Modified lignin as replacement of carbon black in elastomers- For the development of sustainable tyre technology

The substitution of carbon black with modified lignin- Green tyre technology

Ersättningen av kimrök med modifierad lignin i bildäcksgummi- För utvecklandet av grönare bildäcksteknologi

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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

In the name of Allah, the Most Gracious, the Most Merciful

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ABSTRACT

Due to its large flexibility, low-price, large availability, and properties lignin is seen as an important compound with a wide range of applications. The increasing demand of fossil-based rubber materials is causing a serious threat to the environment and it is contributing to plastic- and marine pollution, ozone depletion and carbon dioxide emission (CO_2) [1,2]. Numerous toxicological researches highlight that Carbon black may act as a universal carrier of wide variety of chemicals of varying toxicity to the human body [3,4]. Consequently, researcher endeavours in finding sustainable and eco-friendlier alternatives. The aim of this thesis was to further investigate the possibilities of replacing carbon black with modified lignin in rubber elastomeric materials- for the development of sustainable tyre technology. The research questions for this thesis were divided in four parts:

- How does lignin (unmodified and modified) structure affect the mechanical properties in the rubber compound?
- How does lignin affect the cross-link and vulcanisation in the rubber compound?
- How does lignin affect the dispersion of the rubber compound?
- Which modification of lignin is more compatible with the rubber compound?

Lignin is the second most abundant biopolymer on earth (after cellulose) and is mainly extracted from black liquor, which is obtained as a by-product from the pulp- and paper. In this study, pure lignin was obtained from Lignoboost process (Lignocity) and underwent an esterification process of aldehydes (1. Protonic, 2. Butyric, 3. Isobutyric 4. Methacrylic and 5. Crotonic). LignoCity 2.0 is a project focusing on the development of sustainable products and processes connected to lignin.

The structure of the modified lignin was characterized using a FTIR-spectra. Furthermore, seven different rubber compounds were produced at Anva Poly Tech, which is a company that manufactures rubber materials in Sunne, Sweden. The mechanical testing involved: Tensile strength, IRHD, Hardness, Rebound Resilience and Rheometer curve. It was observable that the addition of lignin in rubber compounds did not significantly improve the mechanical properties compared to conventional carbon black. However, the rheometer curves of the lignin samples clearly indicate an increase in scorch time and that lignin takes part in the vulcanization process, thus the delay in crosslinking phase.

In addition, it was visible that the fully replacement of carbon black with lignin (unmodified and modified) increased the elongation at break. Furthermore, the FTIR spectra indicated a complete and successful modification of lignin. In addition, compared to unmodified lignin, it was visible that the modified lignin significantly improved the mechanical properties. Therefore, it was possible to conclude that the configuration and double bonds of the aldehydes had an impact on the vulcanization process. Butyric and isobutyric lignin were the better choices compared to the other lignin samples.

SAMMANFATTNING

De rådande miljöproblemen som: plast- och gummiutsläpp i havet, växthusgasutsläppet och den ekologiska utarmningen i kombination med den ökande efterfrågan av fossilbaserade material har lett till en ökad satsning på att hitta mer hållbara och miljövänligare alternativ [1,2]. Kimrök i gummimaterial utgör en del hälsorisker och samtidigt har negativ påverkan på miljön. Flertals studier visar att långtidsexponering av kimrök kan ge allvarliga lungproblem och även cancer [3,4]. På grund av dess stora tillgänglighet, låga kostnad och unika egenskaper anses lignin vara en möjlig och intressant framtidskandidat för ersättande av fossila produkter.

Syftet med denna studie var att undersöka möjligheterna om att ersätta kimrök med modifierad lignin i gummimaterial för utvecklandet av 'grönare däckteknologi'. Frågeställningarna i detta arbete var uppställda i fyra i olika delar:

- Hur påverkar tillsättningen av lignin (omodifierad och modifierad) gummiblandningens mekaniska egenskaper?
- Hur påverkar tillsättningen av lignin tvärbindningarna och vulkningen i gummiblandningen?
- Hur påverkas tillsättningen av lignin gummiblandningars dispersion?
- Vilken modifikation av lignin är mest kompatibel med gummimaterialet?

Lignin är en organisk biopolymer som är den näst mest (efter cellulosa) förekommande biomassan i naturen och produceras som en biprodukt från pappers- och massa industrin. Ren lignin erhålls genom extraktion från svartlut med diverse isolations metoder. I detta arbete erhölls lignin genom Lignoboost processen från Lignocity. Lignocity 2.0 är ett projekt som syftar till att utveckla, kommersiella och effektivisera hållbara processer och produkter med fokus på lignin.

I detta arbete modifierades ligninet genom en s.k. esterfierings process av fem olika aldehyder 1.Propionic, 2. Butyric, 3. Isobutyric, 4 Methacrylic och 5 Crotonic som sedan undersöktes i en FTIR-spektra. Sju olika gummiblandningar skapades (inklusive ett gummi som endast innehöll kimrök och ett gummi som ej innehöll kimrök eller lignin). Gummiblandningarnas mekaniska egenskaper undersöktes hos på följande sätt: Dragstyrka, IRHD (Hårdhet), Hårdhet, studselasticiteten och reometrisk karaktärisering

De ligninbaserade gummiblandningarna gav ingen signifikant förbättring i de mekaniska egenskaperna. Dock visade den reometriska kurvan att tillsättning av lignin gav en ökning i bränntid samt att ligninet gav en förskjutning i tvärbindningsfasen. Vidare gav den reometriska kurvan en indikation på att ligninet deltog i vulkaniseringsprocessen. Isobutyric lignin hade den högsta bränntiden. Det var även bevisat att tillsättningen av lignin gav en ökning i töjning. Modifieringen av lignin gav en signifikant förbättring av de mekaniska egenskaperna jämfört med omodifierad lignin. FTIR-spektrumet av ligninproven indikerade på en lyckad modifiering och koppling av aldehydgrupperna.

Trots att de ligninbaserade gummiblandningarna inte förbättrade de mekaniska egenskaperna så kunde intressanta kopplingar mellan aldehydens konfigurationer, dubbelbindningar och vulkaniserings processen göras. Butyric och isobutyric visade bäst resultat jämfört de andra ligninproven.

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1. INTRODUCTION

Over the past decades, the global demand for petroleum and energy-based materials have increased significantly. Environmental problems correlated to plastic- and marine pollution, ozone depletion and carbon dioxide (CO_2) emission have led to critical demands in finding eco-friendlier alternatives. Moving towards a bio-economic society requires sustainable framework processes, prominent strategies, and renewable materials. Petroleum based products are derived from crude oil and natural gas. Due to the operating conditions, high emission of hydrocarbon and reduced sulphur gaseous occur during the process [1]. In 2018, Sweden emitted (excluding adsorption) 51.8 million ton of greenhouse gases, which makes it a reduction of 1.8 % compared to 2017 [2].
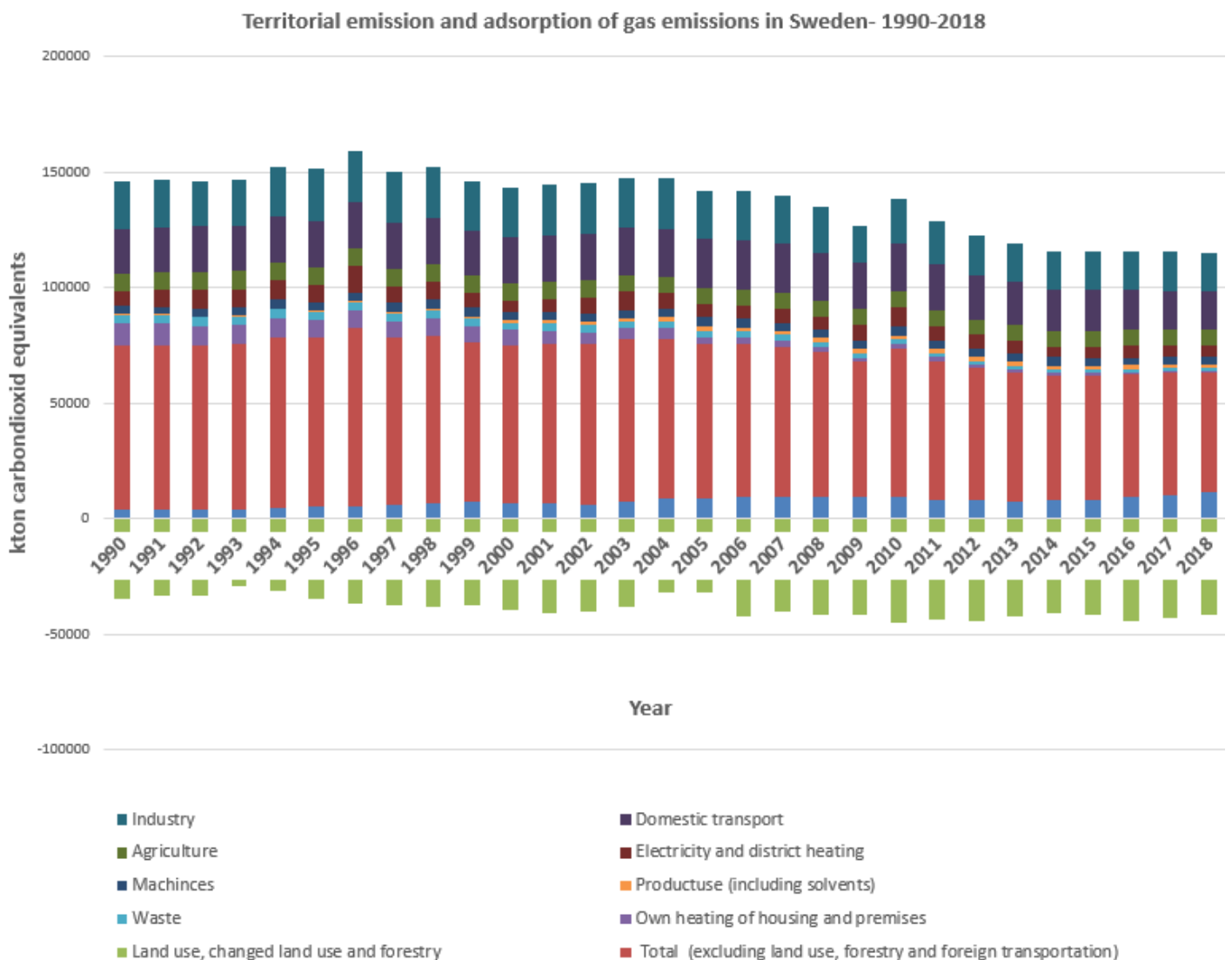

