vial was again shaken well at room temperature to homogenize the mixture. 100 µl of TMDP was introduced into the vial using gastight syringe. The mixture is shaken for few minutes to confirm no precipitates are formed. Then the whole phosphitylated lignin solution is transferred to 5mm NMR tube to record the NMR spectrum.

NMR acquisition parameters

The NMR spectra were recorded on a Bruker AVANCE 600 MHz spectrometer. A 90° pulse was utilized with a 25-second pulse delay along with inverse gated decoupling for the quantitative acquisitions. A line-broadening factor of 5 Hz was used and the time domain (TD) size was 192K. For each spectrum more than 900 scans were collected to increase signal to noise ratio.

6.2 Experimental set-up for rubber compound preparation

6.2.1 Materials

Table 7 Reference tire tread formulation of the compound used in this study

Ingredients		Supplier	Amount (phr)
Rubber			
SSBR	SPRINTAN^{TR} SLR 4602	Trinseo Deutschland GmbH, Schkopau, Germany	75
BR	BUNA® CB 24 (high cis content)	Arlanxeo Deutschland GmbH, Leverkusen, Germany	25
Filler system			
Lignin	HTC Lignin grade SQ243-00341	Suncoal Industries GmbH, Berlin, Germany	80
Process oil			
TDAE	Treated Distillate Aromatic Extract, VIVATEC 500	Hansen & Rosenthal KG, Hamburg, Germany	33
Cure Activators			
ZnO	Zinc oxide	Sigma-Aldrich Chemie, Germany	2.5
St.Ac	Stearic acid	Sigma-Aldrich Chemie, Germany	2.5
Antidegradants			
TMQ	2,2,4-trimethyl-1,2-dihydroquinoline	Flexsys, Belgium	2
6-PPD	N-(1,3-dimethylbutyl)-N’-Phenyl-p-PhenyleneDiamine	Flexsys, Belgium	2
Cure system			
S	Sulfur	Sigma-Aldrich Chemie, Germany	2.2
DPG	1,3 Diphenyl guanidine	Flexsys, Belgium	0.25
TBBS	N-Tert-Butyl-2-BenzothiazoleSulfenamide	Sigma-Aldrich Chemie, Germany	1.5
TBzTD	Tetrabenzylthiuram disulphide	Sigma-Aldrich Chemie, Germany	0.5

For the investigation, a modified tire tread formulation from Michelin's green compound was used as a base formulation by replacing silica filler with HTC lignin as shown in **Table 7**. The quantity of the used ingredients was calculated based on parts per hundred rubber (phr). Polymer blends of functionalized solution styrene butadiene rubber [S-SBR with medium styrene (21.1%) & high vinyl (62.1%) content, Mooney viscosity (ML1+4@100 °C) of 63] and neodymium butadiene rubber [BR with high cis content of 96% & Mooney viscosity (ML1+4@100 °C) of 44] were applied for this study.

6.2.2 Sample preparation

The in-situ modification of lignin with surface modifier as well as mixing of the ingredients was performed on a laboratory scale tangential internal mixer (Brabender Internal mixer 350S) with a chamber volume of 390 cm^3. The heating and cooling of the mixing device is achieved by passing oil through the inner tubing in the chamber walls. The temperature of the oil is controlled by an external unit that can be set to the desired temperature. The mixing device is connected to a driver which is computer and software (winmix) controlled. The software is used to set the mixing parameters. Apart from the external heating, the desired temperature of the mixer (max. 250 rpm) during mixing can also be controlled manually by adjusting the speed of the rotor (max. 350 rpm).

6.2.2.1 Mixing procedure

The compounds were mixed in two stages in the internal mixer with specified mixing parameters as represented in **Table 8**. The first stage of mixing involves mixing of all the compounding ingredients except of curatives. The resulting mixed compounds are termed as "masterbatch". The second/final stage of mixing is carried after a maturation period of approximately 16 h at 23 °C which involves mixing the masterbatch with the curatives. The achieved final compound is termed as "green compound".

Table 8 Mixing parameters for the two stage mixing process

Mixing stages	***Masterbatch mixing***	***Final mixing***
Initial mixer temperature (°C)	50	50
Rotor speed (rpm)	50	30
Fill factor (%)	70	70
Mixing time (min)	10	5
Dump temperature (°C)	140-150	90-100

The desired final dump temperature of the compound mentioned in Table 8 is controlled by adjusting the rotor speed. The final dump temperature is recorded by a thermocouple. After each mixing stages, the compounds were sheeted out using Schwabenthan Polymix 80T two-roll mill operating with a gap of 2.5mm.

The order of mixing is also one of the influencing factors which can affect the mixing efficiency due to the differences in structure, viscosity and cure behavior of the added chemical ingredients. Therefore, a specific sequence of addition of compounding ingredients were followed as tabulated in **Table 9**. Due to the fluffiness and unpelletized form of the HTC lignin, the filler was added in four equal portions for easier incorporation.

Table 9 Mixing sequence

Mixing time (min:sec)	***Masterbatch mixing***
0:00	Open ram & add polymer
0:20	Close ram
1:00	Open ram & add 1st part of filler
1:20	Close ram
2:00	Open ram & add 2nd part of filler
2:20	Close ram
3:00	Open ram & add 3rd part of filler
3:20	Close ram
4:00	Open ram & add 4th part of filler, ZnO, St. Ac., TMQ, 6PPD
4:20	Close ram
5:00	Open ram & sweep
5:20	Close ram & adjust rotor speed
10:00	Dump

6.2.2.2 Curing of the compounds

The cure characteristics were determined using an elite Rubber Process Analyzer (TA Instruments, US) at 160 °C for 30 minutes at 1.667Hz frequency and 6.98% strain according to ISO 3417. T_{90} was used as the optimum curing time .

The rubber compounds were finally cured in a Wickert laboratory press WLP 1600/5*4/3 at 160 °C and 100 bar pressure with their respective optimum cure time (T_{90}). For different in-rubber tests, the sample size and curing conditions are varied as mentioned below in **Table 10**.

Table 10 Curing conditions for different test samples

Cure time	**Test**	**Sample dimension**
T_{90}+2 mins	Tensile DMA	Slab of 90*90*2mm
T_{90}+5mins	Hardness, Rebound resilience	Cylindrical specimen of 12.5 mm thickness

6.2.3 Characterization of compounds

The technical properties of the mixed compounds were characterized by the following standard procedure.

6.2.3.1 Characterization of green compound

6.2.3.1.1 Mooney viscosity

The final compound's viscosity was determined using a Mooney viscometer 2000E (Alpha Technologies) at 100 °C according to ASTM D1646 using a large rotor. The Mooney values are represented as ML (1+4) 100 °C. The mean shear rate of the rotor was 1.25 s^{-1}.

6.2.3.1.2 Payne effect

Filler-filler interactions were determined by Payne effect measurements. The measurements were performed by RPA elite Rubber Process Analyzer (TA instruments) at 100 °C. The values of storage modulus (G') were recorded under shear deformation with a strain sweep range of 0.56-100% at a frequency of 1 Hz.

6.2.3.2 Characterization of cured compounds

6.2.3.2.1 Tensile properties

For tensile test, the vulcanized sheets were die-cut to dumbbell shaped specimens. The test was performed in a Zwick/Roell Z1.0 Universal Tensile Tester (Germany) at a cross-head speed of 500 mm/min, according to ASTM D412. Five specimens were used in each case for the evaluation of the tensile data. The mean values of tensile properties taken from these five specimens are reported.

6.2.3.2.2 Hardness test

The hardness of the samples was measured with a Zwick 3150 hardness tester, Shore A type, according to DIN 53505 at 23 °C. Three measurements from each of three specimens were taken and average of the three specimens were reported.

6.2.3.3 Rebound resilience

The rebound resilience measurements were carried out with cylindrical specimens using Zwick/Roell 5109 Rebound Resilience tester according to DIN 53512. The test was performed at room temperature of 23 °C and 70 °C.

6.2.3.4 Dynamic mechanical analysis

For DMA test, cylindrical shaped specimens of 10mm diameter were die-cut from the 2mm thickness sheets prepared for the tensile tests. The temperature sweep test was carried out using a DMA Eplexor 9 (Netzsch Gabo Instrument) in a double shear mode. The measurements were divided into two segments with different dynamic strains as shown in **Table 11**. The low strain was maintained at low temperature in order to avoid the compound’s stiffness effect, whereas the high strain was used to investigate the dynamic properties at elevated temperatures, when the rubber samples elasticity is more profound.

Table 11 Test conditions for DMA

Segment	Temperature (°C)	Strain (%)	Frequency (Hz)
1	-40 to +10	1	10
2	+10 to 60	3	

6.2.3.5 Determination of Crosslink density

The crosslink densities of the rubber compounds were measured by swelling experiments. Prior to the swelling test, the cured samples were extracted in a Soxhlet apparatus with acetone for 48 h to remove low molecular weight polar substances like unreacted accelerators, curatives or curing by-products. The extracted samples were dried in a vacuum oven at 40 °C for 24 h.

The acetone extracted specimens were immersed in toluene at room temperature for one week. At the end of the immersion period, the samples were removed and blotted with filter paper and transferred to the weighing bottle to obtain the weight of the swollen vulcanizates. Afterwards the samples were dried in a vacuum oven for 24 h at 105 °C to obtain the dried weight. The crosslink density per unit volume (V_e) was calculated according to Flory-Rehner **equations 6.2** and **6.3** [91]:

$$V_e = \frac{-[ln\,(1 - V_r) - V_r + \chi V_r^2]}{V_s\,(V_r^{\frac{1}{3}} - \frac{V_r}{2})} \qquad \textbf{(6.1)}$$

where the volume fraction of polymer in the swollen gel at equilibrium (V_r) can be calculated as,

$$V_r = \frac{m_r}{m_r + m_s(\frac{\rho_r}{\rho_s})} \qquad \textbf{(6.2)}$$

And where χ is the Flory-Huggins polymer-solvent interaction parameter (χ= 0.37 for SSBR/toluene system & for BR/toluene χ= 0.34); V_s is the molar volume of solvent; m_r is the mass of the rubber network; m_s is the mass of the solvent in the swollen sample at equilibrium conditions; ρ_s and ρ_r are the densities of the solvent and rubber, respectively. In this study, the value of χ =0.36 is used. This value is calculated with reference to the polymer-solvent interaction parameters of the individual polymers and their amount in the blend.

7 Experimental results and discussion

7.1 Understanding the reinforcing potential of HTC lignin

7.1.1 Background

The addition of certain particulate fillers like carbon black or silica reinforces the rubber by enhancing broad range of mechanical properties and this has been studied in numerous investigations [26, 92-93]. Based on these investigations, it is generally accepted that filler-rubber interaction and filler network structure are the predominant factors determining the degree of filler reinforcement. Therefore, this study concerns on understanding the degree of reinforcement provided by HTC lignin as such, to gain insight into behavior of HTC lignin filler particles with elastomer. In particular, the effect of characteristics of HTC lignin (surface area) on the rubber properties in comparison to the unfilled rubber and conventional filler reinforced rubbers will be investigated under this study.

7.1.2 Experimental

The investigation was performed with three differently filled systems (HTC lignin, carbon black and silica/silane) and an unfilled (gum) system. The used grade of fillers for this study is tabulated in **Table 12**.

Table 12 Fillers used, source and their specification

Filler & grade	**Supplier**	**Specific density (g/cm^3)**	**Specific surface area (BET) (m^2/g)**
Carbon black, N330	Orion Engineered Carbon, Germany	1.8	78
Silica, ULTRASIL 7000®	Evonik Industries AG, Germany	2.0	171
HTC lignin, SQ243	Suncoal Industries GmbH, Germany	1.4	38

The mixing formulation and mixing conditions as described in **Section 6.2 (Table 7 & 8)** were used for HTC lignin and Carbon Black (Cblack) mixing. A similar mixing procedure as described in **Table 9** was followed for the silica filled compound, with an extra inclusion of the coupling agent Bis(triethoxysilylpropyl)tetrasulfide silane (TESPT/Si69® - purchased from Evonik Industries, Germany) of 6.2 phr added to the formulation. This is because silica fillers are hydrophilic in nature which makes them incompatible with the hydrophobic polymer. Also, the silane coupling agent improves the dispersion and processability of silica filler. The mixing formulation for silica is tabulated in **Table 13**. During vulcanization, the well-known phenomenon observed for silica-TESPT/Si69® silane is that the dissociated sulfur containing part of the silane and/or active sulfur released from silane starts to react with rubber leading to the formation of additional silica-silane-rubber covalent bonds and/or rubber crosslinked products [94]. This results in a higher crosslink density in comparison to other filled system. Usually, sulfur correction (addition of free sulfur to other filled systems) is done to compensate this effect. For this study, sulfur correction was not taken into account for HTC lignin and Cblack filled compounds.

Table 13 Mixing formulation for coupling agent added compounds

Mixing time (min:sec)	***Masterbatch mixing***
0:00	Open ram & add polymer
0:20	Close ram
1:00	Open ram & add 1st part of filler, ½ coupling agent
1:20	Close ram
2:00	Open ram & add 2nd part of filler, ½ coupling agent, oil
2:20	Close ram
3:00	Open ram & add 3rd part of filler
3:20	Close ram
4:00	Open ram & add 4th part of filler, ZnO, St. Ac., TMQ, 6PPD
4:20	Close ram
5:00	Open ram & sweep
5:20	Close ram & adjust rotor speed
10:00	Dump

In addition to this adjustment, TDAE oil was neglected for the unfilled compound (gum) and the mixing of this compound was done for 5 mins and finally it was dumped at 100 °C. All the compounds were validated in terms of their processability (Mooney viscosity) and static mechanical properties (hardness and tensile strength) and dynamic mechanical properties.

7.1.3 Results and discussion

Processability of the HTC lignin compounds

Figure 7.1 shows the filled compound's viscosity in comparison to the unfilled/gum compound. Generally, the increase in viscosity of filled compounds is attributed to the hydrodynamic effect of the filler, filler-filler and filler-rubber interactions. Besides the increased viscosity of HTC lignin compared to gum rubber, the contribution from the above-mentioned parameters seems to be considerably low compared to silica and Cblack filled compounds. One of the reasons is the lower specific surface area of the HTC lignin filler in comparison to Cblack or silica (**Table 12**).

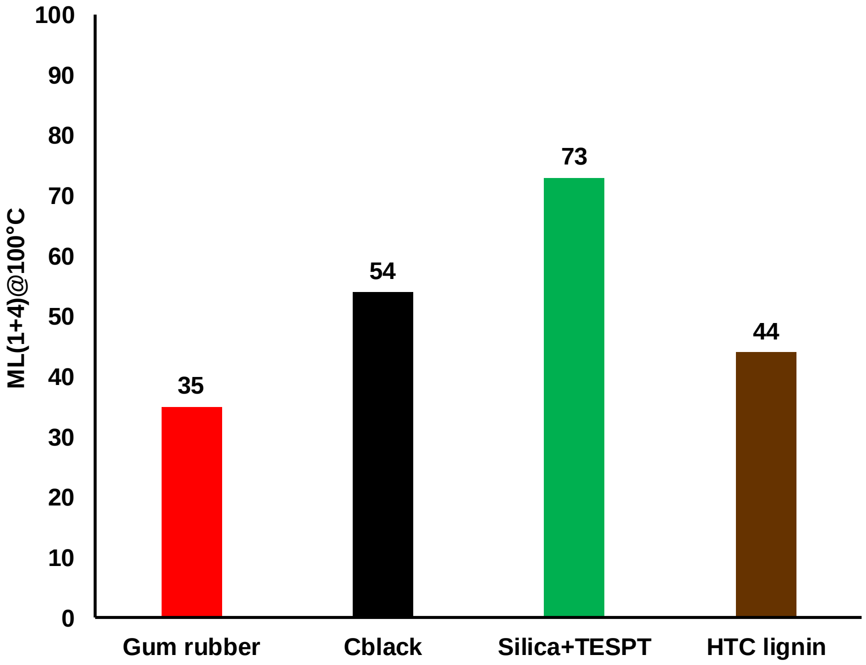


Figure 7.1 Mooney viscosity of the different filled compounds

Influence of HTC lignin on filler-filler interaction

It can be seen from **Figure 7.2**, in contrast to the filled compounds, the gum rubber shows a linear viscoelastic behavior without any change in dynamic modulus G' with respect to the applied strain amplitude, which is the contribution from the polymer network (physical entanglements) alone. For filled rubbers, a typical decrease in the G' with increasing strain amplitude (Payne effect) is observed due to the breakage of loosely bound network. This can be explained by two models: (i) filler structural breakdown model based on filler-filler physical interactions for instance, van der Waals interactions, hydrogen bonds and London forces and (ii) filler-matrix interaction model based on labile bonding of polymer chains to the filler surface resulting in trapped entanglements [95]. The filler network structure and strength influences the dynamic behavior of the filled rubber [96]. Among the investigated fillers, HTC lignin shows lower G' value at high strain and low strain indicating weaker filler-filler interactions as well as filler-polymer interactions.

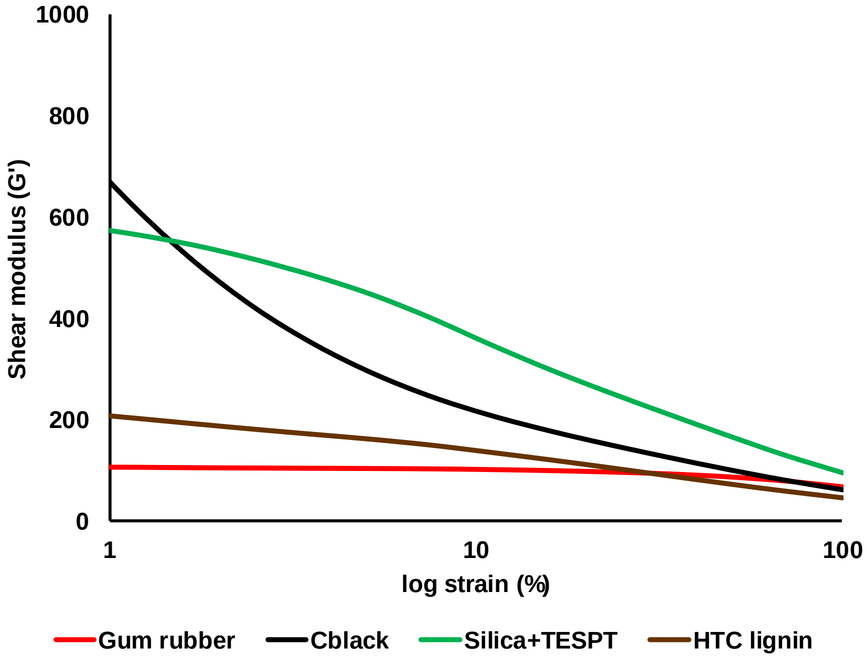


Figure 7.2 Payne effect of different filled compounds

Influence of HTC lignin on cure properties and crosslink density

The curing characteristics of the compounds with different filled systems are shown in **Figure 7.3.** The HTC lignin compound shows better scorch safety (higher scorch time) and lower minimum (M_L) and maximum torque (M_H) value compared to conventional fillers. This suggests that the surface of HTC lignin is acidic which can adsorb the basic accelerator and cure activator delaying the vulcanization. This hypothesis is also confirmed by the crosslink density measurement as shown in **Figure 7.4** which demonstrates a reduced value in comparison with other fillers. The increase in crosslink density of different filled system in comparison to unfilled rubber is due to the presence of additional filler-filler and filler-polymer interactions provided by the incorporation of fillers and it also depends on the used filler type.