Figure 1. *Territorial emission and adsorption of gas emission in Sweden between 1990-2018 [2]*

In the recent years, the policy effort to reduce greenhouse gases has increased significantly. The Swedish Climate policy framework, which is the most important climate reform in Sweden's history, is aiming to reach zero net emissions of greenhouse gases into the atmosphere by 2045. Furthermore, the reform contains a climate policy that will provide societies and businesses with long-term and sustainable conditions for the transition to a bio-economic society [5]. However, a fully society transition takes time and the implementation of biorefineries is a difficult and complex task. An immense challenge is to replace petroleum-based rubber with biodegradable composites. Rubbers are mainly used in different type of tyres and a passenger vehicle tyre contains approximately 47 % rubber [6].

Due to the increasing demands of automotive and trucks, the tyre market is heavily increasing with a global production of billions of tyres per year. Its highly complex structure and shape requires advance materials and the tyre industry is extensively reliant on petroleum and non-renewable materials. From an engineering point of view, the waste management of tyres is a challenging task and today, tyres constitute a large amount of solid waste. The increasing disposal waste is causing an emerging threat to the ecology, seafood, waterways and ourselves [7]. In her work, Sofi [7] highlights that today, 1000 million tyres reach their end-life every year and by 2030s, 5 times more tyres are approximated to be discarded on regular basis. Several studies mentions the possibility of using scrap tyres as a fuel source. According to Ruwona et.al [8], waste tyres are good fuel resources and have the potential to produce sustainable- and renewable energy.

Despite the vast achievements, the existing techniques for tyre-derived fuels are not commercial and scalable, hence the reason why other techniques need to be further investigated. Over the past decades, lignocellulosic materials and biobased rubbers have become increasingly obtrusive. Numerous researcher endeavours in finding eco-friendlier substitutes for the petroleum-based composites. One possible solution could be the replacement of carbon black with modified lignin in a rubber-blend for the development of a sustainable tyre technology. The aim of this master thesis is to further investigate the mechanical properties and behaviour of modified lignin-based rubber elastomeric materials. The research questions for this thesis are formulated accordingly:

- How does lignin (unmodified and modified) structure affect the mechanical properties in the rubber compound?
- How does lignin affect the cross-link and vulcanisation in the rubber compound?
- How does lignin affect the dispersion of the rubber compound?
- Which modification of lignin is more compatible with the rubber compound?

The experimental part of this project has been split in two different activities:

- Chemical modification (esterification) of kraft lignin: Propionic, Butyric, Isobutyric, Methacrylic and Crotnic. All lignin samples will be further characterized in a FTIR-spectra

- Production of lignin-based rubber. The characterization of the rubber compound will be further studied at Anva PolyTech, Sweden.

The results of this study will give a better understanding of the lignin-based rubber blends and its complex behaviour when interacting with natural rubber. Furthermore, it will have a significant importance for the rubber industry, as well as pulp and paper industry for the sustainable enhancement of lignin residual.

1.1. BIOREFINERY

The concept of biorefinery is not new, however it is becoming more mainstream due to industry financing and concerted efforts from government policies, researchers, and academia. In a biorefinery, sustainable- and "greener" materials, power, fuels, heat (usually as a by-product) and value-added chemicals are obtained. Mostly, all types of biomass can be treated and upgraded in a biorefinery (e.g starch, wood, straw, waste, algae and sugars) [9].A typical delineation when discussing different types of biorefineries is between the biochemical and thermochemical pathways. There are also various techniques for upgrading and conversion that exists as separate processes. Generally, the most important feedstocks in biorefineries are sugars, starch, and lignocellulosic materials. Lately, the interest in lignocellulosic materials has increased and prominent accomplishments have been made. In Sweden, many efforts have been done to increase the use of lignin into value-added products. LignoCity 2.0 is a project focusing on the development of sustainable products and processes connected to lignin. The

idea behind the concept is to speed up the business process aswell as giving the opportunity for scale up production of high-quality lignin. The testbed is located at Bäckhammar, Sweden where the lignin is extracted from black liquor by Lignoboost process. In this study, Kraft lignin is obtained from LignoCity and further treated [10].

1.2. LIGNOCELLULOSIC BIOMASS

The general term of lignocellulose refers to plant dry matter (biomass) and includes straw, wheat stover, algae, corn and others. It is the most economical and highly renewable feedstock in the world [11]. Lignocellulosic biomass accounts for approximately half of the plant matter generated by the photosynthetic processes. The main components of lignocellulose are cellulose, hemicellulose and lignin where they together are chemically bound and deeply permeated to each other. The three natural polymers form a stiff material that in plants builds the main constituent of the cell wall, adding chemical recalcitrance -and physical resistance to the structure. However, its physical and chemical properties are causing problem for further treatment and its industrial valorisation into biomaterials and bioenergy, thus the discussion of isolation and characterization method are essential [12]

The industrial application of lignocellulosic biomass are treated in different ways depending on its sources (trees species): softwood, hardwood and herbaceous. In general, softwood is a woody plant comes from gymnosperm tree and is characterized by its evergreen needle-like leaves and naked seeds. Woody plants belonging to angiosperms are classified as hardwoods and are also known as flowering plants. Hardwoods are usually broad-leaved and have enclosed seeds (fruits). Herbaceous (often referred as grasses), are often low growing plants and they tend to have soft green steams.

There are different types of herbaceous plants. Annual herbaceous completes its life cycle from germination to forming seeds in 1 year and then dies. However, biennial and perennial herbaceous plants have living parts that further grows in the next season and only the leaves and stem dies. A graphical representation of lignocellulosic structure is presented in figure 2 and the composition of softwood, hardwood and herbaceous are observed in table 1 [12,13].
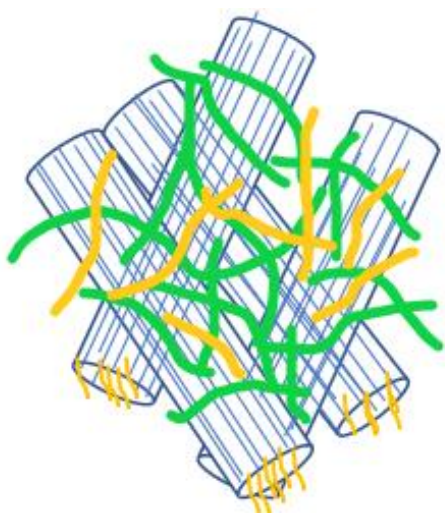
Figure 2. *A schematic illustration of lignocellulose composite material of cellulose, hemicellulose and lignin: Blue: cellulose, green: lignin and orange: hemicellulose, reproduced form reference.*

Table 1. The chemical composition of different lignocellulosic material [12]

Source	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Hardwood	40-55	24-40	18-25
Softwood	45-50	25-35	25-35
Herbaceous	25-40	25-50	10-30

1.2.1. CELLULOSE

Cellulose is the most abundant biopolymer on earth. It is mainly synthesized by plants but can also be produced by some bacteria. Cellulose is a linear syndiotactic, fibrous, water-insoluble and high molecular weight homopolymer composed of glucose monomers (D-anhydroglucopyranose units) [12,14]. The glucose monomers are linked via β-(1→4) glycoside linkage. Compared to starch, cellulose is a straight chain and no branching or coiling occurs in the biopolymer [15]. The arrangement of the β conformation with OH groups coordinated on the molecular plane make the chain to extend in linear fashion. The hydrogen bond between the hydroxyl group in one chain and the oxygen atom in the same or neighbouring chain forms microfibrils with high tensile strength. Cellulose plays an extensive role in the stability of the cell wall and is present in all plants and in some bacteria. The (1→4) linkage in cellulose creates a linear glucan chain which generates a 180 ° rotation of every glucose with respect to its neighbours [12,16]