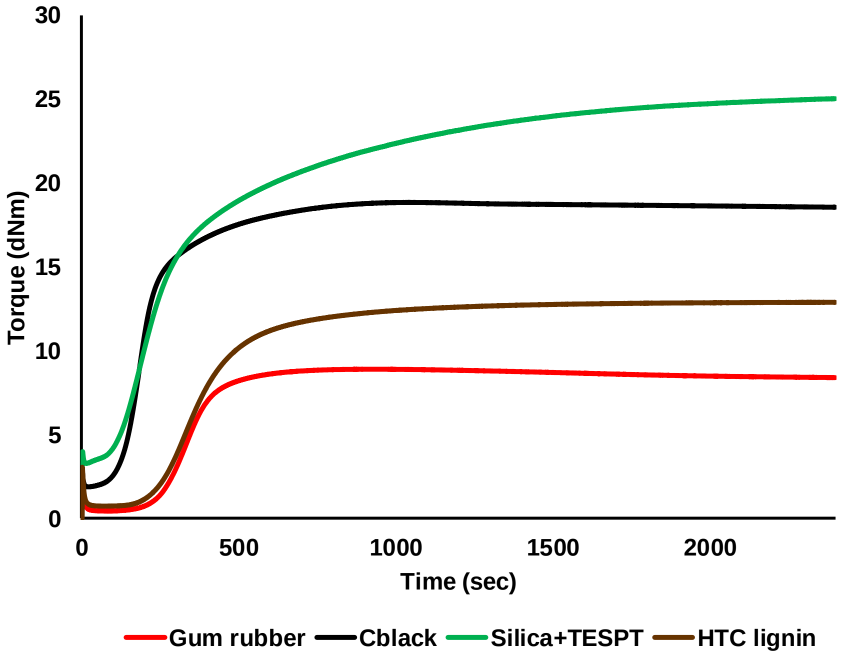


Figure 7.3 Cure behavior of different filled compounds

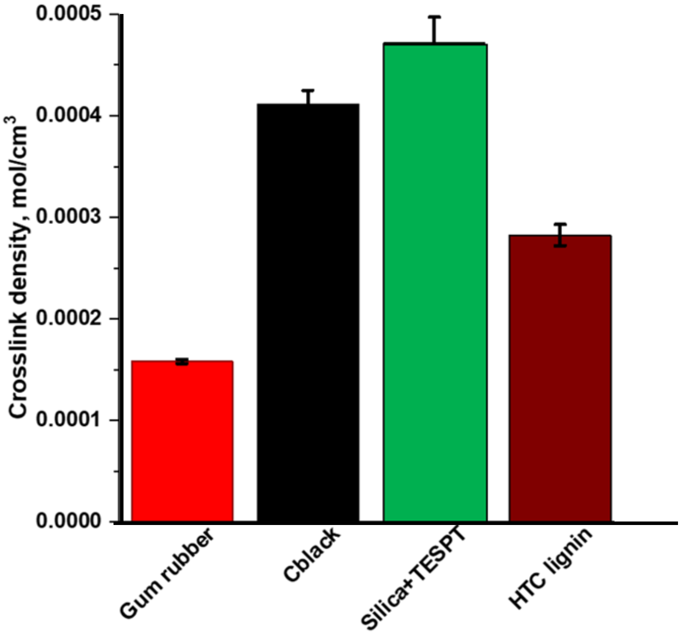


Figure 7.4 Crosslink density of the compounds

Influence of HTC lignin on hardness of the compound

The hardness of the rubber compound is strongly influenced by the type and density of used fillers and crosslink density. The hardness results of the compounds **(Figure 7.5)** are inline with the Payne effect results and crosslink density measurements. As expected, the filled compounds show higher hardness value in comparison to the gum compound, whereas the obtained hardness of HTC lignin is lower in comparison with conventional fillers due to its low density, weaker filler structure and crosslink density.

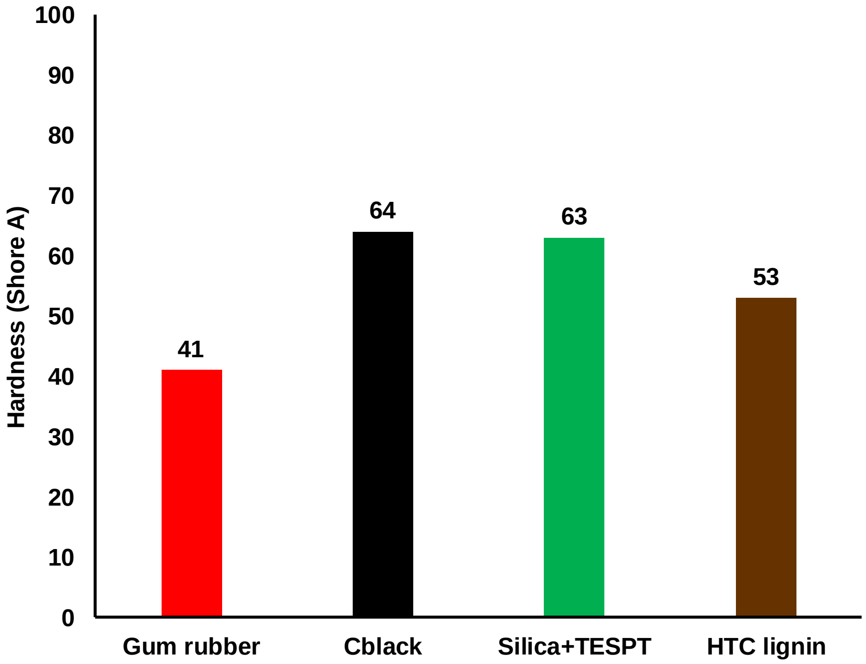


Figure 7.5 Compound hardness

Influence of HTC lignin on mechanical and dynamic properties

The mechanical properties of the different compounds are shown in **Figure 7.6.** The HTC lignin compound shows improved modulus at 300% and 100% elongation (M300 and M100) and tensile strength in comparison with the gum rubber. The obtained values are inferior compared to conventional fillers which is mainly due to the reduced crosslink density, weaker filler-filler as well as lower filler-polymer interaction (confirmed by Payne effect).

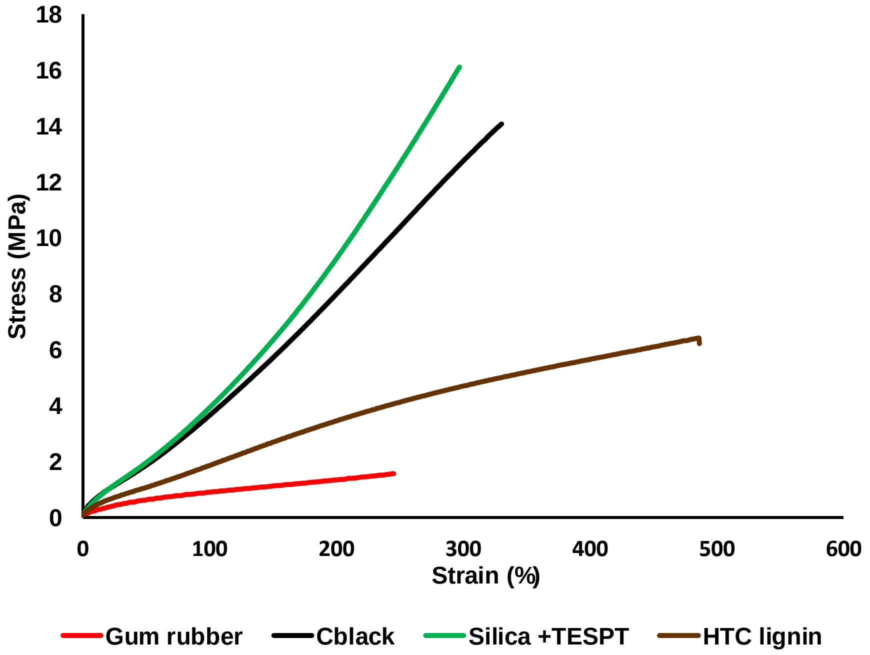


Figure 7.6 Mechanical properties of the different compounds

Figure 7.7 displays the temperature dependent viscoelastic behavior of the unfilled gum and filled compounds. The viscoelastic behavior represented by the loss factor, tan delta, greatly impacts the tire performance properties such as rolling resistance and traction (snow/wet/dry). It can be observed from **Figure 7.7** that the viscoelastic glass transition temperature of filled vulcanizates are affected by the type of the used filler. The variation in the intensity of tan delta peaks in the glass transition region for the rubber samples evidently suggests that the extent of interaction between the rubber-filler and filler-filler of these systems plays a vital role in the dynamic modulus of the rubber. In the present study, gum and HTC lignin compounds exhibit the highest peak in comparison to the conventional fillers. This can be attributed to the low polymer-filler and filler-filler interaction of HTC lignin (also confirmed by Payne effect results) which results in lower immobilized rubber molecules. This eventually leads to an increase in the viscous component in comparison to the conventional fillers.

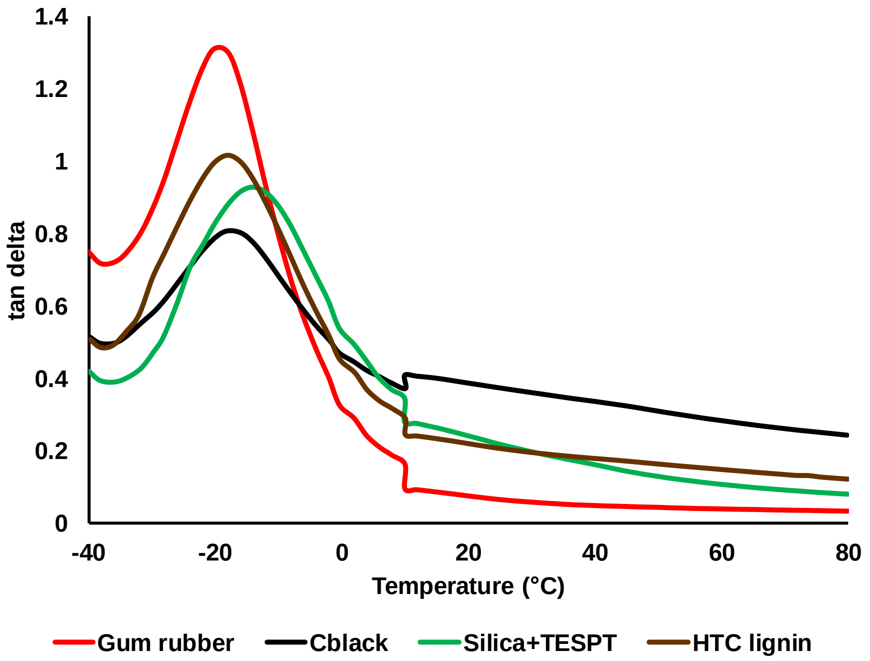


Figure 7.7 Dynamic mechanical properties of the different compounds

The wet grip property of the tire can be indicated by tan delta at 0 °C (higher the value, better the wet grip). Among the filled compounds, silica shows better wet grip behavior which can be attributed to its polar and hydrophilic surface compared to the HTC lignin and carbon black surface.

The rolling resistance property of the tire is indicated by tan delta at 70 °C. The HTC lignin filled compound shows the lower tan delta at 70 °C in comparison to Cblack but higher value compared to silica. This indicates lower rolling resistance in comparison to Cblack but higher than the expected one for the silica/silane system. The increased hysteresis of both HTC lignin and carbon black can be related to the physical interaction of filler and polymer chains which can cause either slippage or adsorption and desorption of polymer chains increasing the compound’s dynamic hysteresis in contrast to the chemical linkages of silica filler with the rubber which restricts polymer mobility. In contrast, the low hysteresis of HTC lignin could be related to the weaker filler networks and lower surface area in comparison to the carbon black fillers.

7.1.4 Summary

The present study was undertaken to give a more detailed analysis of the reinforcing potential of HTC lignin in comparison to the conventional fillers. It can be observed that HTC lignin provides inferior rubber properties (mechanical properties, hardness, dynamic properties). The probable reasons for this low reinforcing potential can be related to physical characteristics: (i) low surface area (ii) polarity difference between polar HTC lignin and non-polar polymer. As a result, the compatibility between HTC lignin and polymer is affected leading to weak filler-polymer interaction. The fundamental study also gives an indication that the surface chemistry of HTC lignin not only leads to weak filler-polymer interactions but also hinders the vulcanization reaction which results in a reduced crosslink density. This leads to the conclusion that a chemical modification of the HTC lignin filler is essential to improve its reinforcing potential.

7.2 Characterization of HTC lignin

Surface modification/ functionalization of fillers is one of the most effective approaches to improve interfacial adhesion between a rubber and filler. Filler characterization was carried out to elucidate the complex surface chemistry of HTC lignin which can help in predicting their interaction with the rubber matrix. ^{31}P NMR was used for the characterization of filler in this design study. This will be discussed in detail in this section.

7.2.1 Determination of different functional groups of HTC lignin

7.2.1.1 Background

Surface modification of filler depends not only on the nature of the used surface modifier but also on the filler surface chemistry like the type of the functional group, their reactivity, concentration etc. [32]. As elaborated in **Chapter 4**, native lignin is an irregular heterogeneous aromatic polymer. And during biomass processing (isolation techniques) or post-treatment processes, the heterogeneity and structural complexity of lignin are typically increasing. Therefore, a detailed understanding of the structure and functional groups of the used HTC lignin is critically important for their modification since their chemical nature differs. This design study employed phosphitylation as **described in Chapter 4, Section 4.2.3.1 and Chapter 6, Section 6.1.1** (followed by ^{31}P NMR) for quantifying different types of hydroxyl groups, such as aliphatic, and various phenolic hydroxyl groups as well as carboxylic groups. These groups are considered to be the major lignin functionalities important for analyzing the lignin structure [98]. Among all the spectroscopic techniques, ^{31}P NMR was preferred due to its faster, simpler and more reliable quantification approach.

7.2.1.2 Results and discussion

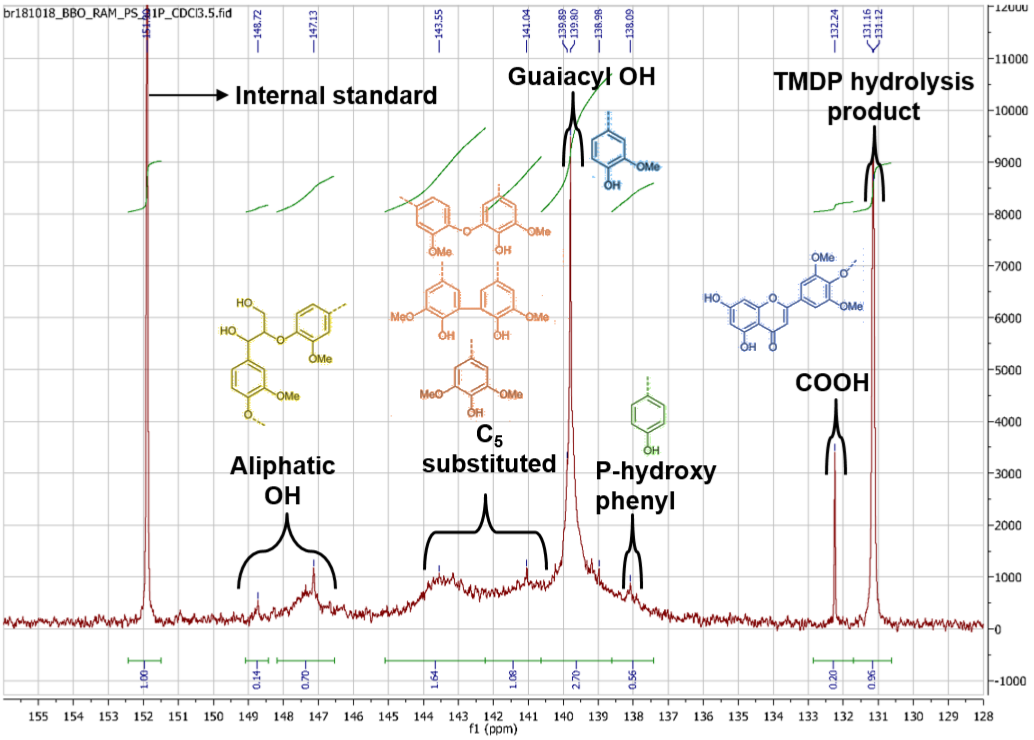


Figure 7.8 ^{31}P NMR spectrum of the HTC lignin under study.

The reaction of 2-chloro-4,4,5,5–tetramethyl-1,3,2-dioxaphospholane (TMDP) with different functional groups of the HTC lignin generates different phosphite products which cause characteristic changes in the chemical shift values. The resulting ^{31}P NMR spectrum of HTC lignin is shown in **Figure 7.8**. The assignment of chemical shifts (δ/ppm) for different phosphitylated hydroxyl groups was conducted according to the relative position specified in literature [54, 97]. The amount of different functional groups are quantitatively determined by integration of the peak areas. **Table 14** summarizes the results of a quantitative ^{31}P NMR analysis of TMDP phosphitylated HTC lignin.

Table 14 Composition and distribution of hydroxyl groups of used HTC lignin quantified by ^{31}P NMR

Different hydroxyl groups		**Amount (mmol/g)**
Aliphatic OH		0.9
5-substituted OH	**Phenolic OH**	3
Guaiacyl		3
p- Hydroxy phenyl		0.6
Carboxylic OH		0.2

The amount of different functional groups presented in **Table 14** was calculated based on the used internal standard (IS) as shown in **equation (7.1)** and is expressed in mmol of functional groups per gram of dry lignin.

$$Amount\ of\ OH\ per\ g\ of\ lignin\ = \frac{R *\ mole\ quantity\ of\ IS\ in\ NMR\ sample}{Dry\ weight\ of\ lignin\ sample\ (g)} \tag{7.1}$$

Where, $R = \frac{Integration\ of\ spectral\ region\ of\ interest\ (I_{OH})}{Integration\ of\ IS\ region\ (I_{IS})}$

Among the various hydroxyl groups, it can be observed that a majority of HTC lignin is composed of phenolic hydroxyl groups and only a minor amount of aliphatic and carboxylic OH groups is present. Syringyl units (S-units) and G-condensed units are reported together as total 5-substituted phenolic –OH. The large amount of 5-substituted -OH groups indicates that a high degree of condensation via ether bond and C-C coupling has occured during biomass treatment. Also, the result features that the major phenolic hydroxyls appeared to be guaiacyl (G-units) phenolics with a minor amount of p-hydroxyphenyl groups indicating that HTC lignin is basically a softwood lignin [40].

7.2.1.3 Conclusions

Quantitative ^{31}P NMR spectroscopy has been used to study the structure of HTC lignin. The study also gave understanding of the different functionalities on the HTC lignin surface. The amount and presence of different functional groups such as phenolic, alcoholic, carboxylic acids and various condensed phenolic units were determined. Eventhough, the study gives an indication that HTC lignin's structure can be compared to that of carbon black structure containing hydrogen (mostly in aromatic rings) and number of different oxygen-containing groups (namely, phenol, carboxyl etc), both are distinct exhibiting different surface chemistry. From the study, it can be reported that the concentration of functional group decreases in the following order: phenolic –OH> aliphatic –OH> –COOH groups. Of these, phenolic –OH groups are considered as active sites for filler modification. The principal reasons are as follows: (i) based on the current study, it is considered as the major functional group of HTC lignin (ii) also, the conclusions of a preliminary reactivity study using the most reactive silane thiocyanatopropyl triethoxy silane (Si264®) [98] highlighted that the phenolic hydroxyl groups are reactive towards ethoxy group of the silane. Further, it is published in literature that phenolic moiety is one of the most important functionalities which affects the physical and chemical properties of lignin [99].

7.3 Surface modification of HTC lignin using silane coupling agents

In rubber industry, for more than a decade, bifunctional organosilane coupling agents are extensively used as surface modifiers to enhance the compatibility between hydrophilic filler (in particular, silica) and hydrophobic polymer matrix [100]. In principle, silane coupling agents are composed of a silicon atom attached to two functional groups of different reactivity (X-Si(OR)$_3$). X represents an organo-functional group which is bonded to the silicon atom by a short alkyl chain (e.g., tetrasulfide, -alkyl, mercapto-alkyl, vinyl, etc.) and it can react with the organic polymer during vulcanization. OR represents a readily hydrolyzable alkoxy group (e.g. OCH_3 , OC_2H_5 or $O(H_4C_2\,O)_5(CH_2)_{12}CH_3$) and this reacts with inorganic materials like filler during mixing [101-102]. As a consequence, silane coupling agents act as a bridge between a filler and polymer to enhance the rubber-filler interaction and, thus provide a significant improvement in properties. This silanization reaction is explained for silica as filler and depicted in **Figure 7.9.**

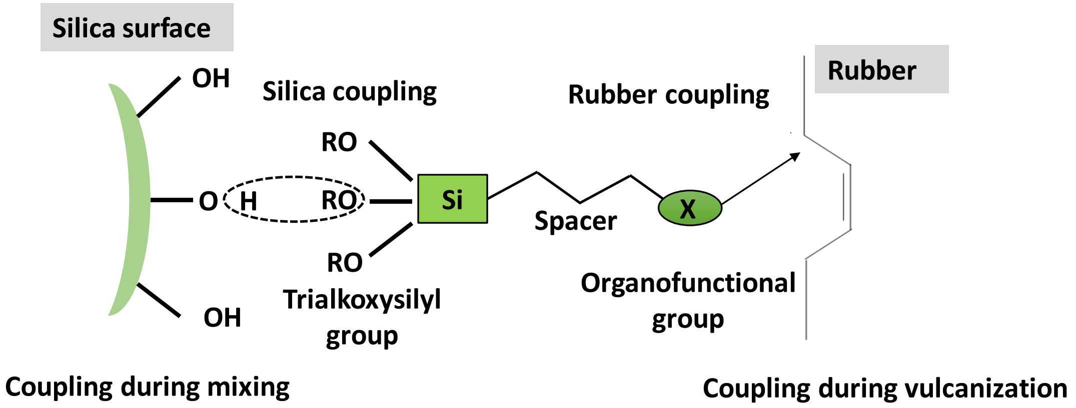


Figure 7.9 Reaction mechanism of silane as a coupling agent [103]

It is established that the application of these intermediate agents improves the reinforcing efficiency of silica filler in rubber compounds [100, 104]. Thus, for this design study, silane coupling agents were selected as surface modifier for HTC lignin.

7.3.1 Screening of different silane coupling agents by in-situ modification

7.3.1.1 Background

Several different rubber silanes have been developed and investigated for silica fillers [104-105]. Each silane has its own advantages and disadvantages [104]. Some of the silanes developed over a period of time are shown in **Figure 7.10.** These silanes differ in their chemical structures, sulfur rank, and functionalities. Initial screening tests were performed as it is of paramount importance to select the right surface modifier which can remarkably improve the mechanical properties of HTC lignin filled compounds. Sulfur-functional silanes were preferred for this initial screening as they are able to participate directly in sulfur vulcanization of HTC lignin filled rubber compounds. Also, the modification/silanization reaction is carried out in-situ. This means that HTC lignin, silane coupling agent, rubber and other ingredients are simultaneously introduced into a thermo-mechanical internal mixer. The objective of this study is to understand the coupling efficiency of the selected silane and the reinforcement of HTC lignin filled compounds.

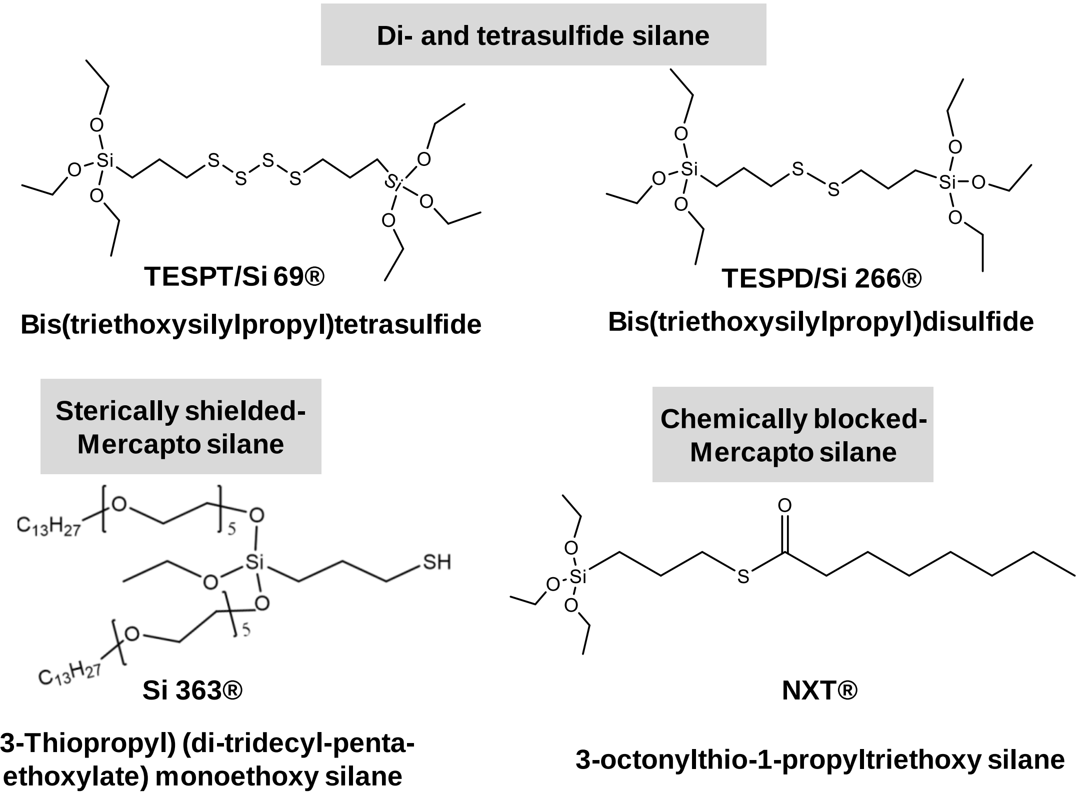


Figure 7.10 Different coupling silanes

7.3.1.2 Experimental

For this screening, some of the commercial silane coupling agents from each category as described in **Figure 7.10** (TESPT/Si69, NXT, Si363) were selected. The amount is kept as 6.2 phr similar to Michelin's green tire recipe irrespective of the filler surface area. Assuming Si69 silane as reference silane, the quantities of the other used coupling agents were adjusted equimolar. Also, considering the two reactive sites of Si69 silanes, double molar quantity of the other coupling agents was added. However, equimolar and alkoxy equivalent calculation resulted in a higher amount of Si363 silane (23 phr) leading to difficulties in the processing of the compounds. Thus, an amount of 9 phr was used for this study. Addition of a lower amount of Si363 silane than the equimolar amount to Si69 is also common in silica technology [106]. Due to the structural differences between the three silane types as shown in **Figure 7.10,** the amount of total sulfur in the compound varies. This, in turn, affects the network formation, therefore a sulfur correction is required. Assuming all the other already discussed influences, a sulfur correction was not taken into account to avoid further complications.

The experiments were carried out using the reference tire tread formulation shown in **Table 15** with a variation in type and amount of used silane coupling agent. A reference compound without silane is also mixed to understand the influence of different coupling agents.

Table 15 Types and amounts of the investigated silanes

Coupling agents	Supplier	Molecular weight (g/mol)	phr
Si69*	*Evonik Industries, Germany*	*532.5*	*6.2**
NXT	*Momentive, Germany*	*365*	*8.5*
Si363	*Evonik Industries, Germany*	*987.5*	*9*
SSBR-75; BR-25; HTC lignin-80; TDAE- 33; ZnO-2.5; St. Ac- 2.5; 6 PPD-2; TMQ-2;S-2.2; TBBS-1.5; DPG-0.25; TBzTD-0.5 ***reference silane 6.2 phr = 15mmol**			

The mixing conditions and mixing procedure as described in **Table 8 &Table 13** were used for this study. The compounds were investigated in terms of their cure and other physical properties.

7.3.1.3 Results and discussion

Cure properties

The cure behavior of different silanized compounds are shown in **Figure 7.11**. It can be observed that the addition of silane decreases the scorch time of the compound i.e., kinetics of vulcanization is improved .This suggests that the addition of silane increases the compound’s basicity and also facilitates in shielding the acidic phenolic hydroxyls from adsorbing the basic accelerators and cure activators. This improvement in kinetics is achieved without affecting the processability of compounds for Si69 and NXT silane, whereas for Si363 silane, the scorch safety is inferior due to the presence of unblocked mercapto groups which is more reactive to the vinyl groups of the rubber [94]. The better scorch safety of NXT silane, on the other hand, can be related to its bulky blocking end-group on the reactive mercapto function [94].

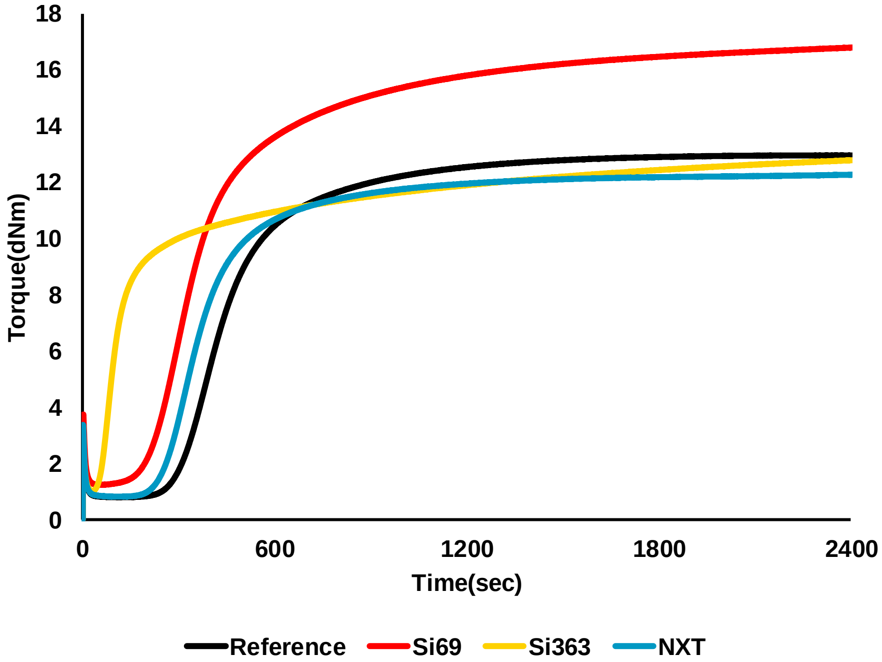


Figure 7.11 Cure properties of the silanized compounds

The increase in minimum (M_L) and maximum torque (M_H) of Si69 compounds compared to other silanes can be explained by the higher sulfur rank of Si69 which can donate some of its sulfur to the compound rising the free sulfur amount and consequently contributing to polymer-filler interaction during mixing and extra crosslinking during vulcanization respectively. Also, a reduction of stiffness of the final vulcanizate of Si363 could be caused by the plasticizing effect of long alkoxy groups, whereas with NXT containing compound, it could be due to the interaction of HTC lignin with the octanoyl group restricting the de-blocking reaction to occur. This might hinder the mercapto function to react with the vinyl groups of the polymers reducing its coupling efficiency.

Payne effect

The Payne effect of different silanized uncured compounds are shown in **Figure 7.12**. The increase in shear modulus at small and high strain can be related to filler-filler and filler-polymer interactions respectively (Chapter 4, Section 4.1.2).

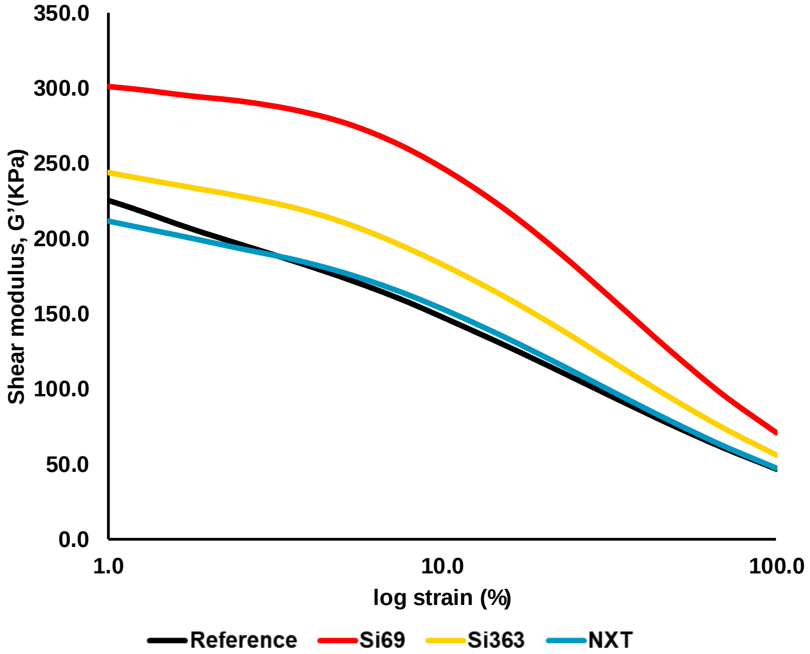


Figure 7.12 Payne effect (uncured) of the compounds with different silanes

The addition of silanes (Si69 , Si363) increases the G' at lower strain which is in contrast to the silica/silane system [32-33]. The higher filler-filler interactions i.e., stronger filler networking of the Si69 silanized HTC lignin filled compounds can be explained by the following theories: (i) the interaction of Si69 to the lignin particles and simultaneous self-condensation of silane creating a 'lignin clusters'. This formed cluster structure can trap the rubber molecules increasing the effective volume fraction of the filler contributing to a high modulus at low strain. This kind of silane self-condensation reaction is highly favourable and more pronounced with Si69 silane due to its structure containing a higher number of ethoxy functionalities (six groups). Upon increasing the strain amplitude, the trapped rubber molecules are released decreasing the G' value. (ii) The resulting cluster structure can also lead to poor micro-dispersion of the fillers in the rubber matrix (iii) The known effect from cellulose is that an irreversible structural change of cellulose fiber can occur by increased crystallinity and fiber aggregation by hydrogen bonds when exposed to temperature which is known as "hornification" [107]. This suggests that a similar kind of structural change might also occur in lignin during this intensive mixing process. Lignin can undergo oxidation when exposed to high temperature i.e.,150 ºC-250 ºC. Beyond 250 ºC, the oxidized lignin can undergo crosslinking /condensation reactions [108]. A thermo-oxidation and condensation of HTC lignin can increase the polarity of the lignin surface which might result in higher filler-filler interactions. This oxidation might occur during mixing where HTC lignin is exposed to a mixing temperature of 150º C which can lead to the formation of carboxylic acid moieties. And these groups can further undergo condensation reaction (between carboxylic acid group and a hydroxyl group (self-condensation of lignin)) to form an ester which might be catalyzed by silanes (or other reactive modifying agents with a suitable functional group). This might result in a condensed lignin structure which is denser. The probability of this reaction is very low and is less pronounced as it is a not noticeable effect in the presence of other silanes. (iv) The high sulfur rank of Si69 silane which can donate its sulfur at high processing temperature leading to formation of filler-polymer interaction / polymer-polymer interaction in the mixer. This effect is also observed for Si363 silane containing the sterically blocked mercapto groups where the early radical breakage of the S-H bond can cause a coupling reaction towards vinyl groups of the polymers during mixing resulting in a pre-scorch effect (which is also in line with lower scorch safety of these compound). The resulting filler-polymer interaction not only increases the G’ at low strain but also at high strain. And this theory is true and valid when comparing the results of NXT silane which can’t deblock the octanoyl groups protecting the mercapto functionality at lower mixing temperature (140-150ºC) resulting in lower filler-filler and filler-polymer interactions.

Mechanical properties

Figure 7.13 presents the stress-strain behavior of different silanized compounds. Among all the compounds, the Si69 silanized compound shows the best improvement in the stress-strain properties which is due to the coupling efficiency in addition to its sulfur donating effect creating an additional increase in crosslink density. The NXT silanized compound shows identical properties to that of the reference compound clearly indicating poor filler-polymer interactions which is in line with the results of the Payne effect. This leads to the assumption that the thioesters are not deblocked to release mercapto groups which can then couple to the polymer chains increasing the filler-polymer interaction unlike Si363 silane.

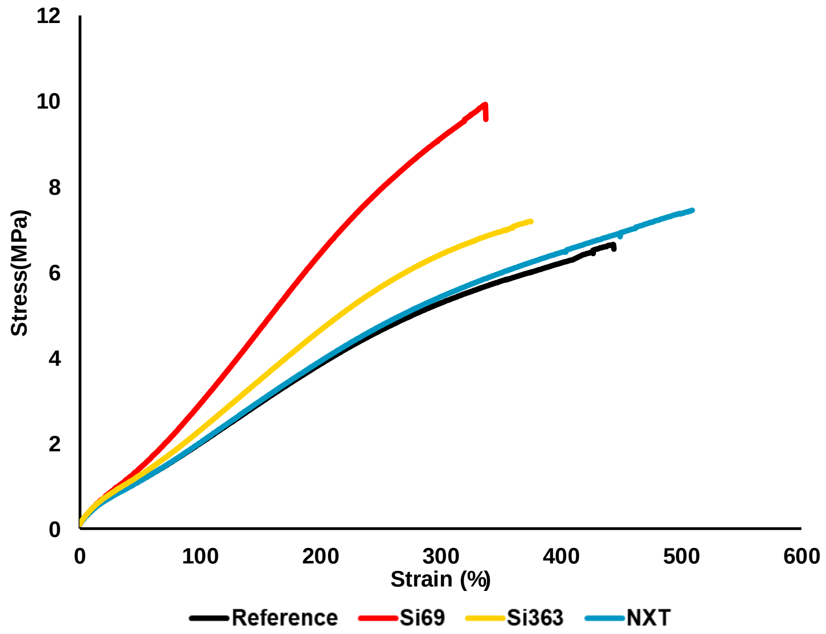


Figure 7.13 Mechanical properties of the vulcanizates containing different silanes

Compound hardness

The hardness results shown in **Figure 7.14** are in line with the Payne results, especially G‘ at low strain. The increase in filler-filler network increases the hardness of the compound. This means that Si69 and Si363 silanes are creating filler network structures which can reinforce the rubber.