Several cellulose chain forms crystalline or para crystalline lattice. The lattice is stabilized by both intermolecular and intramolecular hydrogen bonds. Furthermore, the intramolecular and intermolecular hydrogen bonds ads crystalline fibre structure to cellulose. The abundancy of lateral protruding hydroxyl groups has a strongly influence on the hierarchical organization of the biopolymer. Due to the interaction of linear chain, a dense network of superior hydrogen bonds can easily be formed. There are several identified crystalline structures of cellulose. Natural cellulose is known as cellulose I and cellulose II. Cellulose I occur as two allomorphs denominated Iα and Iβ. Cellulose has a degree of polymerization from 500 to 15 000 glucose units, making cellulose one of the longest biopolymers in earth [15]. The chemical structure of cellulose with its reducing and non-reducing ends is illustrated in figure 3.
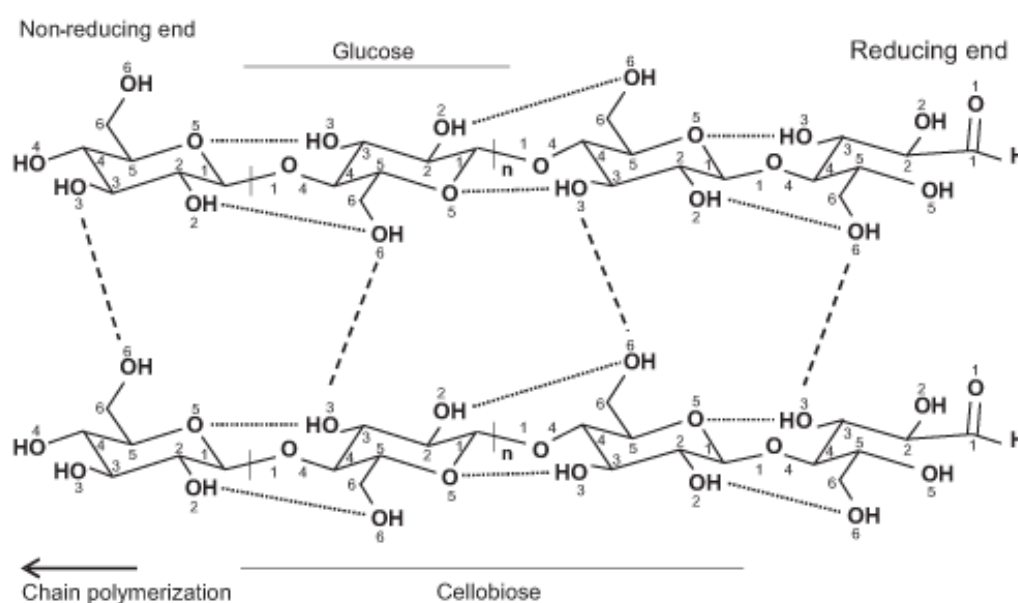

Figure 3. *The structure and inter- and intramolecular hydrogen bonding sequence in cellulose I. The dotted lines represent intramolecular hydrogen bonding and the dashed lines represent the intermolecular hydrogen bonding [15]*

There are other crystalline polymorphs of cellulose such as cellulose IIII, IIIIII, IVI and IVII which are obtained artificially by heat or chemical treatments [15]. Cellulose has a wide variety of applications. Generally, cellulose is obtained from cotton and wood pulp for industrial use. In paper and pulp industry, cellulose is the dominating constituent of paperboard, paper and card stock [17]. Cellulose (fibers) is also used in textiles which is made

from linen, cotton and other plant fibres. Cellulose derivates is also common in the pharma industry, such as microcrystalline cellulose (MCC) [18]

1.2.2. HEMICELLULOSE

Hemicelluloses are mainly built by various sugar with different substituents that are arranged in different proportions. The chemical composition depends on plant type and location on the cell. Depending on feedstock sources, the heteropolymer have side chains that is composed of pentoses (xylans), alternating units of mannose and glucose (glucomannans or mannans) or galactose units (galactans). Unlike cellulose, the degree of polymerization of hemicelluloses is usually lower than cellulose and it consists of 50-3000 sugar units [12]. The classification of hemicelluloses is based on the sugar residue as glucans, mannans and xylans. Usually hemicellulose is grouped in different subtypes depending on developmental stage, plant species, tissue type and various subclasses. Furthermore, based on the hydration of the fibres (low hydration polysaccharides and hydrocolloids) these subtypes are categorized in two general groups. The main function of low hydration polysaccharides is to stabilize and support the cell wall through covalent interaction with lignin and hydrogen bond interaction with cellulose. Hydrocolloids primarily function as a raw material storage system and extracellular energy and as a water retention mechanism in seeds [19].

Compared to cellulose which is crystalline, hemicellulose is amorph and it dissolves in water at temperature above >180 ° C. The chemical structure and frequency of hemicelluloses varies depending on feedstock resources. In hardwood and herbaceous plants, hemicellulose is mainly composed of xylans and glucomannas dominates in softwood. As for glucose in cellulose, xylan connects β-D-xylopyranose units with 1→4bonds. Furthermore, xylans is divided in homo-xylans, gluucuronoxylans, arabinoxylans and glucuronoarabixylans [20]. The heterogenous and complex structure of hemicellulose is an obstacle for its industrial utilization. A common strategy for the valorisation of hemicelluloses is the fermentation of its fermentable sugars and the production of sustainable products- and chemicals. The partial molecular structure of hemicellulose (glucuronoxylan) is illustrated in figure 4 [12].
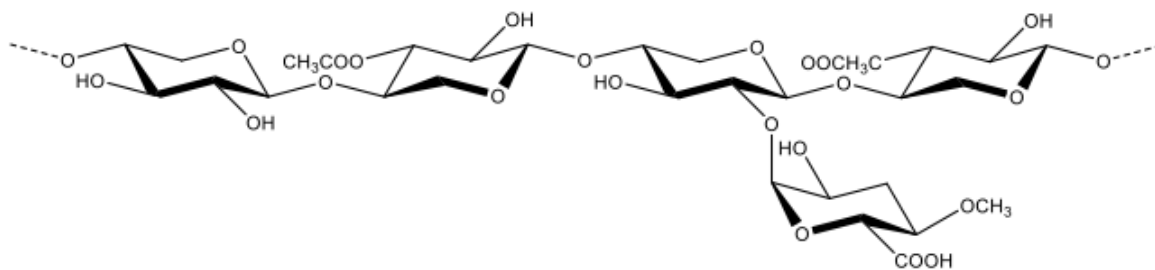
Figure 4. *An illustration of the partial chemical structure of glucuronoxylan [12].*

1.2.3. LIGNIN

Lignin is after cellulose, the most abundant biopolymer on earth. It is an amorphous, heterogeneous, aromatic and complex organic polymer that is synthesized from precursors (monolignol monomers) coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol. Usually, these precursors are known as C9 units or phenylpropane, where the hydroxyl group is bonded to C4 unit [21].

Furthermore, C3 and C5 unit may contain substitutions with one or two methoxyl groups. Hence, the aromatic ring with three alcohols are called, guaicyl (G), *p*-hydroxyphenyl (H) and syringyl (S) [21].

It is reported that the composition of lignin changes and develops during cell development. T. Fukushima [20] mention in his work that middle lamella and cell corners in conifers are primarily enriched in p-hydroxyphenyl lignin. It is further followed by the deposition of guaiacyl lignin in the secondary wall, middle lamella. The late deposited of syringyl lignin was detected in the secondary wall. Guaicyl lignin, which is known as softwood lignin consists of coniferyl alcohol and a minor amount of sinapyl alcohol-derived units. Hardwood lignin also contains sinapyl alcohol and coniferyl alcohol. However, the ratio of the monomer composition differs. Hardwood lignin is known as guaiacyl-syringyl lignin. In herbaceous lignin (grass lignin), p-coumaryl alcohol is the dominating monomer unit and it is also termed as guaicyl-syringyl lignin [23].

Usually, the monolignol units of lignin in tree and plant species are determined by H/S/G ratio, which directly describes the composition of *p*-hydroxyphenyl (H), syringyl (S) and guaicyl (G).The H/S/G ratio in hardwood is 5-33/ 33-80 / 20-54. In softwood the ratio is typically between 0-5 / 95-100 / 0 and 5-33 / 33-80/ 20-54 in grasses [24]. The main function

of lignin is to prevent the swelling of it in water and make the plant cell waterproof. Furthermore, the biological functions of lignin are to "glue" the cells together and make the cell wall stiff. It has also been well documented that lignin assists the wood towards biological degradation by increasing the resistance [25]. The monolignol units in lignin and are presented in figure 5 and a representative structure of lignin is shown in figure 6
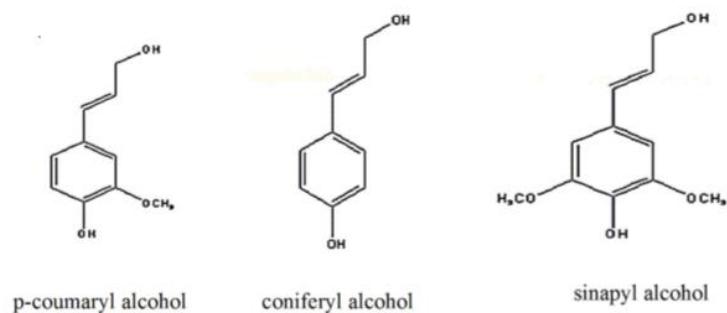