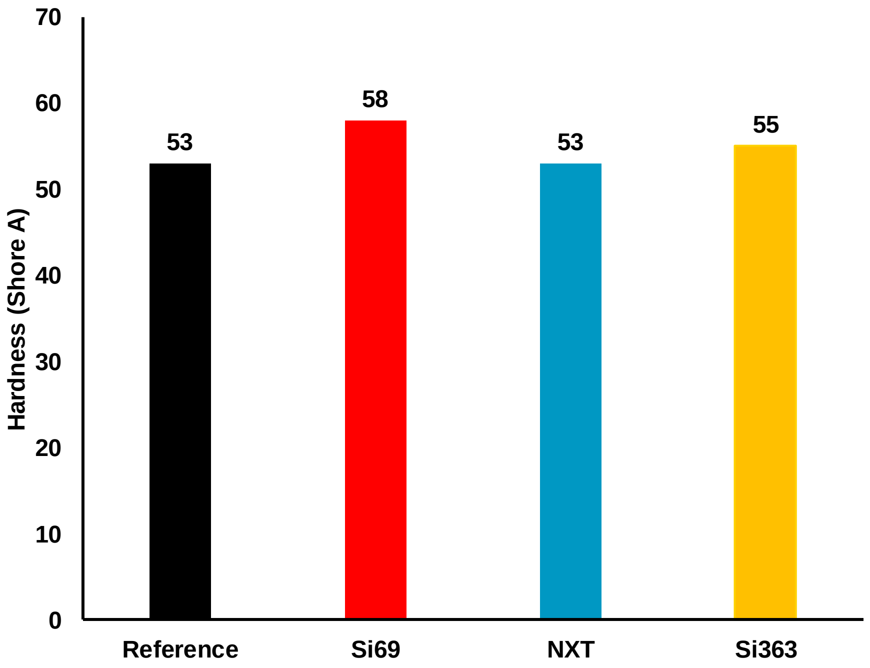


Figure 7.14 Hardness of the vulcanizates

Rebound resilience

The rebound resilience can be indirectly correlated with the DMA results. The higher the rebound value higher the compound's elasticity i.e., lower the tan delta. Rebound resilience of different silanes at 70 °C shows improvement in the dynamic behavior of the compound, in comparison to the reference (without silane) as depicted in **Figure 7.15**. This improvement can be related to an improved filler-polymer interaction provided by the silanes. For Si363 and Si69, this interaction is provided by chemical linkages between filler and polymer resulting in lower dynamic hysteresis. In case of NXT silane, this is solely related to hydrophobation effect which makes the filler more compatible with rubber, however the absence of chemical linkages between filler and polymer resulted in lower elasticity. This is also in line with the other achieved properties.

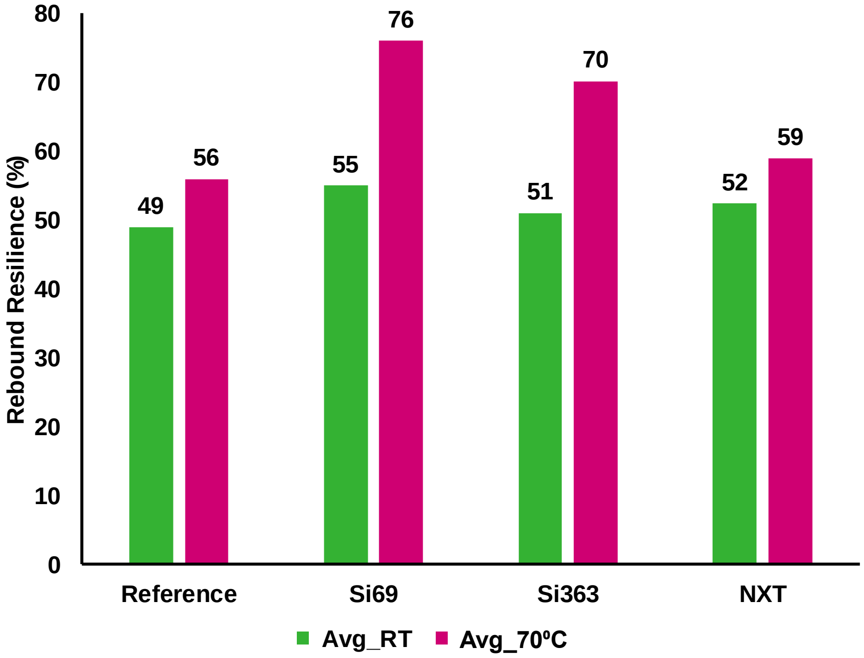


Figure 7.15 Rebound resilience of the vulcanizates

7.3.1.4 Summary

Different coupling silanes (Si69, NXT, Si363) were used as surface modifier for HTC lignin. The comparative study of the properties of compounds and vulcanizates containing HTC lignin silanized by these different coupling agents, shows their different coupling efficiency and its impact on the rubber reinforcement by HTC lignin. Among these silanes, NXT gives the poorest overall properties indicating that the deblocking reaction was hindered by the presence of HTC lignin which leads to poor filler-polymer interactions. The use of Si69 and Si 363 silane results in an improvement in compound properties which is mainly due to the presence of polymer reactive groups i.e, tetrasulfide and mercapto group respectively that take part in the vulcanization leading to strong polymer-filler interaction. Also, the silanization reaction between the lignin and the silanes (Si69 & Si363) resulted in increased filler-filler interactions, which is assumed to be due to several theories described under Payne effect. This increased filler-filler interaction doesn’t have a negative effect on compound hysteresis which is contrary to the silica/silane system [32-33]. Based on the results, Si69 silane shows the overall best performance and better process safety, therefore it was selected to develop an optimized system.

7.3.2 Optimization of modification parameters on silane modified compounds

The previous study concerning different silanes features that the silanization of lignin with Si69 and Si363 leads to an improvement of in-rubber properties compared to the unmodified lignin. The obtained reinforcement is still not sufficient enough and comparable with the conventional fillers. In this aspect, the extent of the silanization reaction is a crucial factor affecting the reinforcing characteristics of the silane modified HTC lignin compounds. Extensive research has been undertaken in understanding the reaction mechanism of TESPT (Si69®) with silica as a filler and influencing parameters of the silica/silane coupling reactions [109,110]. The widely accepted mechanism is proposed by Hunsche et al. and this theory concludes that coupling reaction follows a two-step primary reaction involving hydrolysis of silane in the presence of water leading to ethanol emission followed by chemical coupling of hydrolysed silane to a silanol group of the silica by the release of water and a secondary reaction involving condensation of neighboring silane molecules which are attached to the silica surface [110]. However, recent investigations by Blume et al. highlighted the flaws of this coupling mechanism and proposed a new model based on certain research questions and considerations. This new model of coupling mechanism is depicted in **Figure 7.16** [111]. The summary of the findings are (i) not all the silanol groups of silica are reactive towards silane, therefore the amount of these reactive silanes (isolated and geminal) are important for the silane coupling (ii) only 25% of all Si-OHs are reactive (iii) the presence of water favors the silanization reaction but a direct coupling seems to be a possible mechanism in the absence of water (iv) the accessibility of silanol groups by the silane i.e., the distance that separates the silane reactive silanols (isolated and geminal) is crucial for the coupling reaction [111]. Based on these findings, the following reaction mechanism is proposed: (i) a primary reaction that occurs between one ethoxysilyl group of the coupling agent and silanol group (preferably, isolated and geminal) of the silica. This can be either direct coupling reaction (in the absence of water) or a hydrolysis reaction (in the presence of water). Here in this model, precipitated silica is used whose surface contains water, therefore a hydrolysis step is proposed. The primary reaction starts at temperatures around 130 °C. (ii) a secondary condensation reaction that occurs between the neighboring silane molecules which are already bound to the silica surface. [112].

Many published literatures concluded that the mixer silanization temperature and time determine the degree of silanization [109, 113]. Therefore, the effects of these parameters on the end-use properties of the HTC lignin filled rubber vulcanizates will be investigated in the current study. The optimization studies were carried out using the most promising Si69 and this will be discussed in the upcoming sections.

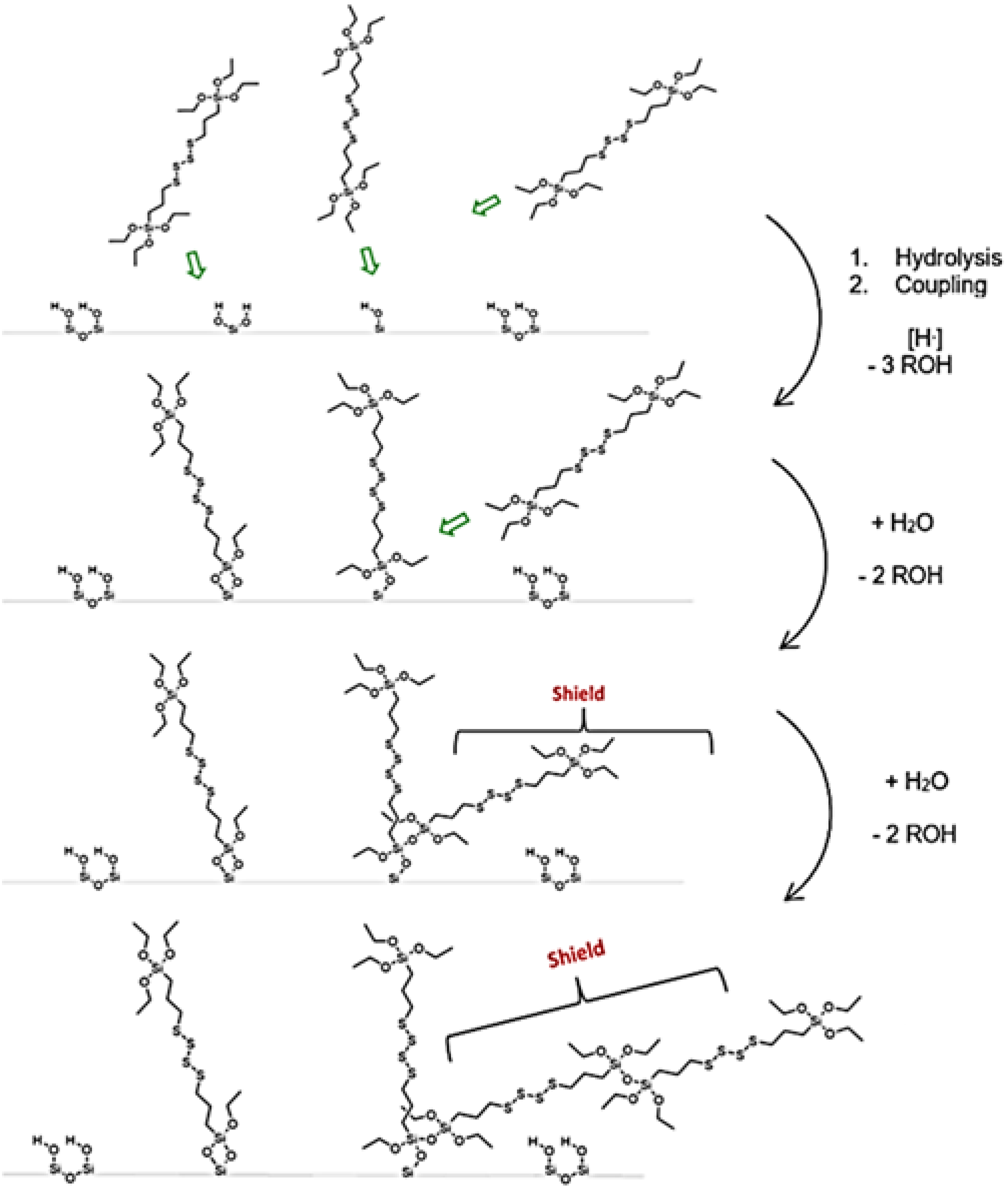


Figure 7.16 Silanization reaction mechanism [111].

7.3.2.1 Influence of mixing parameters: Mixing temperature

This section describes the investigation of the influence of the mixing temperature of a Si69 modified HTC lignin filled compound.

7.3.2.1.1 Experimental

The compounds were mixed in an internal mixer. The mixing conditions and mixing procedure are similar to **Table 8 & 13,** respectively. The only change in the mixing conditions is the variation in the dump temperature of the Si69 compounds representing different silanization temperature. This is tabulated in **Table 16**. The dump temperature was varied by varying the mixer's rotor speed while keeping other mixing conditions and mixing time constant.

Table 16 Obtained dump temperatures of the compounds.

Compound	**Dump temperature (°C)**
Reference (without Si69)	140-150
Si69_DT_140	140-150
Si69_DT_150	150-160
Si69_DT_160	160-170

The mixing formulation for this study is presented in **Table 17**. The compounds were cured using the procedure discussed in Chapter 6, **Section 6.2.2**. Rheological and other physical properties will be carried out using the procedures described in Chapter 6, **Section 6.2.3.1 & 6.2.3.2** at the end of the compound preparation.

Table 17 Compound formulation

Ingredient	**Reference (phr)**	**Si69 (phr)**
SSBR	75	75
BR	25	25
Filler	80	80
Si69	0	6.2
TDAE	33	33
ZnO	2.5	2.5
St. Ac	2.5	2.5
TMQ	2	2
6-PPD	2	2
Sulfur	2.2	2.2
TBBS	1.5	1.5
DPG	0.25	0.25
TBzTD	0.5	0.5

7.3.2.1.2 Results and discussion

Cure properties

The vulcanization behavior of the lignin filled and lignin-Si69 filled compounds is shown in **Figure 7.17**. The curves indicate slight marching behavior. The compounds containing Si69 show a higher inital torque (M_L), maximum torque (M_H) with lesser scorch safety in comparison to the reference (unmodified lignin). The increased initial torque value is related to the compound's viscosity and the higher final torque is related to the increased polymer-polymer interaction due to the additional sulfur of Si69 silane as well as the increased filler-filler and filler-polymer interactions. An increasing dump temperature doesn't influence the scorch safety of silane modified compounds significantly. However, the initial viscosity of the compound is increased to a higher level. This effect is significant for temperature above 150 °C and this indicates that the compound mixed at 160 °C is pre-scorched, meaning that the sulfur moieties of the coupling agent has already partly reacted with the polymer chains, restricting its mobility.

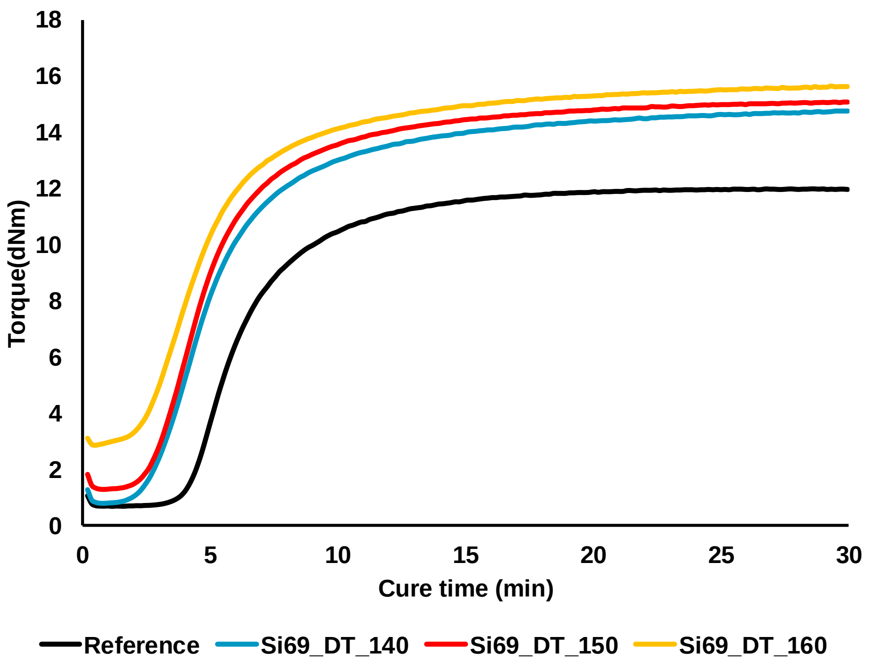


Figure 7.17 Cure behavior of the HTC lignin filled compounds dumped at different temperatures

Mooney viscosity and Payne effect

The Si69 modified lignin compounds show higher viscosities with increasing dump temperature in comparison with the reference lignin as tabulated in **Table 18**.

Table 18 Viscosity of the compounds

Compounds	***Mooney viscosity (MU)***
Reference	*45*
Si69_DT_140	55
Si69_DT_150	65
Si69_DT_160	125

The Mooney viscosities gradually increase with higher dump temperature. Whereas for the compound mixed and dumped between 160-170 °C, there is an abrupt increase in the obtained values. The former effect can be explained by the oxidation and resulting self condensation of lignin leading to a denser filler structure with increasing dump temperature (**Section 7.3.1.3**, “Payne effect theories”). For compounds mixed above 160 °C, apart from the above-mentioned hypothesis, the increase of the Mooney values can be attributed to the contribution from the coupling reaction (crosslinking) between Si69 silane bonded to the lignin and rubber causing further restriction for polymer mobility. This leads to worse processabilityof the compound compared to the other compounds. The increase in the viscosity of the compounds can be indirectly related to dispersion behavior. Compared to other two temperatures, the dispersion behavior of fillers for the compounds dumped at 160 °C might be inferior.

The addition of Si69 to lignin increases the G’ values at both lower and higher strain as shown in **Figure 7.18**. These results are in line with the Mooney values. The increase of G’ at low strain values can be explained by previously explained theory of oxidation and self-condensation of lignin to denser structure affecting the dispersion behavior of them in the rubber matrix.

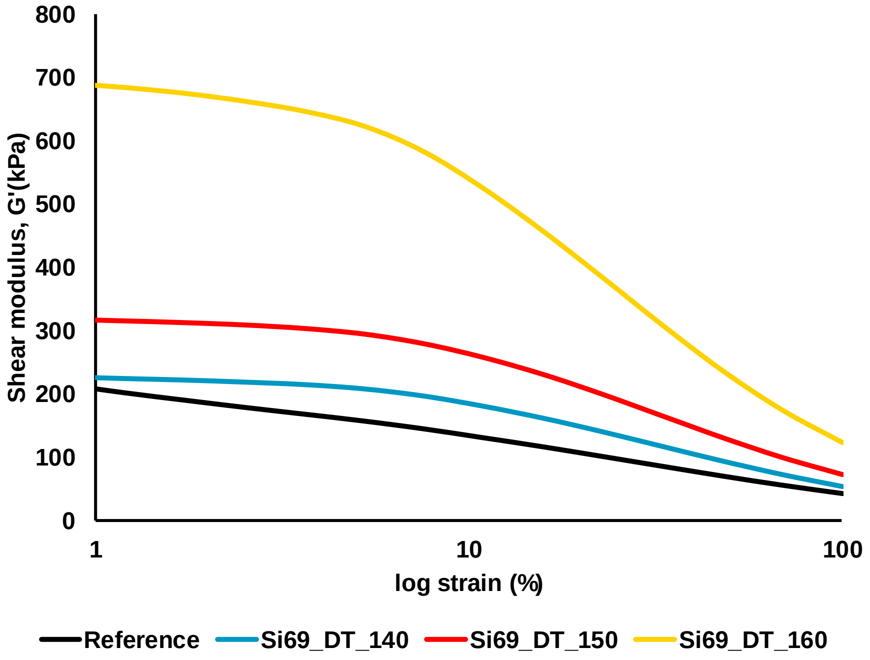


Figure 7.18 Payne effect of the uncured compounds

The increase of G' at higher strain value is related to polymer-filler interactions. With increasing dump temperature, the filler-polymer interactions are increased due to the increased coupling reaction between rubber and Si69 bonded lignin surface. However, the compound dumped above 160 °C shows a significant increase in the interaction level which is due to both lignin-rubber and rubber-rubber interactions.

Mechanical properties

The addition of Si69 significantly improves the compound's tensile behavior and also modulus at 100% and 300% compared to unmodified lignin as shown in **Figure 7.19**. Unlike the effects observed in the case of the storage modulus G' and Mooney viscosity, the reinforcing effect with increasing mixing temperature (from 140 to 160 °C) are not that significant and are less pronounced. This indicates that degree of silanization is not improved with increasing mixing temperature. For the compound mixed and dumped above 160 °C, the modulus and tensile strength is increased with decreasing elongation at break which can be related to the increased crosslink density resulting in a stiffer compound. This is in line with the Mooney viscosity results and Payne results showing a significant rise for the compound dumped above 160 °C.

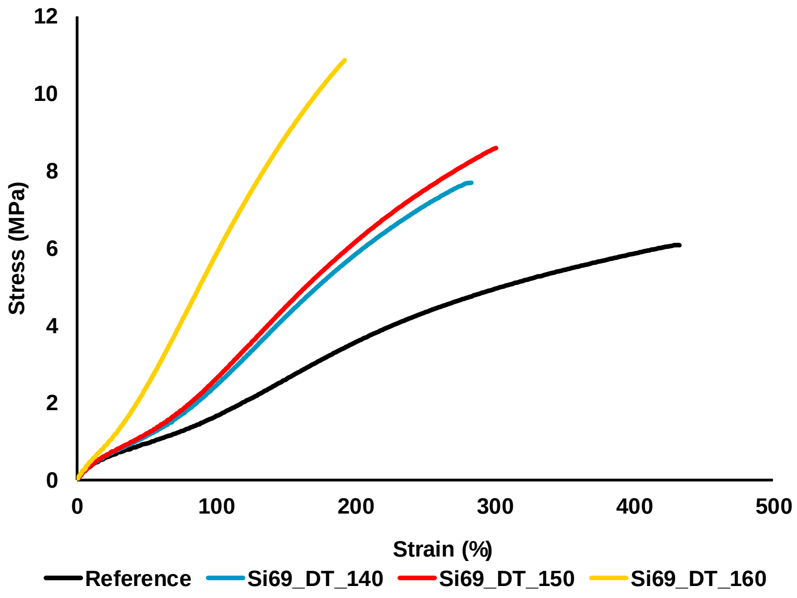


Figure 7.19 Mechanical properties of the vulcanizates compounded at different temperatures

Hardness

The hardness of the cured compounds dumped between 140 to 160 °C are also not that significant in comparison to the compounds dumped between 160 to 170 °C. This also highlights that degree of silanization is not increased with increasing dump temperature.

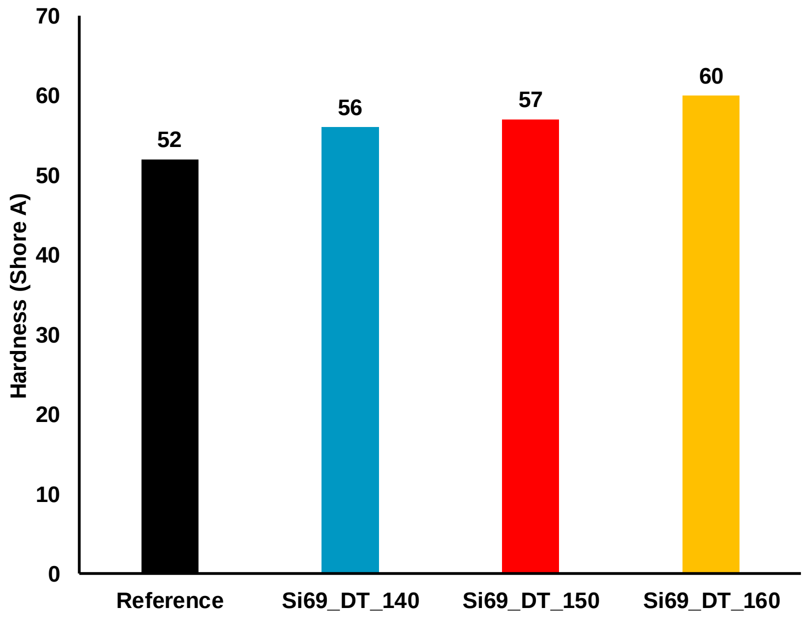


Figure 7.20 Hardness of the vulcanizates

Rebound resilience

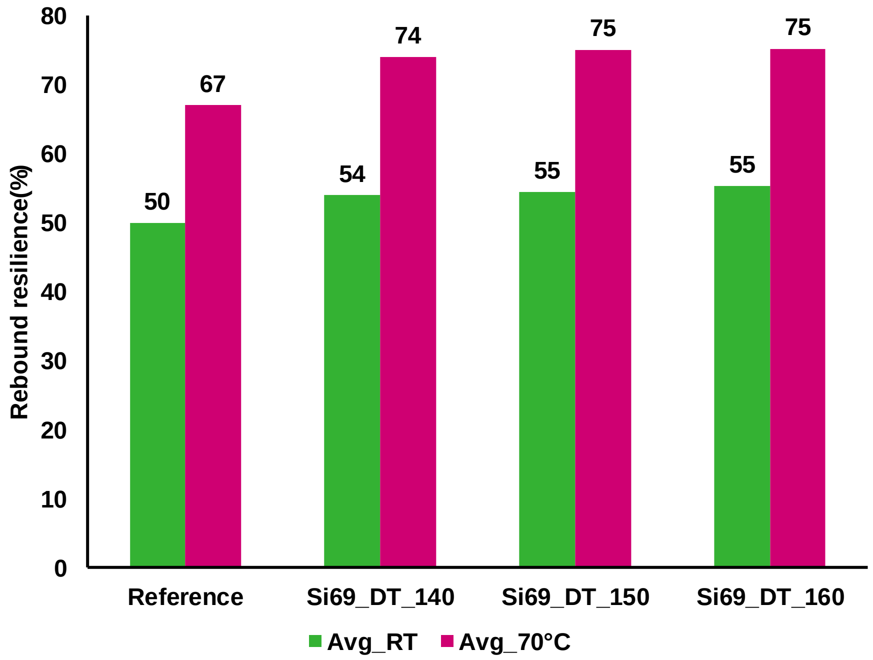


Figure 7.21 Rebound resilience of the vulcanizates

Compared to the reference, the compounds filled with silanized HTC lignin show a higher resilience value due to the formed chemical linkages between the rubber and filler in the presence of Si69. However, mixing at different temperatures doesn't influence the compound's resilience significantly as presented in **Figure 7.21**. This could be due to the two effects contradicting with each other i.e., the denser lignin structure and the increased crosslink density at higher mixing temperature.

7.3.2.1.3 Summary

The results of this experimental work shows that mixing at 140 °C to < 160 °C ensures an optimal performance characteristics of HTC lignin reinforced rubber compounds. Also, an increasing dump temperature gives an indication that it there is an increase in the oxidation and self-condensation of lignin leading to a denser structure. It also gives an assumption that the sulfur silane also promote and catalyzes this condensation reaction. This structure leads to worse dispersion of the filler resulting in a negligible increase in-rubber properties (mechanical, hardness and rebound). Nevertheless, this hypothesis need to be further confirmed by mixing reference (without silane) at different temperatures. Whereas, temperatures above 160 °C support also the reaction between the rubber matrix and sulphur moieties of Si69 which leads to a pre-scorch affecting the compound's processability. This also increases the crosslink density of the compound resulting in improved properties. This is confirmed by the results of the tensile strength, the

M300% and M100% values and the higher Mooney viscosity. Based on the obtained results, the dump temperature range between 140-150 °C is selected to achieve a compromise between the performance and processability.

7.3.2.2 Influence of mixing parameters: Mixing time

This section describes the investigation of the influence of the mixing time of a Si69 modified HTC lignin filled compound.

7.3.2.2.1 Experimental

The compounds were mixed in an internal mixer. All series of experiments were done based on a tire tread compound as shown in **Table 17**. The mixing conditions and mixing procedure are similar to **Table 8 & 13**. The only change in the mixing condition is the variation in the total mixing time for Si69 based compounds which represents different silanization time as tabulated in **Table 19**. In case of the reference compound (without any silane), the total mixing time is 10 mins without silanization. Based on the outcome of the previous study, an optimized dump temperature of 140-150 °C is selected for all compounds.

Table 19 Obtained mixing time of the compound.

Compound	**Total mixing time (mins)**
Reference (without Si69)	10
Si69_10min	10
Si69_12min	12
Si69_14min	14

The compounds were cured using the procedure described in Chapter 6, **Section 6.2.2**. Rheological and other mechanical properties were carried out using the procedures described in Chapter 6, **Section 6.2.3.1 & 6.2.3.2** at the end of the compounds' preparation.

7.3.2.2.2 Results and discussion

Cure properties

The vulcanization behavior of the reference compound and Si69 modified HTC lignin filled compounds prepared with different mixing times is shown in **Figure 7.22**. With increasing silanization time, the minimum (M_L) and maximum (M_H) torque of the silane modified HTC lignin filled compounds are increased which is due to an increased degree of silanization.

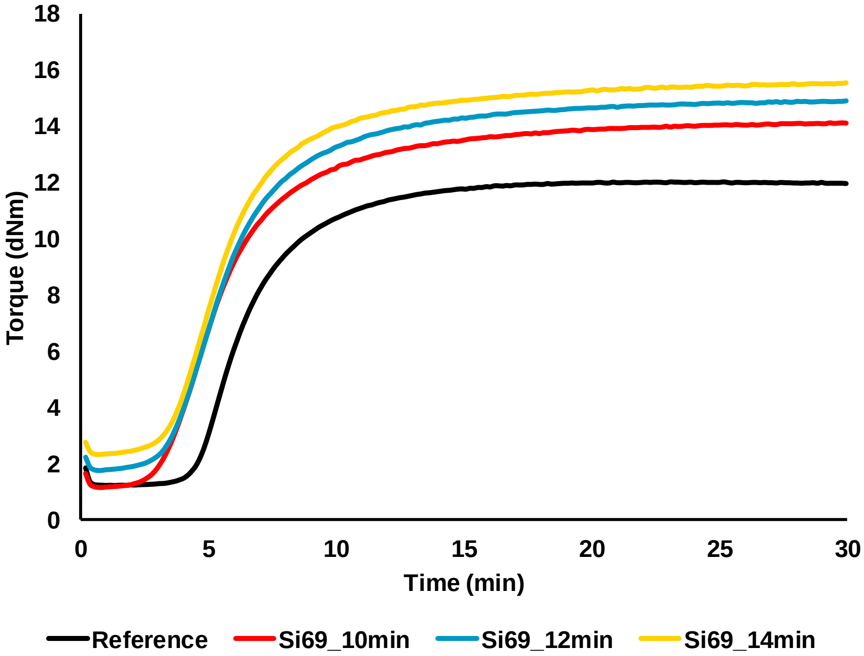


Figure 7.22 Cure behavior of the compounds

Mooney viscosity and Payne effect

As presented in **Table 20**, it can be seen that the Mooney viscosity of the silane-modified HTC lignin filled compounds increases with increasing mixing time and this is in line with the minimum torque (M_L) of the cure curves.

Table 20 Mooney viscosity of the uncured compounds

Compounds	***Mooney viscosity (MU)***
Reference	*45*
Si69_2min	55
Si69_4min	75
Si69_6min	86

The increase in Mooney viscosity with longer mixing time can also be explained by the similar "lignin self condensation" phenomenon described in **Section 7.3.2.1** which results in denser filler structure**.** This formed structure can also cause a worse filler dispersion. The observed values are not adverse compared to the values obtained with increasing mixing temperature. Also, the pre-scorch behavior of compounds mixed for a longer mixing time is less pronounced. This is further confimed by the Payne effect measurements presented in the following.

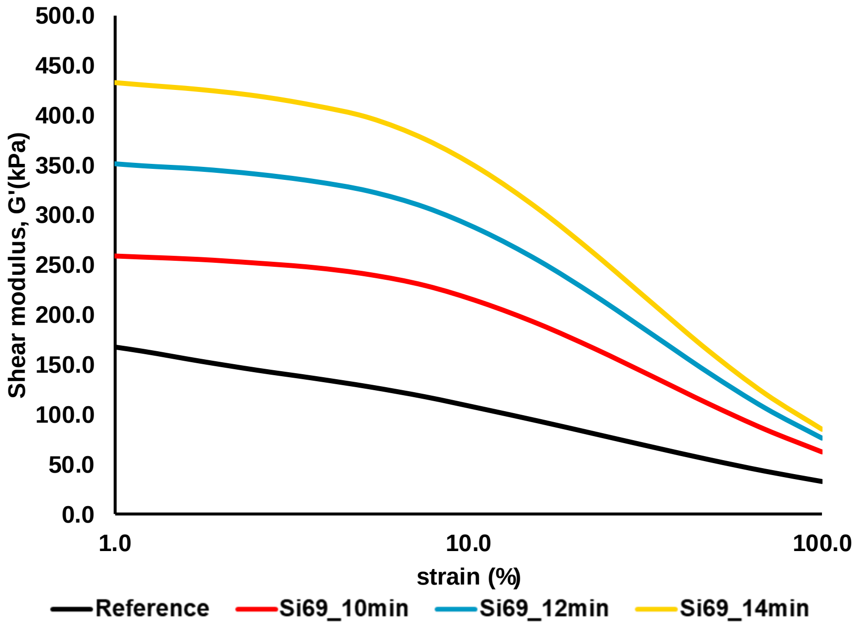


Figure 7.23 Payne effect of the uncured compounds

The Payne effect results (**Figure 7.23**) are also in line with the Mooney viscosity values. A longer mixing time increases the filler structure increasing the filler-filler interactions as well as filler-polymer interaction.

Mechanical properties

The tensile strength and modulus at 100% and 300% results are depicted in **Figure 7.24** are in a good agreement with the results of the maximum torque (M_H). This improved reinforcing efficiency with increasing silanization time clearly indicates that the filler-filler and filler-polymer interaction is increased. In addition to these effects, the increased modulus and decreased elongation of the vulcanizate mixed above 12 mins can be attributed to the pre-scorch effect of the compound (filler-polymer interactions & polymer-polymer interactions) which increases the overall crosslink density of the compound, resulting in a stiffer compound. This is also in line with the Mooney viscosity and Payne effect results showing a significant rise for the compound with increasing mixing time.

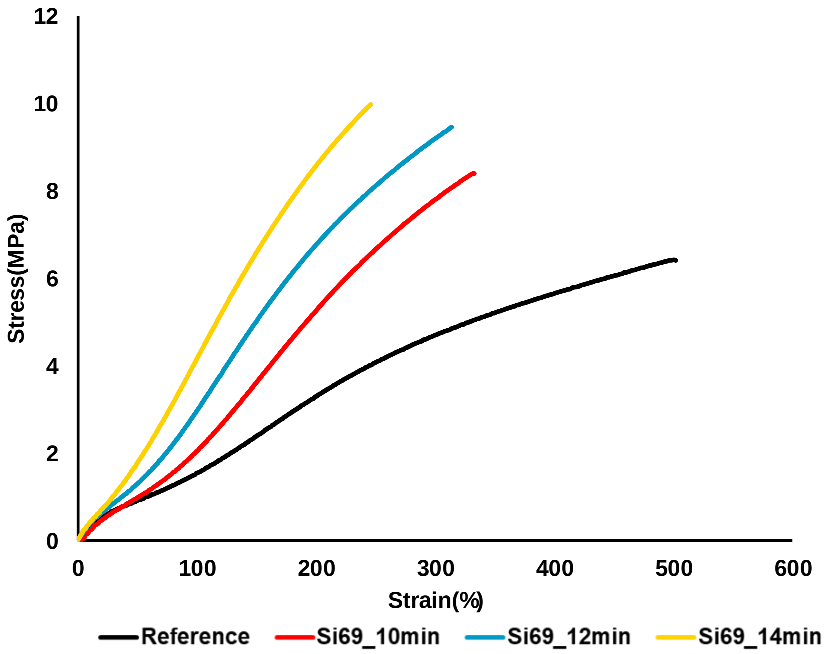


Figure 7.24 Mechanical properties of the vulcanizates

Hardness

The increase in hardness of the silane-modified-lignin filled compounds with increasing mixing time also highlights the formation of stronger filler-filler interactions and filler-polymer interactions in comparison to referencecompound, as presented in **Figure 7.25**. For longer mixing time, this increase is also due to the increase in crosslink density.

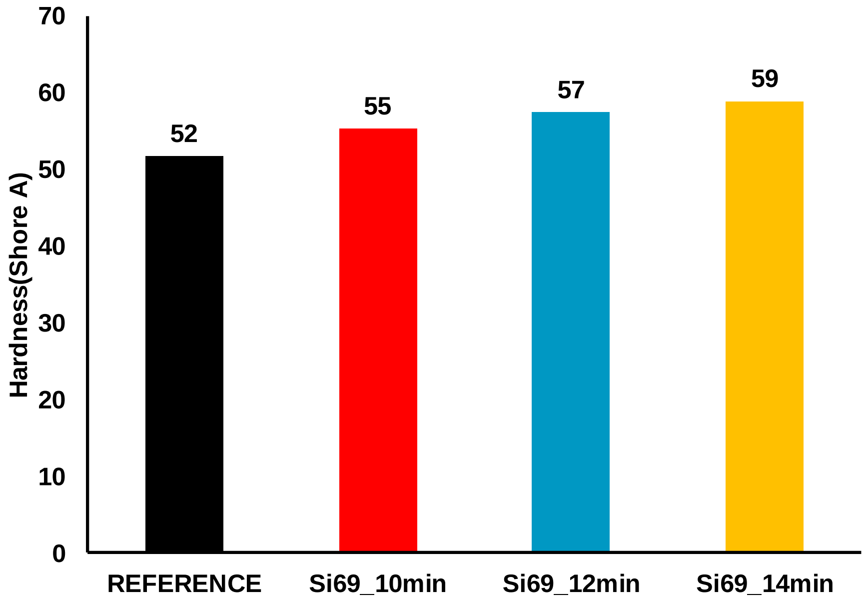


Figure 7.25 Hardness of the vulcanizates

Rebound resilience

Compared to the reference, the silanized compounds show a higher resilience value due to the formed chemical linkages between the rubber and filler in the presence of Si69. However, mixing at different time slightly influence the compound‘s resilience as presented in **Figure 7.26**. This is again attributed to the increased silanization degree.