Figure 5. *The monolignols in lignin: p-coumaryl/hydroxyphenyl, coniferyl/guaiacyl, and sinapyl/syringyl alcohol [23]*
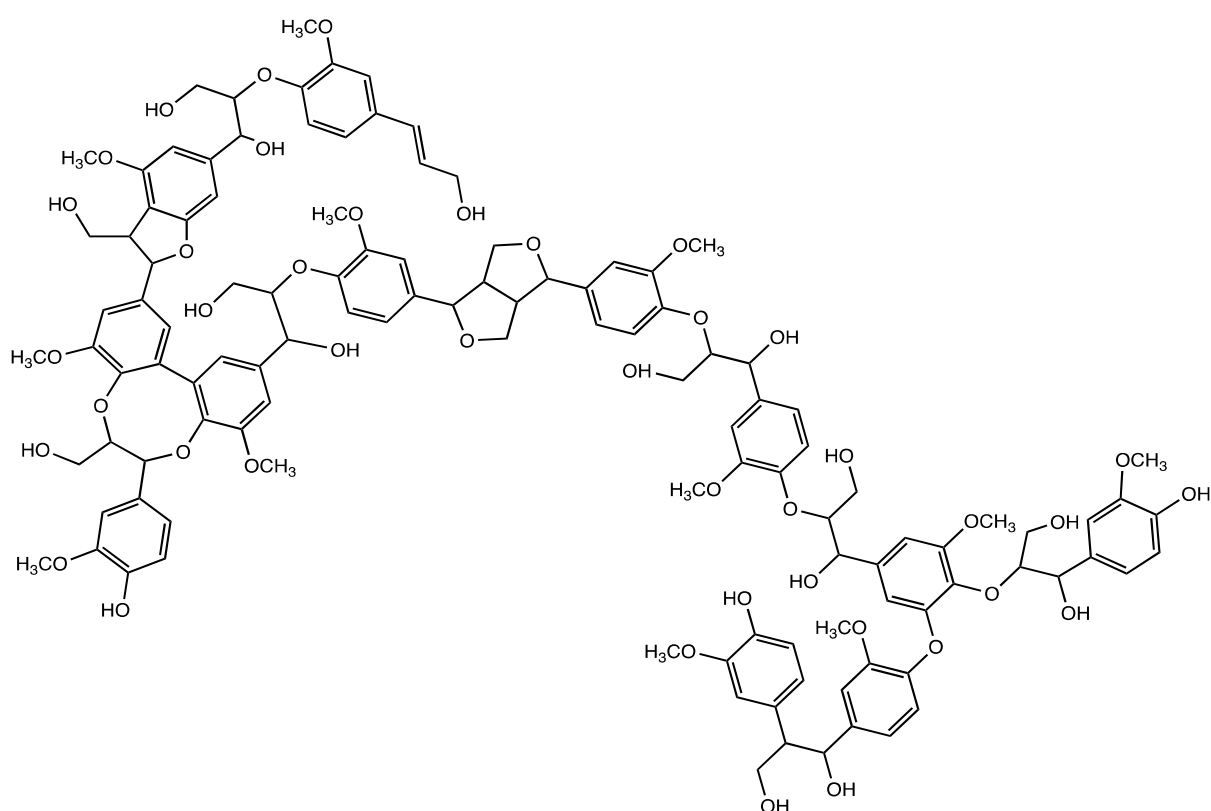

Figure 6. *A hypothetical structure of conifer lignin*

1.2.4. STRUCTURE AND BIOPOLYMERIZATION OF LIGNIN

Holger [26] and Freudenberg, K [27] clarified and gave new structural details of lignin. However, the analytical chemistry and obtaining new data of this biopolymer is a difficult task. Generally, the principles of the biopolymerization of lignin is based on the oxidization of monolignols and phenolic end-groups into resonance stabilized radicals. Furthermore, the radicals forms intermonolignol covalent bonds by undergoing radical-radical coupling. Monolignols is either oxidized directly or indirectly by oxidative enzymes (laccases and peroxidases) [25].

The phenolic end groups on lignin are also involved in coupling reaction and furthers forms covalent bonds in three different way: I. End-group radical and monolignol radical, II. two end group radicals or III. Two monolignol radicals. Thus, several different of intermonolignol bonds are created, of which β-0-4 ether is the most dominating. Ethers between aromatic rings (1-O-4 ether and 4-O-5 ether) and various types of carbon-carbon bonds (5-5, β-1, β-5 and β-β) are formed [25]. A representative illustration of the principle of lignin bio polymerization is presented in figure 6 [25].

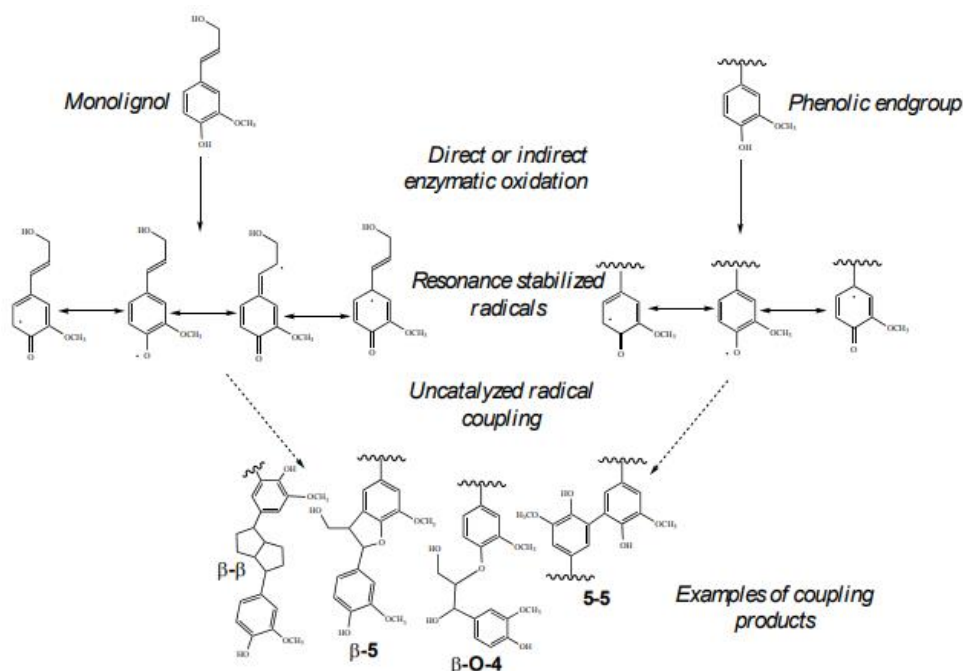**Figure 7.** *Principles lignin bio polymerization [25]*

In the irregular and three-dimensional network of lignocellulosic composite, lignin acts as a matrix, enveloping hemicellulose, and cellulose. Generally, good compatibility between

different components in any composite material plays an extensive role as it affects the mechanical properties. Lignin can easily form non-covalent bonds with carbohydrates, due to its large availability of functional group. An example is the richness of aromatic and aliphatic hydroxyls where lignin can form hydrogen bonds. Furthermore, it is also confirmed that lignin and carbohydrates (especially hemicellulose) are covalently bond and forms lignin-carbohydrate complexes (LCC). It is further believed that the covalent bonds between the lignin and hemicelluloses exists in the form of ether and ester linkages, examples of ester and ether bonds are illustrated in figure 8 [12, 25, 27].
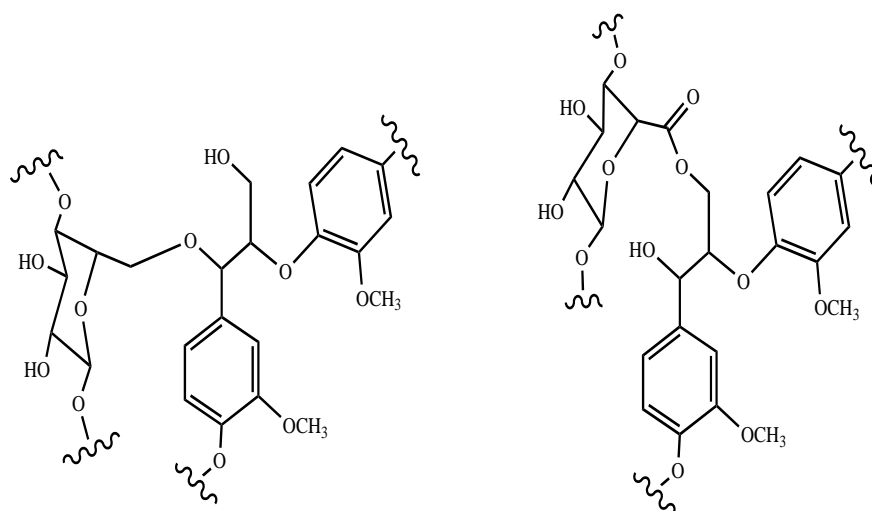

Figure 8. *Ether (left) and ester (right) covalent bonds between lignin and hemicellulose*

1.3. ISOLATION TECHNIQUES

The irregular and heterogenous structure of lignocellulose composite material where lignin, cellulose and hemicellulose are interconnected by a myriad of chemical and physical interaction. They are further embedded to each other at molecular level, which causes major obstacles for the isolation process of lignin. In order to be further exploited and treated, these biopolymer needs to be separated by drastic methods from each other which usually changes its native conformation [12]. Consequently, the isolation of lignin in its unaltered and native form is impossible, hence the discussion of isolation method is essential when studying the implementation of lignin in rubber blends. No isolation technique is currently commercial for the quantitative extraction of residual or native lignin without the risk of damaging (structural changes) the lignin.
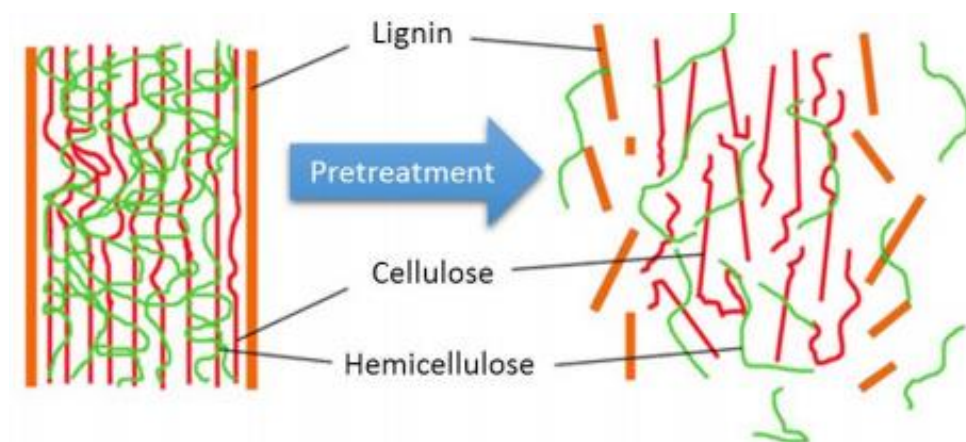
Figure 9. *Illustration of the pre-treatment on a lignocellulosic material [12]*

As mentioned before, the chemical composition of lignin varies in different feedstocks. Hence, the isolation method is dependent on raw material and desirable end- product. There are several developed isolation techniques of lignin: pyrolysis, steam explosion, CO_2 explosion, ammonia explossion, ozonlysis, acid/alkaline hydrolysis, mechanical comminution organosolv and biodegradation. Based on chosen extraction method, the structure and chemical composition of lignin will differ [29]. Today, impure lignin is mainly obtained as a by-product from paper industry where the desired product is cellulose. Lignin that is obtained from industrial processes are often referred as technical lignin. These processes are divided in two groups: sulfur-free and sulfur based. Kraft lignin originates from the sulphate process and is extensively used by pulp and paper industry and constitutes 85 % of the total lignin production in the world. Generally, the kraft pulp process is the main technique for the conversion of coniferous wood to pulp which generates the highest pulping yield compared to other alkaline pulping techniques. In the cooking process, approximately 90-95 % of lignin is dissolved into white liquor (sodium sulphide and sodium hydroxide). Due to the alkaline conditions in the cooking process, various bonds, usually the β-O-aryls are cleaved, and the molecular fragments gets further solubilized. Higher amount of phenolic hydroxyl groups are present in kraft lignin due to the cleavage of etheric bonds. Furthermore, the oxidative environment of the cooking causes kraft lignin to form condensed structures and incorporate sulfur. The range of sulfur content in kraft lignin is approximately 1-2%. Lastly, at the end of the kraft cooking, lignin is precipitated from black liquor. Figure 10 represents the industrial processes for the treatment of technical lignin [12, 29]
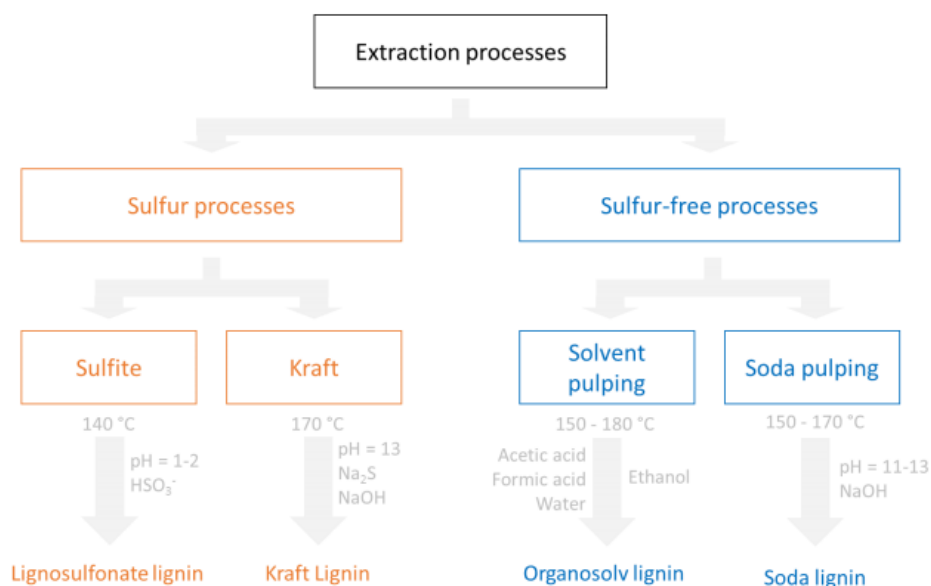
Figure 10. *Sulfur-based and sulfur-free (industrial) process for the production of technical lignin [12]*

1.3.1. LIGNOBOOST PROCESSS: FURTHER TREATMENT OF KRAFT LIGNIN

As mentioned before, efforts have been made in the development of isolation method. Generally, lignoboost process obtain black liquor from an evaporation plant and it is further precipitated by acidification (CO_2) and filtered using a chamber press (Filter 1 in figure 11). Furthermore, the lignin is re-dispersed and acidified after the filtration. In this step, lignin forms a slurry and is filtered and washed which is illustrated in figure 11 "chamber press filter 2". Due to the re-dispersion of the filter cake in a liquid, at a temperature and pH near to final washing liquor, the concentration gradients during the washing stages will be low. Subsequently, any change in solubility, pH level and most of the change in ionic strength will take place in the slurry and not in the filter cake. The filtrate obtained from "chamber press filter 1" in figure 11 is recycled to the black liquor evaporation plant (usually after taking the feed stream to LignoBoost). The aim is to avoid any decrease in lignin concentration in the stream fed. Furthermore, the obtained filtrate from chamber press filter 2 in figure 11 is recycled to the weak black liquor. However, it can also be used for washing the oxygen delignified or unbleached pulp. Thus, the Lignoboost process is an effective technique for the extraction of lignin from black liquor in Kraft mills [30]
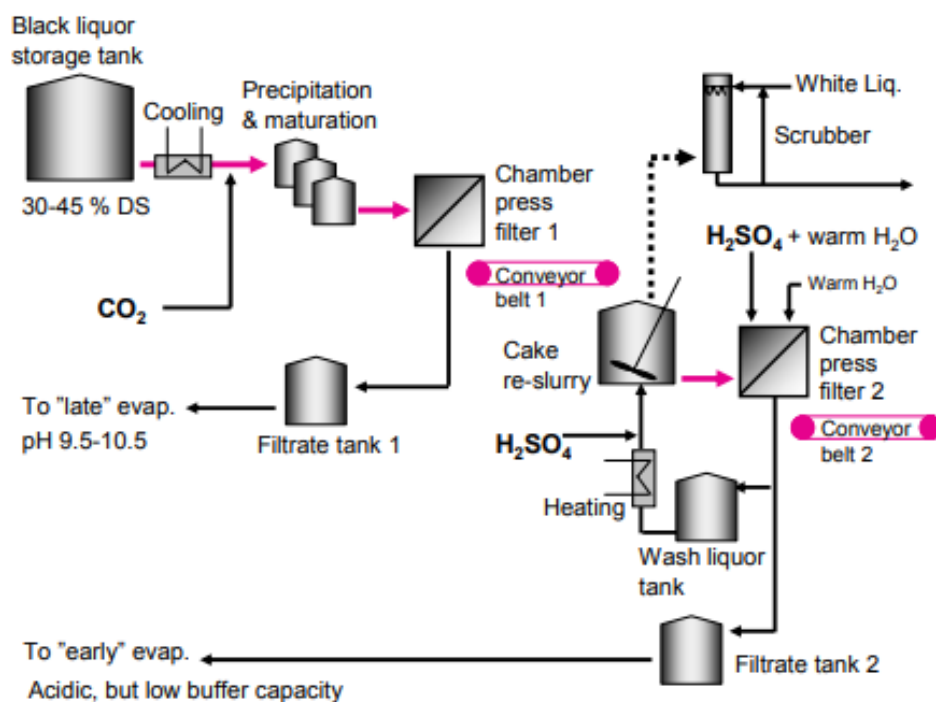
Figure 11. *General layout of the LignoBoost process [30]*

1.4 APPLICATIONS OF LIGNIN

Lignin has a wide variety of industrial applications. Lack of toxicity, bulk availability and cost efficiency in combination with the growing demand for renewable materials and chemicals creates numerous potential industrial application routes. Lignin can be further upgraded by modification makes it useable as polyolefin, rubber packing, rubber intensifier, filler in vinyl ester etc. Usually, due to its properties, kraft lignin are mainly used in high end applications such as in printing inks, modifier/extender, in foam fire extinguishers [31, 32].

It has been proven that lignin can be used as a flocculent, dispersing agents, auxiliary or thickener for paints, coatings etc. Due to its chemical structure, lignosulfonate is used to prevent the settling and clumping of undissolved particles in suspensions. Lignin is also used as the binder for glass wool building insulation [31]. Norgebey, E et.al [32] highlighted that adding lignin fibres to bitumen increased the viscosity of the binder at lower and higher temperature for. Furthermore, an increase in the recovery component and rutting resistance of bitumen at higher temperature were observable.A new study indicated that lignin can be used as UV and fire protection [33]. Lately, efforts have been made in utilization of lignin for fuel production [34]. Moreover, studies have been made on lignin as a filler in plastics [35, 36].

1.5 TYRE TECHNOLOGY

In 1845, Robert William Thompson patented the first pneumatic tyre [37]. However, due to durability issues and low market share (soild rubber was still dominating), it never went to production. The air-filled tyres started to gain popularity after a northern Irishman, named John Boyd Dunlop obtained a patent for pneumatic bicycle tire in 1889. The real breakthrough for automotive was pioneered by Édouard and André, usually known as the Michelin brothers. Furthermore, the development of tyres was accelerating and Goodyear Tire and Rubber Company, named after George Good year, invented vulcanized rubber in 1898. In over 50 years, pneumatic tyres for automobile were built up of an inner tube containing compressed air and an outer tube that provided traction and protection [38]. In 1948, Michelin introduced the first steel-belted radial tyres in Europe. Radial tyres usually contain rayon, nylon or polyester. The name 'radial tyre' is due to the casing which is reinforced and supported by a belt of steel that operates around the circumference of the tyre. Due to its properties and functionalities, radial tyres have many advantages such as: better steering characteristics, less rolling resistance (which increases gas mileage) and longer tread life. Despite the pros, radial tyres have harder riding quality which is not preferred [38].

Today, there are approximately 455 factories that manufactures pneumatic tyres. The global production is over 1 billion tyres/year. Firstly, the tyre rubber is manufactured in a rubber industry and it usually contains natural/synthetic rubber, carbon black and several chemicals that will be further discussed in this thesis. Furthermore, the tyres are formed on a drum and cured in a press under press and heat. Heat causes a polymerization reaction where the rubber monomers start to bond and forms elastic molecules. The biggest tyre manufacturers today are Bridgestone, Micheline, Goodyear, Continental and Pirelli where each producer uses their own elements to increase the durability and performance [39].