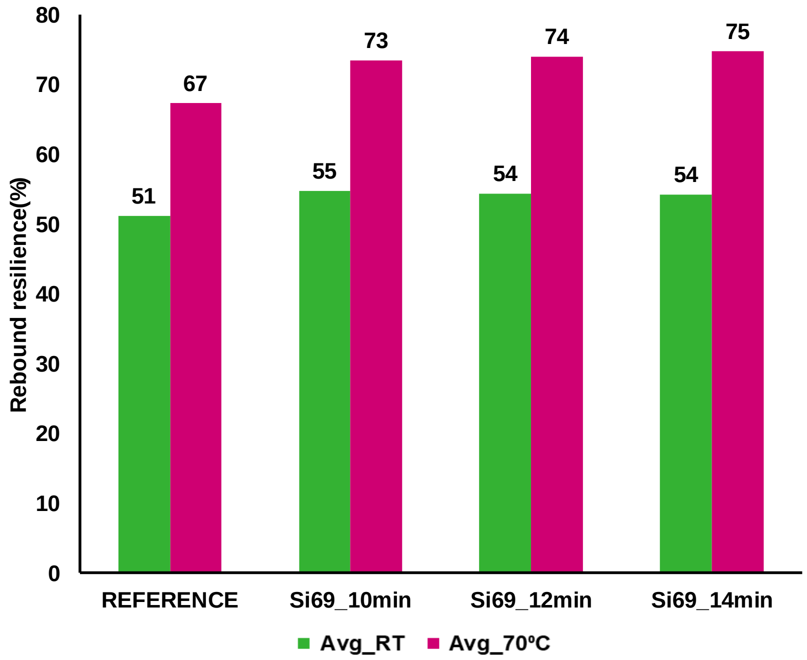


Figure 7.26 Rebound resilience of the vulcanizates

7.3.2.2.3 Summary

Based on this study, it can be concluded that unlike silanization temperature, the silanization time strongly influences the reinforcing behavior of silane modified HTC lignin. Increasing the silanization time creates more bonding of Si69 to the lignin surface (increase in degree of silanization) and also results in a self-condensation of lignin leading to denser structures. This increases both the filler-filler interaction and filler-polymer interaction. It is confirmed by Payne effect and Mooney viscosity results. Nevertheless, a longer mixing time also increases the Mooney viscosity of the compound which can affect the processability. This observed value is not significant in comparison to the observed effect for the mixing temperature of 160 °C. Therefore, a mixing time between 10-12 mins is selected as optimum to achieve a compromise between the performance and processability. A second mixing stage can also be introduced to avoid pre-mature crosslinking and further increase the silanization efficiency.

7.3.2.3 Use of plasticizer as a possible compatibilizer for silane-modified HTC lignin

The impact of a bio-based oil on the compatibilization of filler and rubber in comparison to the conventional TDAE will be investigated in this section.

7.3.2.3.1 Background

In-situ compatibilization with low molecular weight chemicals is one of the strategies to enhance the compatibility between filler and polymer. One of the low molecular weight chemicals in tire formulation is a plasticizer oil. It is considered to be an indispensable ingredient in a tire compound as it enables the use of higher amounts of filler and high molecular weight polymers. Safe mineral based process oil Treated Distillate Aromatic Extract (TDAE) is widely used in the tire tread formulation [114, 115]. Therefore, for this whole design study it is preferred as a reference. The use of a more polar oil as an alternative to TDAE can improve the compatibility of polar lignin filler. For this purpose, a bio-based polar oil was selected due to their low cost, non-toxicity, wide availability and renewability [114]. The recently introduced bio-based polar oil Vivamax 500 was chosen as an alternative to TDAE for this study.

7.3.2.3.2 Experimental

The bio-based oil used for this study is Vivamax 500 (VVM), purchased from Hansen & Rosenthal KG, Germany. The formulation used for this study is similar to the one from **Table 17 (Si69)**, with the variation in oil type. The compounds were mixed in an internal mixer in two stages. The mixing procedure and mixing conditions were similar to these presented in **Tables 8 & 9**. The cure and mechanical properties of the compounds containing the two process oils will be compared and evaluated.

7.3.2.3.3 Results and discussion

Cure behavior

The influence of the oil type on the cure properties is shown in **Figure 7.27**. The compound with VVM demonstrates a faster cure rate and a decreased scorch safety. Similar behavior of VVM is also reported for a silica filled system [115]. This indicates that along with Si69, the polar groups of VVM (fatty acids or esters) is also interacting with the phenolic groups at the lignin surface. This interaction can further hinder the adsorption of accelerators and other cure activators. Also, the increase in the maximum torque (M_H) can also be explained by the stronger filler-filler interaction formed by VVM in addition to the crosslink density and filler-filler networks formed by Si69.

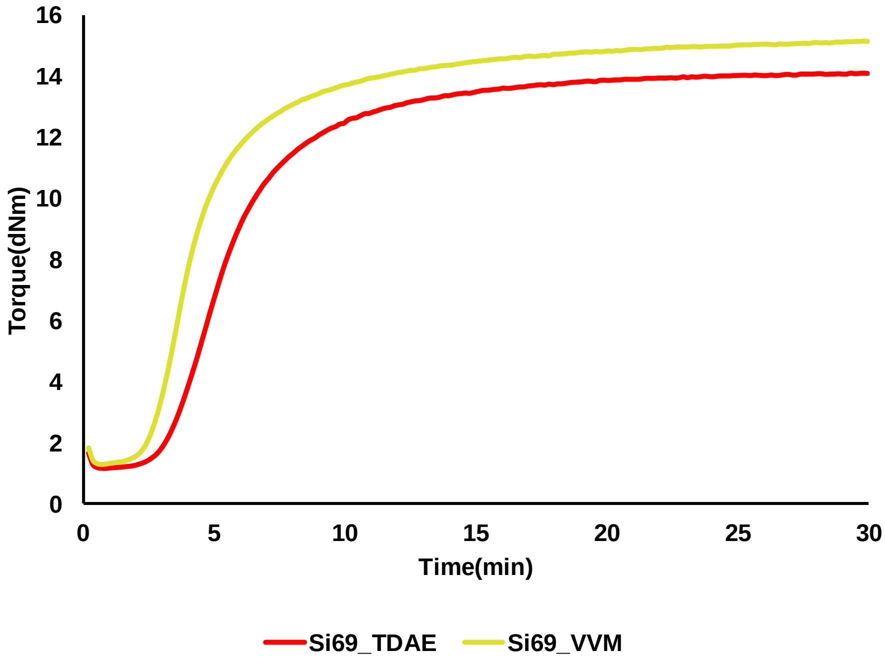


Figure 7.27 Cure behavior of the compounds containing TDAE (Si69_TDAE) or Vivamax 500 (Si69_VVM)

Payne effect

The increase in M_H is also in line with the Payne measurement (an increase in the shear modulus (G') at low strain) as shown in **Figure 7.28.** The magnitude of increase in G' at low strain with VVM oil suggests that along with the lignin cluster structures formed by self condensation of Si69, VVM oil also forms additional structures with lignin by hydrogen bonding. This results also in an inferior micro-dispersion of the compound. Although the presence of VVM oil shows an interaction with lignin, the level of filler-polymer interaction represented by G'at higher strain is similar for both oil types.

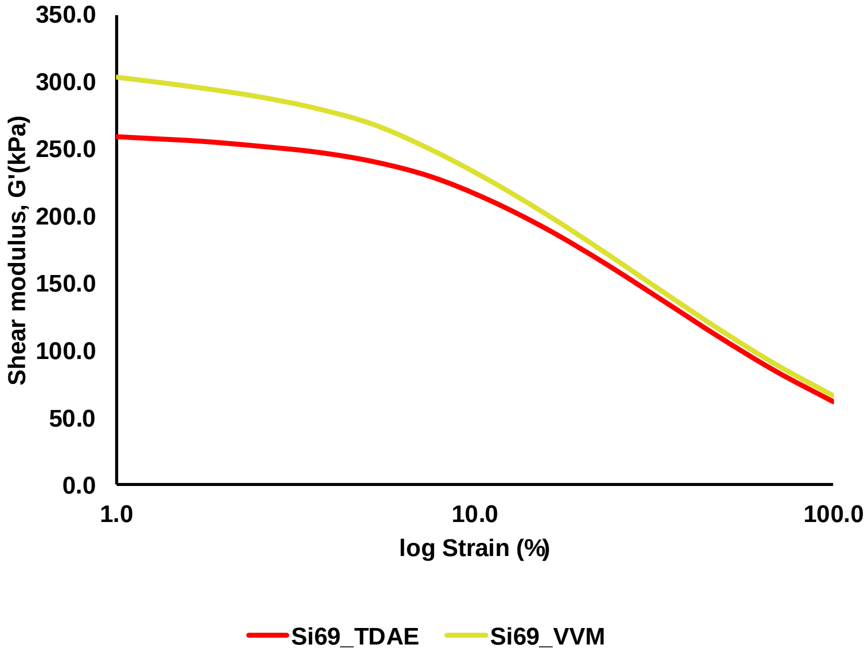


Figure 7.28 Influence of oil type on Payne effect (uncured compounds)

Mechanical properties

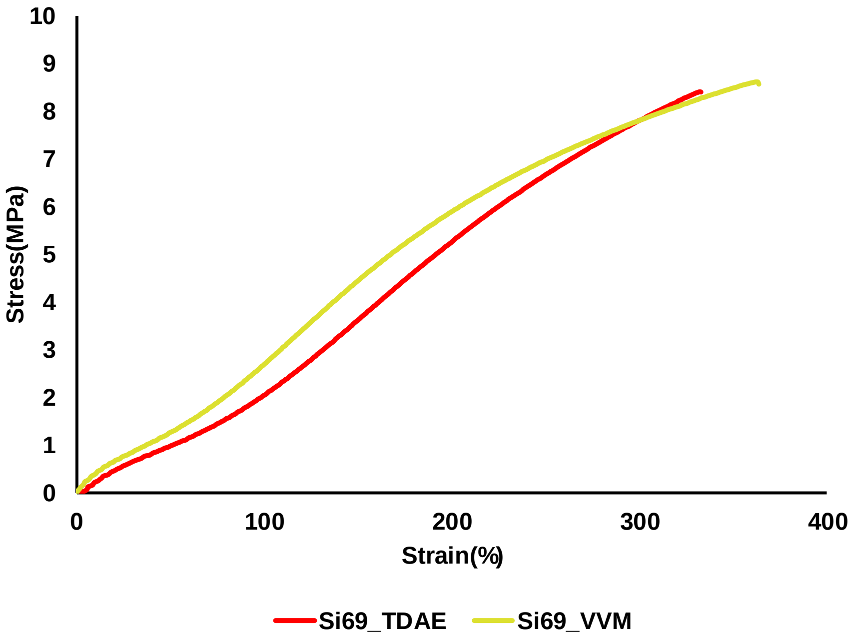


Figure 7.29 Influence of oil type on stress-strain curve of the vulcanizates

The stress-strain behavior of the vulcanizates containing different oils is shown in Figure 7.41.The modulus of the compound is significantly increased with the addition of VVM upto an elongation of 200% which could be related to the increased M_H value presented in **Figure 7.29**. After 200%, the obtained moduli of both systems are comparable which is in line with the Payne effect showing similar filler-polymer interactions.

Hardness

A similar effect can be observed in the hardness results (**Figure 7.30**) The VVM compound has a noticeably higher hardness value which is in line with the higher Payne effect (**Figure 7.28**) and mechanical properties.

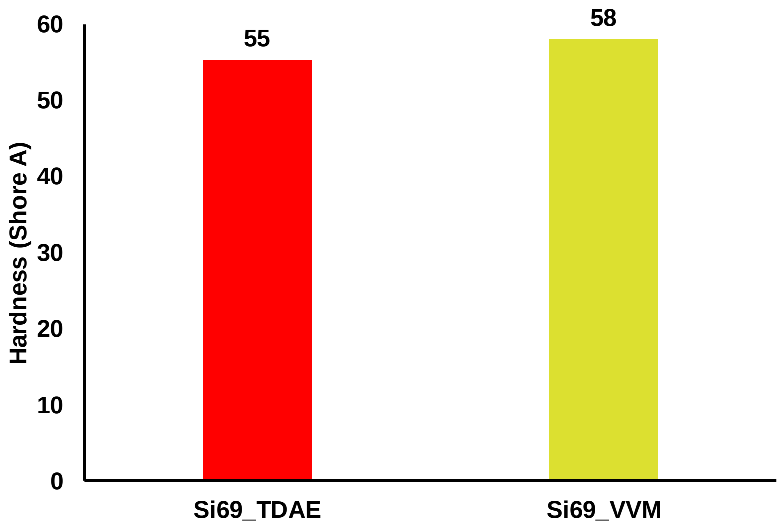


Figure 7.30 Influence of oil type on the cured compound hardness

Rebound resilience

Figure 7.31 presents the obtained rebound resilience for both compounds containing different oil types. The rebound resilience obtained with VVM is lower in comparison to TDAE oil at both temperatures, meaning a lower elasticity which could be due to the increased filler-filler interaction of the Si69_VVM compound (**Figure 7.28**). The VVM oil exhibits a higher polarity than TDAE because of its natural origin (ester groups), thus it will tend to be located close to the HTC lignin particles forming a physical interaction links between them and exhibits hysteresis leading to a lower elasticity.

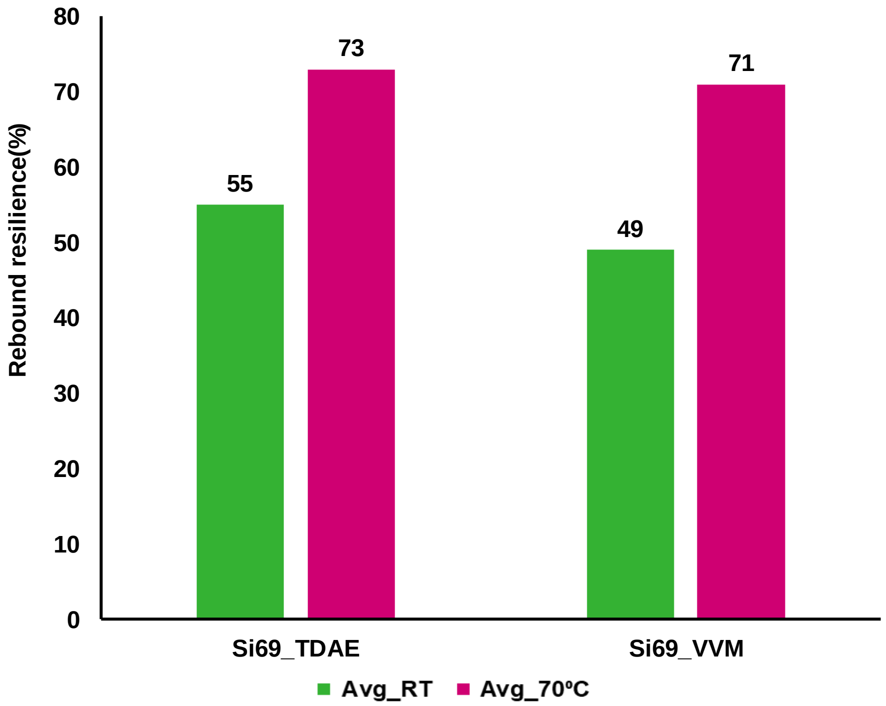


Figure 7.31 Influence of oil type on rebound resilience of the vulcanizates

7.3.2.3.4 Summary

The use of bio-based oil Vivamax 500, as a possible compatibilizer for HTC lignin reinforced rubber is studied. The addition of VVM oil shows a significant improvement in the cure behavior of the compound. With respect to the in-rubber properties, only a slight improvement is observed in comparison to the TDAE oil except resilience property which is deteriorated by introducing VVM oil. This observed effect is related to the higher polarity of Vivamax 500 oil in comparison to mineral-based TDAE which increases the filler-filler interaction of the compound. Based on this study, it is recommended that the addition of both oils (TDAE and Vivamax) together in an appropriate proportion can result in a bettter balance of properties.

7.3.3 Overall summary and conclusions of silane modified HTC lignin

Surface modification of HTC lignin using silane coupling agent enhances the in-rubber properties. Different silane coupling agents are investigated and based on the achieved results, Si69 is selected as the most promising coupling agent for HTC lignin. Although the modified compound shows improved in-rubber properties compared to the unmodified HTC lignin filled compound, the achieved properties are inferior compared to those compounds filled with conventional fillers. Thus, an optimization study involving an improvement in the degree of silanization was carried out to further increase the polymer-filler interaction which enhances also the in-rubber properties. Some of the parameters such as mixing temperature, time and compatibilizer (process oil) influencing the silanization degree were selected and investigated in detail. The obtained results are in contrast to the silica/silane system as tabulated in **Table 21**.

Table 21 Comparing the results of achieved in-rubber properties of Si69 modified HTC lignin

Increase in silanization temperature leads to:		
In-rubber properties	Si69 modified Silica [109]	Si69 modified HTC lignin
Mooney viscosity	↓	↑
Payne effect	↓	↑
Mechanical properties (Tensile strength, M300 & M100)	↑	No change
Hardness	↓	No change
Rebound resilience	↑	No change
Increase in silanization time leads to:		
In-rubber properties	Si69 modified Silica [109]	Si69 modified HTC lignin
Mooney viscosity	↓	↑
Payne effect	↓	↑
Mechanical properties (Tensile strength, M300 & M100)	↑	↑
Hardness	↓	↑
Rebound resilience	↑	↑

Silica is highly polar and consists of siloxane and silanol groups. The silanol groups can interact with each other by hydrogen bonds and can form strong filler-filler interactions leading to silica clusters. This results in difficulties to disperse the filler. The obtained compounds also show high compound viscosities, high moduli at low strain amplitudes, low moduli at high strain amplitudes and low bound rubber contents. To improve the properties of silica-filled compounds, silane coupling agents are generally added to improve the silica-rubber interaction and to decrease the silica-silica interaction. The addition of TESPT silane to silica reduces the Mooney viscosity and the Payne effect, and increases the mechanical properties by improving the filler-polymer interaction. In case of HTC lignin which consists of phenolic –OH groups, the filler –filler interaction and filler-polymer interaction are weak confirmed by Payne effect measurements (**Section 7.1**). Upon addition of silane, all the observed properties such as Mooney viscosity, modulus at low strain (filler-filler interaction) and modulus at high strain (filler-polymer interaction), static and dynamic mechanical properties are increased. The reason for this disparity can be explained by different reinforcing mechanisms exhibited by these fillers. Filler structure plays an dominating role in this mechanism. In case of silica, the structure is reduced by addition of silane which can cover the polar silica surface and makes it well dispersed in the rubber matrix and increases its compatibility with rubber, whereas in case of HTC lignin, the structure is increased either due to the formation of lignin clusters due to oligomerized silanes or self-condensation of lignin due to thermo-oxidation and catalytic effect of Si69 (sulfur silane). These structures determine the further improvement in properties of silanized HTC lignin. The results of optimization study suggest that the parameters affecting degree of silanization also influence the structures formed inside the rubber matrix. The summary from **Section 7.3.2.1** suggested that the higher silanization temperature seems to result in a higher degree of condensed lignin structure but not in an improvement in the degree of silanization resulting in no further improvement in static mechanical and dynamic mechanical properties. In contrary, a longer silanization time at a constant mixing temperature increases the degree of silanization as well as that of the condensed lignin structure enhancing the in-rubber properties. This highlights that even in the former case, there is an observed increase in silanization degree as well as condensed lignin structure but these reactions seems to be contradictory which makes it difficult to identify the effect of the single reaction. Further model compound studies are needed to confirm this hypothesis. More polar oil like Vivamax used in this study also moderately influenced the in-rubber properties.