1.5.1 STRUCTURE AND COMPONENTS

The accelerating development of pneumatic tyres for automotive have resulted in the highly engineered and complex product. Usually, a radial tyre aimed for passenger cars is built up by various components that are fused together. The different rubber components with specific qualities and amounts plays a specific role in within the pneumatic tyre. Usually, a different types of vulcanization agents, protective substances, and processing aids are used in the rubber. Due to the network of steel wires and synthetic fabrics, the rubbery parts are steadily

held together [12]. The main function of the synthetic fabrics is to improve the mechanical properties and reinforce the structure. A typical pneumatic tyre, with some variation, is made up of inner liner, body ply, sidewall, beads, apex, belt package, tread and cushion gum. The different structure elements of a radial tyre are illustrated in figure 12 [39]. As it is visible, the tread is in contact with the ground and it gives the tyre a low rolling resistance and good traction. This is, the reason to why the rubber compound in tread greatly differs from that in the sidewalls. As the tread undergoes environmental stresses, (i.e friction and different forces from the ground), it is supported, and the shape is maintained by the sidewalls. The specific role of the bead (heel, sole, and toe) is to keep the tyre in position on the rim and they are mainly made up of strong steel wirings enclosed by several types of rubber elements [12,38,39].
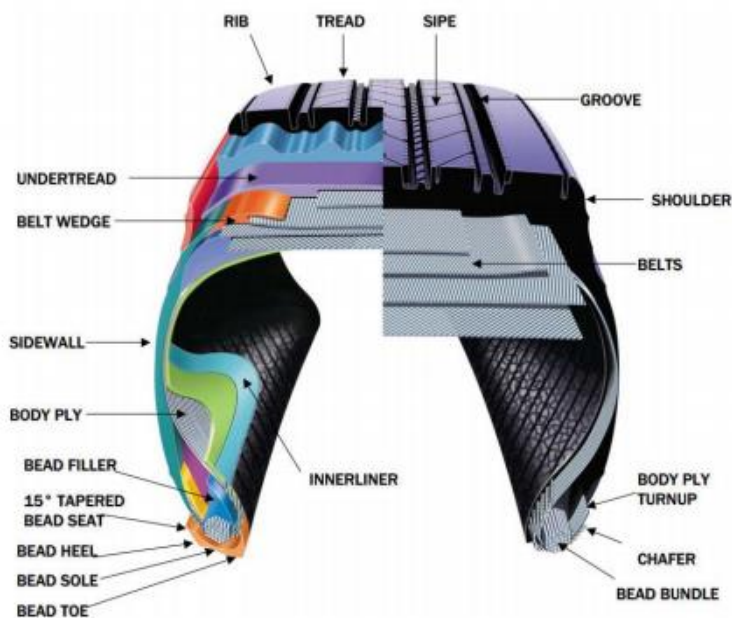
Figure 12. *Main structure elements of a radial tyre [10]*

1.5.2 MATERIALS IN TYRES

As mentioned before, pneumatic tyres must have specific properties in order to utilize their function. Therefore, the choice of the rubber ingredients and construction of tyre is crucial. The main function of the tread is to further provide essential traction or grip for braking, driving, and concerning. The aim of the moulded pattern in the tread is to minimize pattern noise on a variety of road surfaces and to give uniform war in order to channel water out of the footprint. The designing part takes place during the curing or vulcanization of the rubber. For the blends in the sidewalls, it is constructed to further assist and enhance the flex-resistance. The idea of the compounds in the inner liner is to minimize air loss etc [40].

Approximately 200 elements can be used to make a final pneumatic tyre. However, it is possible to categorize the main element used in the rubber compound [12]. Mainly, natural rubber is used to provide and enhance specific performance characteristics to tires, such as fatigue and tear resistance. Generally, in tyre manufacturing, to synthetic rubber polymers are used: styrene butadiene and butadiene rubber. They are often used in combination with natural rubber. Usually, the chemical and physical properties of these rubbers have a great impact on the performance for each component in the pneumatic tyre as well as the overall tyre performance (wear, traction and rolling resistance) [12, 41]

Textiles in tyres are common and they are made of several types fabrics cord that further improve the mechanical properties. The main function of the fabrics is to provide help support and dimensional stability to the automotive. Common textiles are polyester cord fabrics: rayon, nylon and aramid cord fabrics [41].

Fillers, (carbon black and amorphous precipitated silica) are used to reinforce the rubber by improving the abrasion and mechanical properties, such tear resistance and the tensile strength. This furthers enhances the wear performance and traction. Silica is mainly used to improve the rolling resistance. In order to enhance the stability of the tire, various chemicals are used, such as antiozonants and antioxidants. Furthermore, curing systems (zinc oxide and sulfur) are crucial components in the rubber compounds and they have a main role during the tire curing or vulcanization, which is discussed in the section "*VULCANISATION PROESS*" [12, 41]. The main ingredients and average composition of tires are presented in table 2.

Table 2. *Average ingredients and composition in different tyres. OTR* (off the road) [10]*

Ingredients	Passenger tyres	Lorry tyres	OTR*tyres
Rubbers	47 %	45 %	47 %
Carbon Black	21,5 %	22 %	22 %
Metal	16,5 %	25 %	12 %
Textiles	5,5 %	-	10 %
Zinc Oxide	1 %	2 %	2 %
Sulphur	1 %	1 %	1 %
Additives	7,5 %	5 %	6 %

POLYMERS

Elastomers have the characteristics of rubbers (i.e elasticity and flexibility) and are loosely cross-linked polymers. Due to its randomly coiled, long cross-linked composite, it can be stretched and efficiently return to its original shape when environmental stresses are removed. [42 ,43]. As it has weak intermolecular forces between the polymer chain and the crosslinks suppress irreversible flow, the elastomeric chains are highly flexible at temperature above T_g. Hence, the reason why when small stress to the system causes large deformation. It is obvious for this reason that rubber elastomers have low Young's modulus and high elongation at break compared to other polymers [44]. From a thermodynamic point of view when stress is applied to the system/specimen, the randomly coiled chains will align, and they will be stretched in the direction of force. When environmental stresses are released, the specimen will spontaneously move towards maximum entropy (equilibrium). The principle is illustrated in figure 13 [12].

There are numerous types of elastomers, such as styrene-butadiene, block copolymers, polyisoprene, natural rubbers, polybutadiene, ethylene propylene rubber, silicone elastomers, fluoroelastomers, polyurethane elastomers and nitrile rubbers [42]. Elastomeric materials are mainly used in the automobile industry to manufacture, braking systems, tires, interior parts, chassis, etc [43].
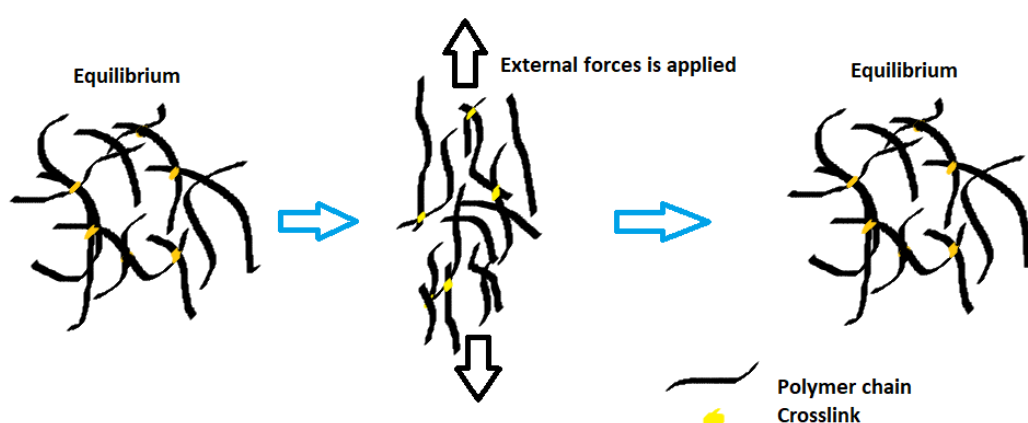

Figure 13. *Crosslinked elastomeric system under applied tensile stress, reproduced from reference*

NATURAL RUBBER

Natural rubber (NR) is created by enzymatic processes in several plants and belongs to the families of Euphorbiacea, Moracea, Apocynacea and Compositea. NR is usually obtained from Hevea Brasiliensis in the form of poly-cis 1,4 isoprene, where it contains over 99,9% cis 1,4 structural units and other components such as fatty acids, resins, proteins and inorganic materials (salts) [45]. Approximately, the average molecular weight in NR is 10^5- 10^6 g/mol and the distribution is bimodal and broad with a polydispersity index between 2-10 Mw/Mn. At the molecular scale, the chain ends are weak since the polymer do not transmit the strength in the chain. High molecular weight polymer such as NR has usually greater tensile strength [46].

Generally, the characterization and properties are far more complex than organic molecules. It is believed that poly-cis,14 isoprene (NR) forms after a series of biochemical reaction which begins with pyrophosphate and isopentenyl within the tree. Its long chains allow for entanglement which helps hold the mass together. Usually, when environmental stress (tensional forces) is applied to the NR latex, such as lifting with a fork, the strands will tend to straighten out and untangle. This is due to the various rotations that occur about single bonds in the polymer backbone and the polymer strand is further uncoiled [46].

Furthermore, when stresses are released, the mass may not return to its original shape or orientation and the 'spaghetti' strands will slide by each other. Another important macro structure property to discuss is the degree of branching of a polymer which affects the glass transition temperature of the rubber. Hence, the reason why stiffening occurs when the temperature is lowered. The glass transition temperature of NR is -72 °C. There are four different isomers of NR: cis-1,4; trans-1,4;1,2 and 3, 4. However, due to is doubles bonds, no rotation around the carbon-carbon will occur [46]. The biochemical reaction is illustrated in figure 14.
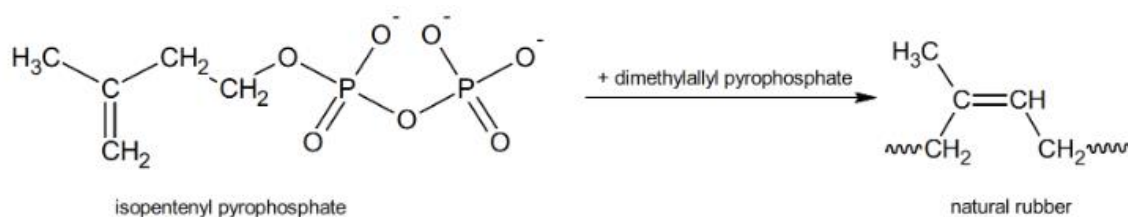

Figure 14. *The biochemical reaction of natural rubber*

SYNTHETIC RUBBER

Today, tyre manufacturers constitutes 70 % of world consumption of synthetic rubbers. Styrene butadiene (SBR) and butadiene (BR) are most the most common rubber polymer in the tyre industry [12]. SBR has lower viscosity grades than NR and due to its irregular molecular structure, it does not crystallize. It is compatible with natural rubber and has a low cost. SBR is mainly produced by free-radical solution polymerization or by emulsion polymerization at a high temperature 60 ℃ (hot rubber) or low temperature 30 ℃ (cold rubber) [47].

Emulsion SBR (ESBR) is more suited for high-performance tyres. Nevertheless, ESBR constitutes nearly 75 % of the world capacity (2015). However, the manufacturing of solution polymerization SBR is increasing. SBR has a highly irregular and random structure and the addition of styrene (compared to butadiene rubber) reinforces the abrasion resistance, improves the strength, and blend properties of polybutadiene [48]. Unlike NR, SBR vulcanizates have lower fatigue resistance, resilience and resistance to cut and growth and tearing. On the other hand, SBR possess improved thermal aging, mechanical cleavage of the chains and resistance towards abrasion [12]. The chemical structure of SBR is shown in figure 16.
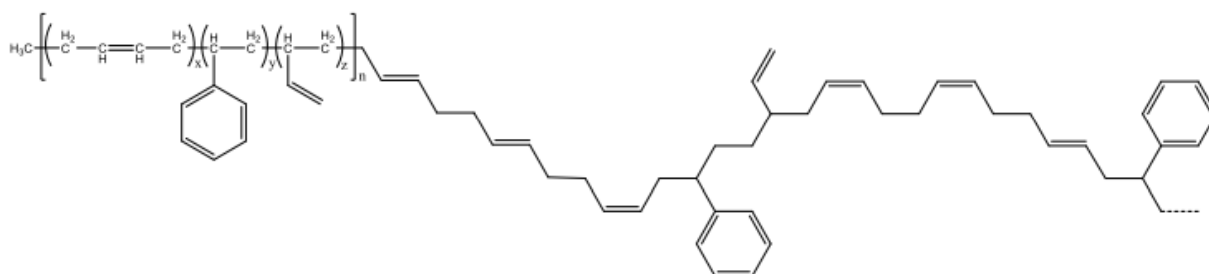

Figure 15. *A chemical structure of styrene butadiene (SBR) [12]*

VULCANIZATION

Vulcanization is a crucial process that occurs in rubber compounding. Rubber elastomeric materials usually retract their original shape after tension forces have been applied (deformation). Vulcanization is often defined as a mechanism that reduces the amount of permanent deformation and further increases the retractile forces after removal of the deforming stress. Hence, the reason why vulcanization of the rubber compound increases while it decreases plasticity. It is documented that there is a proportional relationship between

the retractile force to resist a deformation and the number of network-supporting polymer chains / unit volume of elastomer. The supporting polymer chain between network junctures is a linear polymer and an increase in crosslinks or junctures gives a further increase in the number of supporting chains. Above its melting point, in a un vulcanized high linear polymer, only molecular chain entanglements compose junctures [49].

Although vulcanization is a chemical mechanism where network junctures forms by the insertion of crosslinks between polymer chains, several short chained sulfur crosslinks may be present. These types of sulfur bonds are: a single sulfur atom, a carbon-to-carbon bond, an ionic cluster, a polyvalent organic radical, or a polyvalent metal ion. Generally, for a vulcanization process, the rubber compound that contains various vulcanizing agents is heated in a mould under pressure. It is also common for extruded rubber goods to be heated in salt bath or even hot air [49]. Furthermore, vulcanization generates a three-dimensional network structure and enhances greater stability in the rubber compound. It was discovered by Goodyear in 1839 and since the development of vulcanization process, majority of all rubber products are manufactured using the vulcanization process [50]. The aim of the vulcanization process in a rubber compound is the conversion of a mouldable and plastic substance into one that is elastic and flexible. The introduction in vulcanization process further improves the modulus (stiffness), abrasion resistance, rebound, hardness, and tensile strength, and decreases hysteresis (heat build-up), compression set, elongation and solubility. A brittle, hard and solid rubber compound indicates an excessive crosslinking. The most dominating curing agent used for elastomer, usually diene rubbers: SBR, natural, polybutadiene, nitrile, polychloroprene, and polyisoprene (unsaturated polymer backbones) is sulfur agent. [51].

Generally, there are two different types of sulfur vulcanization: accelerated and unaccelerated. The unaccelerated vulcanization usually contains zinc oxide, sulfur and a fatty acid (stearic acid is common). Compared to unaccelerated, the accelerated vulcanization consists of an accelerator in the system. Furthermore, there is a subcategory to accelerated sulfur, which is sulfur-free systems (known as sulfur-donor systems). Sulfur-donor systems the accelerator supplies the sulfur needed for the network formation, which generally function as sulfur-donor and an accelerator. Today, unaccelerated sulfur vulcanization is not commercial. However, it plays an extensive role as a starting point in the understanding of accelerated vulcanization processes [52].
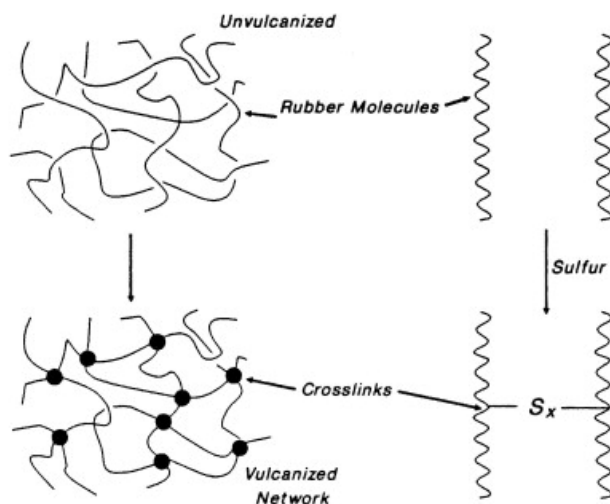
Figure 16. *The formation of sulfur vulcanization process [52]*

To further analyse the important characteristics linked to vulcanization such as scorch time (t_{s2}), optimum cure time (t_{s90}), cure rate and maximum torque (M_H), a rheometer curve is plotted (shown in figure 17). Generally, the vulcanisation curve is divided in three different areas: induction and scorch, curing and overcure. The time needed to begin the cross-linking is referred as scorch time, the maximum torque is related to the quality of the polymer used, the final level of cross linking and the compounding process. Furthermore, after reaching the maximum torque, a crosslink reversion is visible [52]. Generally, there are two distinctively different types of rheometers: Rotational or shear type rheometers and extensional rheometers. Rotational or shear rheometer control the applied shear stress/strain whereas extensional rheometers applies extensional stress. Usually, a raw rubber compound is placed between two heated platens and is further compressed by an applied oscillating force where the degree of vulcanization determines the cure characterises of the rubber and the change in stiffness of the rubber sample. The rheometer test is between 3-5 minutes and the typical standards for this procedure are ASTM D5289, D6024 and D6601 [52].
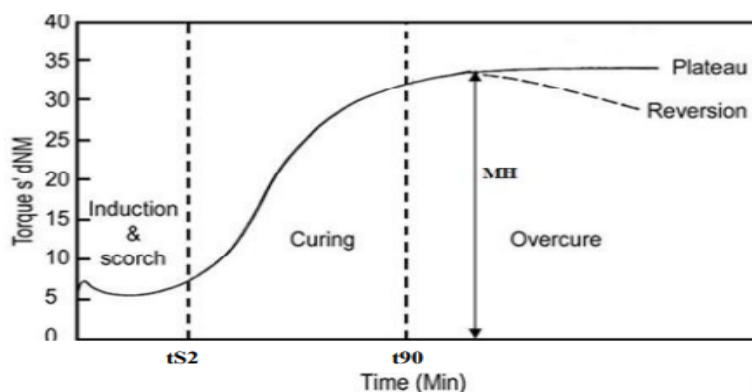

Figure 17. *Vulcanization curve [51]*

FILLERS: CARBON BLACK

The main function of fillers in rubber compounding is to enhance the chemical and-mechanical properties and reduce the cost. For the improvement of properties in elastomeric materials, usually one or more reinforcing fillers is present. Reinforcing fillers usually consists of particles with the dimension in the nanometric domain such as: nanoparticles (three dimensions in nano scale), nanofibers (two dimensions) and nano plates (one dimension). Furthermore, the addition of reinforcing fillers enhances tensile strength, hardness, compression set, viscosity, elongation at break and abrasion resistance [12].

In the tyre manufacturing and rubber industry, carbon black and silica are extensively used as a reinforcing filler. Approximately 93 % of carbon black is used in rubber compounding and it is often classified in two main categories: mechanical rubber goods (i.e hoses and automotive belts) and tyres. Carbon black usually provides enhanced durability and performance to the elastomeric material and is further categorized in N100-N900 series blacks.

The N number, that is included in the naming of different carbon black grades, is directly correlated to the decreasing surface area (ASTM D1765) and denotes normal curing material [54]. Carbon black N375 which is used in this experiment has approximately a surface area of 90 m^2/g and roughly an average diameter of 23-30 nm (high structure). Generally, carbon black is manufactured by the incomplete cracking or combustion of vapours and hydrocarbon gases derived from petroleum feedstocks.