All these studies highlight that the structure of HTC lignin differs significantly not only with carbon black (**Section 7.2.3.1**), but also with silica. Therefore, the existing reinforcing mechanisms and theories doesn’t hold good for explaining the reinforcing behavior of HTC lignin. Further improvement in properties of silane modified HTC lignin can be achieved if the influence of HTC lignin structure on reinforcement is well understood.

8 Project deliverables

The objective of this project is to design a green tread formulation using a bio-based filler system. Under this context, the feasibility of Hydrothermally Carbonized HTC lignin as a filler was studied. A modified Michelin green recipe was used as a reference compound. Initial studies of HTC lignin in rubber compared with conventional fillers (carbon black, silica) suggest a need for its surface modification using coupling agents. The reinforcing potential of HTC lignin is shown in **Figure 8.1**.

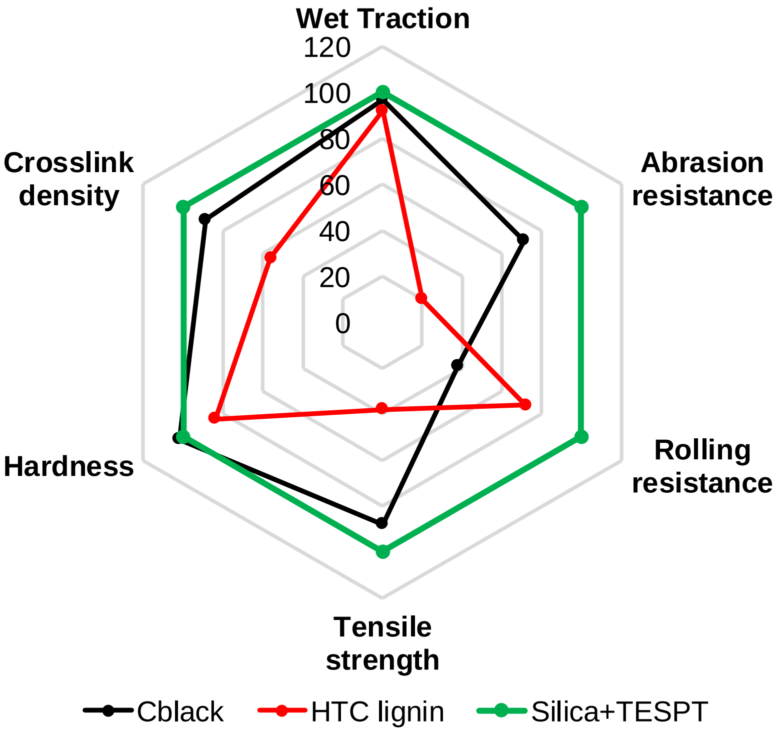


Figure 8.1 Performance summary of HTC lignin in comparison to conventional fillers. *(Obtained values are relative to reference compound (Silica+TESPT). The higher the value the better the properties)*

This design project delivers the following outcomes:

- The first and foremost deliverable of this project is the identification of promising coupling agents by a screening test, bis(triethoxypropyl) tetrasulfide silane (TESPT/Si69®). Addition of this surface modifier had a positive influence on the properties of HTC lignin filled compounds which is the corresponding deliverables from this project. **Figure 8.2** summarizes the key deliverables of the achieved properties (cure, mechanical property as well as key tire performance) of silanized HTC lignin compound using a spider diagram. This chart is based on relative values versus the reference (HTC lignin). The higher the values the better the achieved properties. In case of rolling resistance, a higher rating means a lower rolling resistance. The same is true for the scorch time, higher the rating faster the kinetics of vulcanization without affecting the compound's processability.

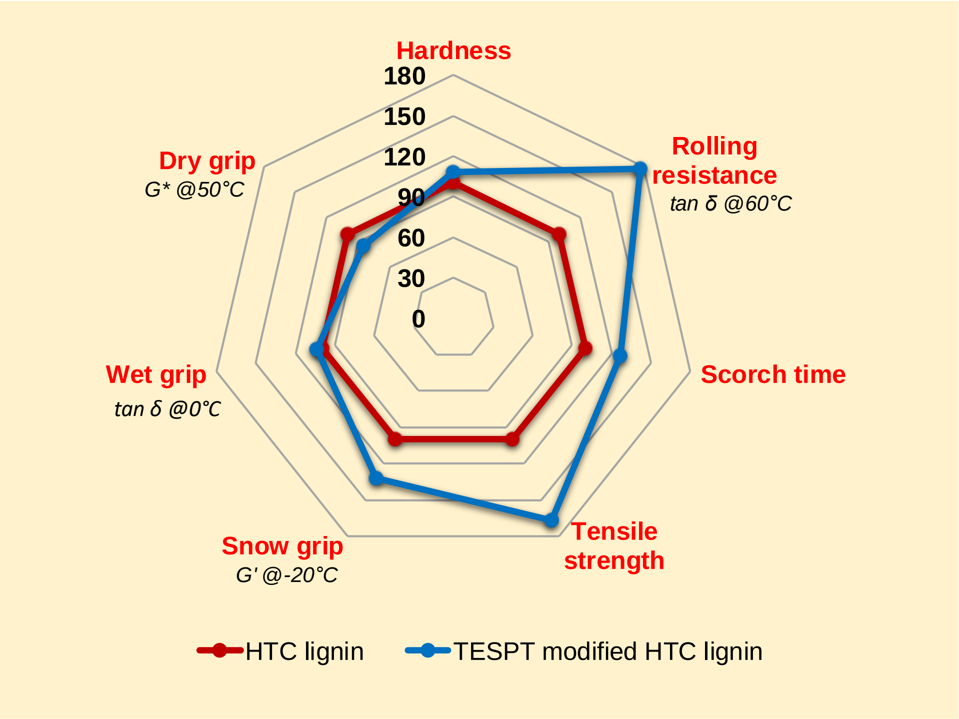


Figure 8.2 Performance summary of prototype compounds

Based on the results, the prototype green tire tread formulation using TESPT modified HTC lignin (Formulation I) is suggested for design implementation as tabulated in **Table 22**.

Table 22 Formulations for the prototype compound

Ingredients	Formulation I (phr)
SSBR_4602	**75**
BR_CB24	**25**
HTC lignin	**80**
TESPT	**6.2**
TDAE	**33**
ZnO	**2.5**
Stearic acid	**2.5**
TMQ	**2**
6PPD	**2**
DPG	**0.25**
TBBS	**1.5**
Sulphur	**2.2**
TBzTD	**0.5**

- The process guide for the silanization of HTC lignin was developed based on the optimization study. This is tabulated in **Table 23.**

Table 23 Optimized conditions for silanization of HTC lignin

Parameters	***Optimum***
Initial mixing temperature	50 °C
Rotor speed	50 rpm
Fill factor	70%
Silanization temperature/dump temperature	140-150 °C
Extent of silanization	4mins
Total Mixing time	12 mins
Process oil	Vivamax 500 in combination with TDAE
Amount of Process oil	33 phr

9 Conclusion & Outlook

9.1 Summary

A growing emphasis on managing the global environmental concerns like increased energy demands and emissions drives tire manufacturers to strive towards sustainable development. Recent scientific studies spotlight the use of renewable alternatives as one of the emerging strategies that can encompass both tire performance and sustainability. The objective of this thesis is to design a greener elastomeric compounds for tire tread application using renewable HydroThermally Carbonized (HTC) lignin as a reinforcing filler. The developed compound should exhibit improved in-rubber properties and tire tread performance in comparison to the conventional fillers (carbon black and silica).

The design cycle using spiral model was beneficial for developing the present project (**Chapter 5, Figure 5.1**). The filler characterization and their specific influence on the properties of a rubber formulation showed that HTC lignin cannot completely replace conventional fillers as it imparted lower mechanical properties in tread compounds (**Chapter 7, Section 7.1 and 7.2**). The study also gain insight that lignin's surface characteristics not only affects the compatibility and interfacial adhesion of filler with rubber but also interfers with the kinetics of curing. Therefore, a surface modification approach using different coupling agents was followed to enhance filler-polymer compatibility resulting in an improvement in in-rubber properties. The overall summary of the thesis can be illustrated using **Figure 9.1**.

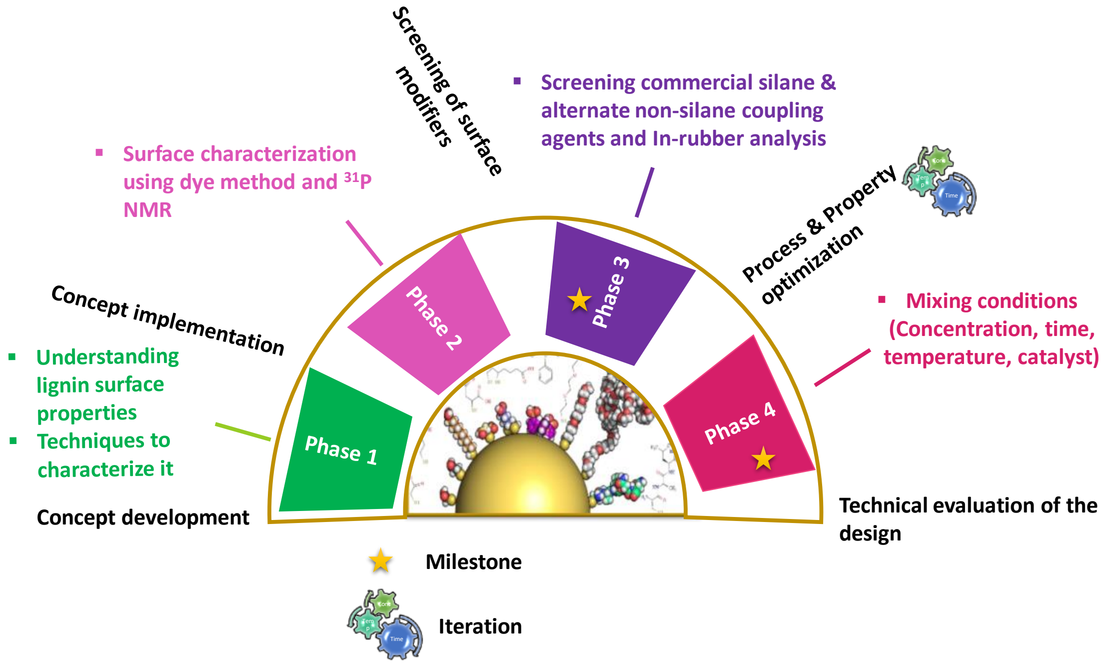


Figure 9.1 Development of a greener tire tread compound using HTC lignin

With this approach, different commercial silanes were investigated as a coupling agent for HTC lignin. Additionally, various non-silane coupling agents were also investigated for HTC lignin. A screening test of different silane (**Section 7.3.1**) and non-silane coupling agents (**Section 7.4**) were carried out to identify the best suitable surface modifier for HTC lignin under each category. Based on the results of the screening test of silane surface modifiers, bis(triethoxypropyl) tetrasulfide silane (TESPT/Si69®) was selected.

The crucial parameters such as mixing parameters (temperature and time), presence of a catalyst and the processing oil type affecting the performance of TESPT modified HTC lignin were identified and optimization studies were undertaken to design a prototype tire tread compound using HTC lignin filler (**Section 7.3.2**). All these factors played a vital role in a further improvement of in-rubber properties. The final conclusions of this study highlighted that a chemical surface modification of HTC lignin using silane coupling agent is one of the feasible solutions to improve the rubber properties filled with HTC lignin. The studies also indicate that the influence of silane on HTC lignin is completely different from that of silica-silane system (**Section 7.3.3**).

In conclusion, the goal of the project was achieved by developing a bio-based filler system (HTC lignin+TESPT) to design a greener rubber compound. The developed compounds show an improvement in all the in-rubber properties in comparison to the pristine HTC lignin compounds. Nevertheless, the achieved performances are still lower in comparison to conventional fillers. This is mainly due to the low surface area of HTC lignin which results in a performance similar to a semi-reinforcing filler.

9.2 Recommendations for Future Works

Surface modification of HTC lignin with coupling agents improves the in-rubber properties. From silica technology, it is well-known that in-situ mixing is a challenging task. Also, during this mixing, two factors need to be taken into account, which are the mixing sequence of specific ingredients and the completion of the modification reaction of HTC lignin with TESPT/Si69®. The pre-requisites for the completion of the modification reaction (mixing temperature, time, catalyst) are thoroughly investigated in this thesis. Secondly, for an enhanced surface modification reaction, it is important to gain knowledge about crucial parameters such as concentration and reactivity of the coupling agent, the phenolic group concentration of HTC lignin and their reactivity and distribution of these groups on the surface of lignin. In this thesis, the first two parameters were taken into account. Knowledge about the distribution of phenolic groups can help to understand the surface coverage of surface modifiers. This influencing factor was not studied in this design project. Furthermore, the coupling efficiency and reactivity of given coupling agents with HTC lignin are not investigated in detail. This could be another valuable information for further design improvement and understanding the reinforcing mechanism. The compounding ingredients such as zinc oxide and DPG which might interfere with the ethoxy groups of TESPT are also crucial for the modification reaction. The influence of these specific ingredients on silanization and their mixing sequence needs to be studied in depth to understand the reinforcing efficiency of TESPT silane.

Another uncovered investigation is the dispersion behavior of HTC lignin in rubber which can bring further explanation for many observed phenomena such as an increase in Payne effect and Mooney viscosity of TESPT modified HTC lignin which is in contrast to the silica-silane system. The investigations in this design project envisaged that structural changes of lignin triggered by thermo-oxidative reaction is one of the phenomenon which affected the above-mentioned in-rubber properties. Here, we have taken into account only the temperature effect, since mixing of silanizaed HTC lignin filled rubber compound is a complex process involving temperature, shear forces and modifying agents, the joint influene of these parameters on these structural changes are unclear. Further studies are needed to understand the influence of a combination of these parameters on structural changes and their effect on dispersion and in-rubber properties.

The present thesis provides an insight into many aspects of HTC lignin reinforcement of rubber, as well as an understanding of crucial parameters affecting the in-rubber properties. On the whole, modified HTC lignin can be highly recommended for the tire tread application as it greatly contributes to the reduction of rolling resistance of tires if the reinforcement provided by HTC lignin is improved further. This means that in future, HTC lignin reinforcement will be of growing importance in tires because of its advantage of reduced fuel consumption in automotive transport and embedding sustainability in tire by reducing it’s environmental footprint. This study is also expected to contribute to the future direction of HTC lignin technology leading also to advancements in the development of other “green” rubber products such as seals and hoses.

10 References

[1] https://markets.businessinsider.com/news/stocks/europe-cis-tire-market-2023-increasing-tire-production-capacity-growing-vehicle-sales-and-expanding-automobile-fleet-driving-market-growth-1027610419, 27/6/2019

[2] https://carbiketech.com/tyre/, 15/11/2019

[3] https://ec.europa.eu/clima/policies/transport/vehicles/cars_en, 15/08/2018

[4] D.J. Schuring, The Rolling Loss of Pneumtic Tires, Rubber Chemistry and Technology 53 (1980) 600-723

[5] P C M Jacobsson, J Neilsen, L Nikiel, W Wampler, S Richardson Improving hysteresis through filler modifications and smart compounding, in Rubber World. 2013.

[6] http://ec.europa.eu./environment/life/project/Projects/files/laymanReport/LIFE06 ENV L 000118 LAYMAN.pdf, 6/7/2018

[7] JR Cho, HW Lee, WB Jeong, KM Jeong, and KW Kim, Numerical estimation of rolling resistance and temperature distribution of 3-D periodic patterned tire, International Journal of Solids and Structures 50 (2013) 86-96

[8] https://www.rubbernews.com/technical-notebooks/making-sustainable-tire-possible, 1/10/2019

[9] https://ec.europa.eu/growth/industry/sustainability_en, 1/10/2019

[10] https://www.ustires.org/whats-tire-0, 31/10/2019

[11] J Dick, E Hull, and K Jackson, Requirements engineering, 3rd edition, Springer, Cham(2017).

[12] R J Wieringa, Design science methodology: principles and practice. In ICSE '10: Proceedings of the 2010 IEEE International Conference on Software Engineering, Cape Town, South Africa, (2010) 493-494

[13] G T Doran, There's a S.M.A.R.T Way to Write Management's Goals and Objectives, Management Review 70 (1981) 35-36

[14] https://www.msds-europe.com/h-statements/, 1/03/2019

[15] M Lahtinen, K Alavi, P Salomonsson, M Hoffmann, and H Fruhmann, Improving Winter Traction and Fuel Economy of Car Tires Using Naphthenic Tire Oils, Journal of Traffic and Transportation Engineering 6 (2018) 35-41

[16] Maghami S, Silica-filled tire tread compounds: an investigation into the viscoelastic properties of the rubber compounds and their relation to tire performance (Doctoral thesis), University of Twente, The Netherlands (2016)

[17] N Warasitthinon and C G Robertson, Interpretation of the tanδ Peak Height for Particle-Filled Rubber and Polymer Nanocomposites with Relevance to Tire Tread Performance Balance, Rubber Chemistry and Technology 91 (2018) 577-594

[18] R Rana, S Nanda, V Meda, AK Dalai, and JA Kozinski, A review of lignin chemistry and its biorefining conversion technologies, Journal of Biochemical Engineering & Bioprocess Technology 1 (2018) 1-14

[19] S Chatterjee and T Saito, Lignin-derived advanced carbon materials, ChemSusChem 8 (2015) 3941-3958

[20] W Dierkes, Economic mixing of silica-rubber compounds Interaction between the chemistry of the silica-silane reaction and the physics of mixing (Doctoral thesis), University of Twente, Enschede (2005)

[21] JWM Noordermeer and WK Dierkes, Carbon Black Reinforced Elastomers, in Encyclopedia of Polymeric Nanomaterials, Shiro Kobayashi and Klaus Müllen, Editors. 2014, Springer Berlin Heidelberg: Berlin, Heidelberg. p. 1-14.

[22] R Rothon, Fillers for Polymer Applications, Springer, Cham (2017).

[23] R Rothon, Particulate fillers for polymers, iSmithers Rapra Publishing, (2002), p 141

[24] E Cichomski, WK Dierkes, JWM Noordermeer, S M Schultz, T V Tolpekina, LAEM Reuvekamp, and A Blume, Effect of the crosslink density and sulfur-length on wet-traction and rolling resistance performance indicators for passenger car tire tread materials, presented at: 188th Technical Meeting of Rubber Division, ACS, (2015)

[25] EM Dannenberg, The effects of surface chemical interactions on the properties of filler-reinforced rubbers, Rubber Chemistry and Technology 48 (1975) 410-444

[26] J Fröhlich, W Niedermeier, and H-D Luginsland, The effect of filler–filler and filler–elastomer interaction on rubber reinforcement, Composites Part A: Applied Science and Manufacturing 36 (2005) 449-460

[27] M Del Carmen Gamero Rodriguez, Studies on the Rubber-Filler Interactions in Tire Tread Compounds (Master thesis), Material science, Tampere University of Technology, Finland (2016)

[28] SS Sarkawi, Wisut Kaewsakul, Kannika Sahakaro, Wilma K Dierkes, and Jacobus WM Noordermeer, A review on reinforcement of natural rubber by silica fillers for use in low-rolling resistance tires, Journal of rubber research 18 (2015) 203-233

[29] DJ Kohls and G Beaucage, Rational design of reinforced rubber, Current opinion in solid state and materials science 6 (2002) 183-194

[30] S Thomas, CH Chan, L A Pothen, J P Joy, and HJ Maria, Natural Rubber Materials: Volume 2: Composites and Nanocomposites, Royal Society of Chemistry, (2013).

[31] J B Donnet, Carbon black: Science and Technology, 2nd Edition, CRC Press, New York (1993).

[32] M J Wang, Effect of polymer-filler and filler-filler interactions on dynamic properties of filled vulcanizates, Rubber chemistry and technology 71 (1998) 520-589

[33] M J Wang, S Wolff, and E Tan, Filler-elastomer interactions. Part VIII. The role of the distance between filler aggregates in the dynamic properties of filled vulcanizates, Rubber chemistry and technology 66 (1993) 178-195

[34] E Cichomski, Silica-Silane Reinforced Passenger Car Tire Treads (Doctoral Thesis), University of Twente, The Netherlands (2015)

[35] E Windeisen and G Wegener, Lignin as Building Unit for Polymers, Polymer Science: A Comprehensive Reference, 10 Volume Set 10 (2012) 255-265

[36] S Laurichesse and L Avérous, Chemical modification of lignins: Towards biobased polymers, Progress in Polymer Science 39 (2014) 1266-1290

[37] SK Khanal, RY Surampalli, TC Zhang, BP Lamsal, RD Tyagi and CM Kao, Bioenergy and biofuel from biowastes and biomass, Amercian Society of Civil Engineers, (2010).

[38] MN Belgacem and A Gandini, Monomers, Polymers and Composites from Renewable resources, Elsevier Science, UK (2008).

[39] M El Marouani, N El Hrech, J El Jastimi, A El Hajji, L Rghioui, S Sebbahi, S El Hajjaji, and F Kifani-Sahban, Lignin and derivative charcoals: Functional groups involved in the adsorption phenomenon, J. Mater. Environ. Sci. (2017) 4313-4322

[40] NAM Aini, N Othman, MH Hussin, K Sahakaro, and N Hayeemasae, Lignin as Alternative Reinforcing Filler in the Rubber Industry: A Review, Frontiers in Material 6: 329 (2020)

[41] E G Lyubeshkina, Lignins as components of polymeric composite materials, Russian Chemical Reviews 52 (1983) 675-692

[42] U Weißbach, S Dabral, L Konnert, C Bolm, and J G Hernández, Selective enzymatic esterification of lignin model compounds in the ball mill, Beilstein journal of organic chemistry 13 (2017) 1788-1795

[43] www.napier.ac.uk/~/media/documents/sebe/cost-action/events/workshop-december-2012/presentations/claudia-crestini_presentation.pdf, 22/6/2018

[44] I Santoni, E Callone, A Sandak, J Sandak, and S Dirè, Solid state NMR and IR characterization of wood polymer structure in relation to tree provenance, Carbohydrate polymers 117 (2015) 710-721

[45] UP Agarwal, RS Reiner, AK Pandey, SA Ralph, KC Hirth, and RH Atalla, Raman spectra of lignin model compounds, presented at: 59th Appita Annual Conference and Exhibition: Incorporating the 13th ISWFPC (International Symposium on Wood, Fibre and Pulping Chemistry), Auckland, New Zealand, 16-19 May 2005: Proceedings, (2005)

[46] F Lu and J Ralph, Non-degradative dissolution and acetylation of ball-milled plant cell walls: high-resolution solution-state NMR, The Plant Journal 35 (2003) 535-544

[47] JJ Bozell, CJ O'Lenick, and S Warwick, Biomass fractionation for the biorefinery: heteronuclear multiple quantum coherence–nuclear magnetic resonance investigation of lignin isolated from solvent fractionation of switchgrass, Journal of agricultural and food chemistry 59 (2011) 9232-9242

[48] Y Brech, J Raya, L Delmotte, N Brosse, R Gadiou, and A Dufour, Characterization of biomass char formation investigated by advanced solid state NMR, Carbon 108 (2016) 165-177

[49] D Ando, F Nakatsubo, and H Yano, Acetylation of ground pulp: monitoring acetylation via HSQC-NMR spectroscopy, ACS Sustainable Chemistry & Engineering 5 (2017) 1755-1762

[50] Y Pu, S Cao, and A J Ragauskas, Application of quantitative 31P NMR in biomass lignin and biofuel precursors characterization, Energy & Environmental Science 4 (2011) 3154-3166

[51] C Fernández-Costas, S Gouveia, MA Sanromán, and D Moldes, Structural characterization of Kraft lignins from different spent cooking liquors by 1D and 2D Nuclear Magnetic Resonance spectroscopy, Biomass and Bioenergy 63 (2014) 156-166

[52] S Y Lin and C W Dence, Methods in lignin chemistry, Springer, Berlin (2012), p. 33-61

[53] E A Capanema, M Y Balakshin, and J F Kadla, A comprehensive approach for quantitative lignin characterization by NMR spectroscopy, Journal of agricultural and food chemistry 52 (2004) 1850-1860

[54] Xianzhi Meng, Claudia Crestini, Haoxi Ben, Naijia Hao, Yunqiao Pu, Arthur J Ragauskas, and Dimitris S Argyropoulos, Determination of hydroxyl groups in biorefinery resources via quantitative 31 P NMR spectroscopy, Nature Protocols 14 (2019) 2627-2647

[55] O Faix, C Grünwald, and O Beinhoff, Determination of phenolic hydroxyl group content of milled wood lignins (MWL's) from different botanical origins using selective aminolysis, FTIR, 1H-NMR, and UV spectroscopy, Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood 46 (1992) 425-432

[56] A Gärtner, G Gellerstedt, and T Tamminen, Determination of phenolic hydroxyl groups in residual lignin using a modified UV-method, Nordic Pulp & Paper Research Journal 14 (1999) 163-170

[57] O Faix, DS Argyropoulos, D Robert, and V Neirinck, Determination of hydroxyl groups in lignins evaluation of 1H-, 13C-, 31P-NMR, FTIR and wet chemical methods, Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood 48 (1994) 387-394

[58] P Månsson, Quantitative determination of phenolic and total hydroxyl groups in lignins, Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood 37 (1983) 143-146

[59] E Adler and S Hernestam, Estimation of phenolic hydroxyl groups in lignin, Acta Chem. Scand 9 (1955) 319-334

[60] L Serrano, ES Esakkimuthu, N Marlin, M Salon, G Mortha, and F Bertaud, Fast, Easy, and Economical Quantification of Lignin Phenolic Hydroxyl Groups: Comparison with Classical Techniques, Energy & Fuels 32 (2018) 5969-5977

[61] J P Butler and T P Czepiel, Determination of phenolic groups in lignin preparations titration with potassium methoxide using dimethylformamide as a solvent, Analytical Chemistry 28 (1956) 1468-1472

[62] M Jablonský, J Kočiš, A Ház, and J Šima, Characterization and comparison by UV spectroscopy of precipitated lignins and commercial lignosulfonates, Cell. Chem. Technol 49 (2015) 267-274

[63] O Goldschmid, Determination of phenolic hydroxyl content of lignin preparations by ultraviolet spectrophotometry, Analytical Chemistry 26 (1954) 1421-1423

[64] C Lapierre and C Rolando, Thioacidolyses of pre-methylated lignin samples from pine compression and poplar woods, Holzforschung-International Journal of the Biology, Chemistry, Physics and Technology of Wood 42 (1988) 1-4

[65] P Whiting, Phenolic hydroxy analysis of lignin by pyrolytic gas chromatography, Paperi ja Puu 10 (1982) 592-595

[66] AS Wexler, Characterization of lignosulfonates by ultraviolet spectrometry. Direct and difference spectrograms, Analytical Chemistry 36 (1964) 213-221

[67] F de Sousa, A Reimann, M Björklund Jansson, and NO Nilberbrant, Estimating the amount of phenolic hydroxyl groups in lignins, 11th ISWPC, Nice, France 3 (2001) 649-653

[68] DK Setua, MK Shukla, Vineeta Nigam, Harjeet Singh, and GN Mathur, Lignin reinforced rubber composites, Polymer Composites 21 (2000) 988-995

[69] O Faruk and M Sain, Lignin in polymer composites, 1st Edition, Elsevier Amsterdam, (2015), 350

[70] JJ Keilen and A Pollak, Lignin for Reinforcing Rubber, Rubber Chemistry and Technology 20 (1947) 1099-1108

[71] B Košíková and A Gregorová, Sulfur-free lignin as reinforcing component of styrene–butadiene rubber, Journal of Applied Polymer Science 97 (2005) 924-929

[72] G Xu, G Yan, and J Zhang, Lignin as coupling agent in EPDM rubber: thermal and mechanical properties, Polym. Bull. 72 (2015) 2389-2398

[73] M Asrul, M Othman, M Zakaria, and MS Fauzi, Lignin filled unvulcanised natural rubber latex: effects of lignin on oil resistance, tensile strength and morphology of rubber films, Int. J. Eng. Sci. Invention 2 (2013) 38-43

[74] C Jiang, H He, P Yu, DK Wang, L Zhou, and DM Jia, Plane-interface-induced lignin-based nanosheets and its reinforcing effect on styrene-butadiene rubber, Express Polymer Letters 8 (2014) 619-634

[75] P Yu, H He, Y Jia, S Tian, J Chen, D Jia, and Y Luo, A comprehensive study on lignin as a green alternative of silica in natural rubber composites, Polymer Testing 54 (2016) 176-185

[76] P Frigerio, L Zoia, M Orlandi, T Hanel, and L Castellani, Application of sulphur-free lignins as a filler for elastomers: effect of hexamethylenetetramine treatment, BioResources 9 (2014) 1387-1400

[77] JJ Keilen and Arthur Pollak, Lignin for reinforcing rubber, Industrial & Engineering Chemistry 39 (1947) 480-483

[78] C Jiang, H He, H Jiang, L Ma, and DM Jia, Nano-lignin filled natural rubber composites: Preparation and characterization, Express Polymer Letters 7 (2013) 480-493

[79] C Jiang, H He, X Yao, P Yu, L Zhou, and D Jia, In situ dispersion and compatibilization of lignin/epoxidized natural rubber composites: reactivity, morphology and property, Journal of Applied Polymer Science 132 (2015) 42044 (1-10)

[80] D Barana, S D Ali, A Salanti, M Orlandi, L Castellani, T Hanel, and L Zoia, Influence of lignin features on thermal stability and mechanical properties of natural rubber compounds, ACS Sustainable Chemistry & Engineering 4 (2016) 5258-5267

[81] I Sagajllo, Lignin as a Compounding Ingredient for Natural Rubber, Rubber Chemistry and Technology 30 (1957) 639-651

[82] SH Botros, MAM Eid, and ZA Nageeb, Thermal stability and dielectric relaxation of natural rubber/soda lignin and natural rubber/thiolignin composites, Journal of applied polymer science 99 (2006) 2504-2511

[83] K Bahl and S C Jana, Surface modification of lignosulfonates for reinforcement of styrene–butadiene rubber compounds, Journal of Applied Polymer Science 131 (2014) 40123 (1-9)

[84] Z Cao, Z Liao, X Wang, S Su, J Feng, and J Zhu, Preparation and properties of NBR composites filled with a novel black liquor–montmorillonite complex, Journal of applied polymer science 127 (2013) 3725-3730

[85] K Bahl, T Miyoshi, and S C Jana, Hybrid fillers of lignin and carbon black for lowering of viscoelastic loss in rubber compounds, Polymer 55 (2014) 3825-3835

[86] T Wittmann and K Bergemann, Particulate carbon material producible from renewable raw materials and method for its production. Priority to DE102015014956.3, 21/11/2015; U.S. Patent 20180340074A1, Publication date: 29/11/2018

[87] T Wittmann and I Richter, Method for extracting lignin from black liquor and products produced thereby. Priority to DE102013013189, 9/8/2013; US9902816B2, Publication date: 12/02/2015

[88] E Atta-Obeng, B D Andoh, M S Seehra, U Geddam, J Poston, and J Leisen, Physico-chemical characterization of carbons produced from technical lignin by sub-critical hydrothermal carbonization, Biomass and bioenergy 107 (2017) 172-181

[89] A Funke and F Ziegler, Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering, Biofuels, Bioproducts and Biorefining 4 (2010) 160-177

[90] C Hepburn, Rubber compounding ingredients: need, theory and innovation: processing, bonding, fire retardants, Part:II, Shawbury: ISmithers Rapra Publishing, UK, (1997), 1-119

[91] Flory, P. J. Thermodynamics of High Polymer Solutions. J. Chem. Phys. 1942, 10, 51-61.

[92] S Wolff, Chemical aspects of rubber reinforcement by fillers, Rubber Chemistry and Technology 69 (1996) 325-346

[93] J Ma, L Zhang, and Y Wu, Characterization of filler-rubber interaction, filler network structure, and their effects on viscoelasticity for styrene-butadiene rubber filled with different fillers, Journal of Macromolecular Science, Part B 52 (2013) 1128-1141

[94] Masaki Sato, Reinforcing Mechanisms of Silica/Sulfide-Silane vs Mercapto-Silane Filled Tire Tread Compounds (Doctoral Thesis), University of Twente, The Netherlands (2018)

[95] GB Ouyang, Modulus, hysteresis and the payne effect: network junction model for carbon black reinforcement, KGK. Kautschuk, Gummi, Kunststoffe 59 (2006) 332-343

[96] J Ramier, C Gauthier, L Chazeau, L Stelandre, and L Guy, Payne effect in silica-filled styrene–butadiene rubber: Influence of surface treatment, Journal of Polymer Science Part B: Polymer Physics 45 (2007) 286-298

[97] M Balakshin and E Capanema, On the quantification of lignin hydroxyl groups with ^{31}P and ^{13}C NMR spectroscopy, Journal of wood chemistry and technology 35 (2015) 220-237

[98] A Blume, Kinetics of the silica-silane reaction, KGK. Kautschuk, Gummi, Kunststoffe 64 (2011) 38-43

[99] E Adler, Lignin chemistry—past, present and future, Wood Science and Technology 11 (1977) 169-218

[100] WK Dierkes, LAEM Reuvekamp, AJWT Brinke, and J WM Noordermeer, Silane coupling agents for silica-filled tire-tread compounds: the link between chemistry and performance, In K.L. Mittal (Ed.), Silanes and Other Coupling Agents 3 (2004) 89-103

[101] P Vondráček, M Hradec, V Chvalovský, and HD Khanh, The Effect of the Structure of Sulfur—Containing Silane Coupling Agents on Their Activity in Silica-Filled SBR, Rubber chemistry and technology 57 (1984) 675-685

[102] P Sae-oui, C Sirisinha, U Thepsuwan, and K Hatthapanit, Roles of silane coupling agents on properties of silica-filled polychloroprene, European polymer journal 42 (2006) 479-486

[103] www.rubber-silanes.com/sites/lists/RE/DocumentsSL/Reinforcing-FillersfortheRubberIndustryEN.pdf, 16/8/2018

[104] H-D Luginsland and C Röben, The development of sulphur-functional silanes as coupling agents in silica-reinforced rubber compounds. Their historical development over several decades, International Polymer Science and Technology 43 (2016) 1-6

[105] K Sengloyluan, K Sahakaro, WK Dierkes, and JWM Noordermeer, Reinforcement efficiency of silica in dependence of different types of silane coupling agents in natural rubber-based tire compounds, KGK Kautschuk, Gummi, Kunststoffe 69 (2016) 44-53

[106] O Klockmann, Processing Of New Rubber Silane VP SI 363, presented at: 2006 International Tire Exhibition and Conference of Rubber & Plastics News, (2006)

[107] Y Li, B Li, W Mo, W Yang and S Wu, Influence of residual lignin and thermal drying on the ultrastructure of chemical hardwood pulp and its enzymatic hydrolysis properties, Cellulose (2019) 26:2075-2085

[108] JL Braun, KM Holtman and JF Kadla, Lignin-based carbon fibers: Oxidation thermostabilization of Kraft lignin, Carbon 43 (2005) 385-394

[109] LAEM Reuvekamp, JWT Brinke, PJ Van Swaaij, and J WM Noordermeer, Effects of time and temperature on the reaction of TESPT silane coupling agent during mixing with silica filler and tire rubber, Rubber chemistry and technology 75 (2002) 187-198

[110] U Goerl, A Hunsche, A Mueller, and HG Koban, Investigations into the silica/silane reaction system, Rubber chemistry and technology 70 (1997) 608-623

[111] A Blume, J Jin, A Mahtabani, X He, S Kim, and Z Andrzejewska, New Structure Proposal for Silane Modified Silica, presented at: International Rubber Conference, IRC 2019, (2019)

[112] W Dierkes, JWM Noordermeer, C Van de Pol, M Rinker, and KU Kelting, Increasing the silanisation efficiency of silica compounds: upscaling, KGK Kautschuk, Gummi, Kunststoffe 56 (2003) 338-344

[113] SS Sarkawi, WK Dierkes, and JWM Noordermeer, Reinforcement of natural rubber by precipitated silica: The influence of processing temperature, Rubber chemistry and technology 87 (2014) 103-119

[114] Chesidi Hayichelaeh, Silica-Reinforced Natural Rubber Tire Compounds with Safe Compounding Ingredients (Doctoral thesis), University of Twente, the Netherlands (2018)

[115] Akansha Rathi, Investigating Safe Process Oils for Tire Tread Application (Doctoral thesis), University of Twente, the Netherlands (2019)

[116] Jungmin Jin, Influence of Compounding and Mixing on Filler Dispersion and Curing behavior of Silica Compounds (Doctoral thesis), University of Twente, the Netherlands (2020)