The properties of carbon black are highly discussed and there are four fundamental properties which gives further instructions on the optimization of the reinforcing filler: 1. Particle size distribution and fineness, influence tint and blackness, 2. The aggregation of the particles and structure within the carbon black particle, 3. Pore-size distributions and porosity influence coverage and viscosity requirements , and 4. The presence of surface functionality influences viscosity, electrical conductivity and wettability [55]. Silhouettes of particles of carbon black morphologies are illustrated in figure 18.
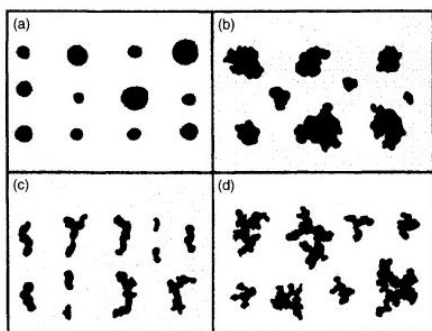
Figure 18. *The morphologies of carbon black particles: a) individual and spherical, b) agglomerated and formed into sphere, c) agglomerated linearly and d) clumps and agglometerated into linear, however it forms branched systems [55].*

OTHER COMPONENTS

Other elements such as stabilizer (which is usually is seen as a fundamental component in rubber compounding) plays a specific role in order to achieve specific requirement. Stabilizer are used namely for protection of the rubber compound. Organic polymers and rubbers are susceptible to aging. There are multiple external agents that affects the rubber materials; oxygen, light, ozone, heat, mechanical stress, metal ions etc. Furthermore, rubbers are specifically susceptible to heat due to the energy needed to break of π-bonds in the C=C bonds to form active relatively low. Thus, the presence of stabilizer in rubber compounding is essential. Other minor components such as plasticizer are also added to the rubber material for further enhancement of flexibility [12]

2. METHOD

The experimental part of this project was split into two different activities: A1. Chemical modification and A2. Rubber compounding. Both activities involved different characterization types that will be further discussed.
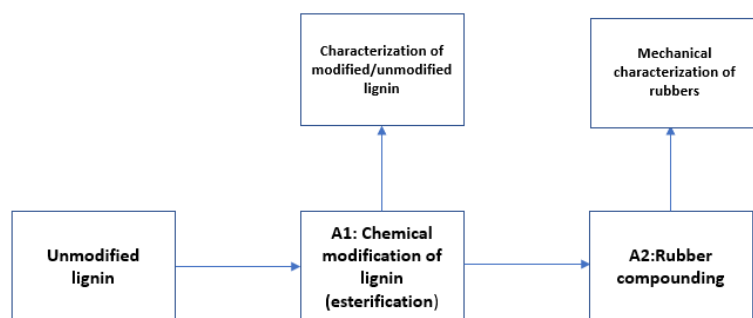

Figure 19. *The overall setup for this experiment*

2.1 EXPERIMENTS

The experimental part of this thesis is further divided: chemicals, equipment, chemical modification of lignin (A1) and rubber compounding (A2).

2.1.1 CHEMICALS

Five hundred grams kraft lignin were obtained from LignoCity2.0 (Research Institution of Sweden, RISE), using the Lignoboost process. All the anhydrides and catalysis shown in table 3 were obtained from Sigma Aldrich Chemicals. The chemical modification and characterization of lignin was performed at Karlstad University, department engineering and chemical science.

Table 3. *The chemicals used for esterification of lignin*

Chemicals	Purity (%)	Abbreviation	Form
Crotonic	95	Cro	liquid
Methacrylic	94	Met	liquid
Isobutyric	97	Iso	liquid
Butyric	98	But	liquid
Propionic	>99	Pro	liquid
1-methylimidazole	99	1-MIM	liquid
Lignin	>99	KL (Kraft lignin)	Pulver (65 % DS)

2.1.2 EQUIPMENT

A1: Reflux system for the modification of lignin, Cary 630 FTIR Spectrometer-Agilent for the characterization of lignin. **A2**: GUIX, GX 2070 Two roll mill for the rubber compounding, Poly 300 S for the rubber samples. The instruments and standards used for the mechanical testing are following: Alpha Technologies Tensometer 200 (serial number 80SIC1083), SS-ISO 37 for tensile-test, for IRHD and Shore A (hardness) Bareiss digitest II (Shore A: serial number DTA 8619, IRHD: DTM 8617), SS-ISO 48, were used. As for rebound resilience Hampden, model EPH-50 (serial number 025), SS-ISO 4662 were used. For weighing the rubber samples, a Mettler PL-1502-S were used. For determining the density, an analytical weight scale Kern ABT 220-4M, SS-ISO 2781 were used.

2.1.3 CHEMICAL MODIFICATION OF LIGNIN

The esterification reactions of lignin were conducted following the procedure suggested by [56] Thielemans and Wool with small adjustment on the extraction part. To avoid spills and odours the chemical modification of lignin was performed under fume hood. Lignin powder were obtained from Lignocity and 45 grams were weighed with an analytical scale and dispersed in a 250 ml round bottom flask with 90 ml of corresponding anhydride. Furthermore, 2, 25 ml of catalyst 1- methylimidazole was added to the solution after stabilizing the temperature at 50 ° C and the esterification reaction was carried on for approximately 180 minutes.

After 180 minutes the reaction was quenched with 750 ml of deionized water and briefly stirred. Butyric, isobutyric and methacrylic lignin formed a batter consistency and could easily be separated from the rest product by decantation. Propionic lignin and crotonic lignin required further separation treatment. The corresponding lignin were equally added in four 200 ml plastic flasks and underwent a repeat centrifugation for 10 minutes (5000 rpm). The clear lignin product was dissolved and transferred to aluminium forms by adding a small amount of acetone. The modified lignin samples were dried under fume hood for several days until constant weight.

Figure 20. *The modified lignin after several days of drying in fume hood.*
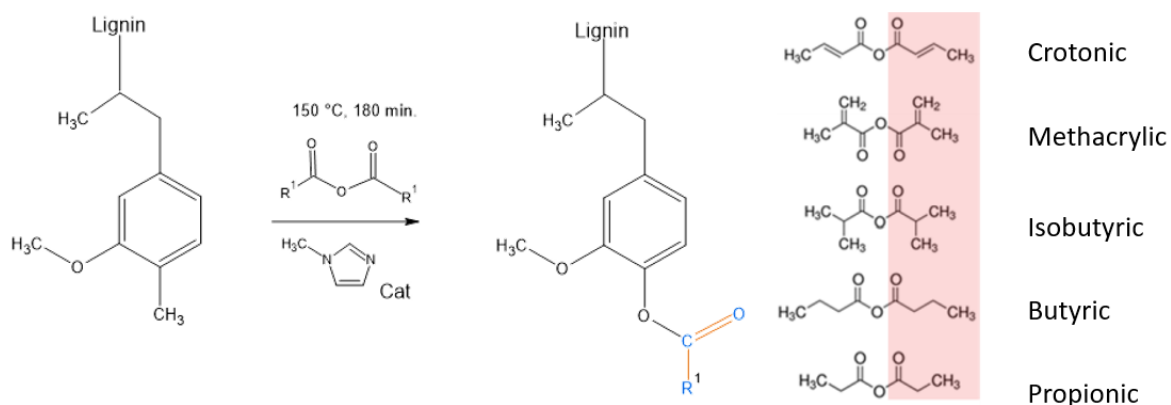
Figure 21. *Overall esterification mechanism of lignin. (Reproduced in Chemsketch from reference [10])*

2.1.4 RUBBER COMPOUNDING

The lignin- based rubber compounds were prepared by mixing several ingredients, shown in table 4, using an open two-roll mixer. The following ingredients followed Barana's preparation of rubber compounding [12]. Firstly, zinc oxide, stearic acid, antioxidant I and antioxidant II were weighed together with an analytical scale and briefly mixed. The chemicals were then gradually introduced in the two-roll mill with natural rubber (CV50). After processing the sample, 30 grams of corresponding modified lignin were increasingly added and further processed. Depending on the homogeneity of the rubber compound, the rpm of the two-roll mill varied. Furthermore, CBS and sulphur were pre-weighed and added into the two-roll mill. The rubber compounds were processed until achieving homogeneity and then transferred to a table. As for carbon black based rubber compound, the same procedure was followed.

To further investigate the mechanical properties of the rubber compounds, the preparation of round buttons and flat samples were essential. For the flat samples, approximately 45 gram of corresponding rubber compound were weighed and pressed for 8 minutes at 160 °C, using Polystat 300 S. The same equipment was used for the round button samples. Furthermore, 10 grams were weighed and transferred in a round metallic form. Multiple samples were simultaneously processed for 12 minutes at 160 °C. All samples were left to cool and rest 24 hours before the characterizing the mechanical properties. The chemicals used in the rubber compounding are presented in table 4. For carbon black and natural rubber, N375 and CV50 were used.

Table 4. *The chemical ingredients used in the rubber compounding. Expressed in parts hundred rubber (phr)*

Ingredients	NEAT	CB	KL	ProL	ButL	IbutL	MetL	CroL
CV 50	100	100	100	100	100	100	100	100
N375		15						
Kl			15					
ProL				15				
ButL					15			
IsoL						15		
MetL							15	
CroL								15
Zinc Oxide	5	5	5	5	5	5	5	5
Stearic Acid	2	2	2	2	2	2	2	2
SULPHUR	2	2	2	2	2	2	2	2
Accelerator (CBS)	2	2	2	2	2	2	2	2
Antioxidant I (6PPD)	1	1	1	1	1	1	1	1
Antioxidant II (TMQ)	1	1	1	1	1	1	1	1
phr tot	113	128	128	128	128	128	128	128

Figure 22a and b. *The rubber compounding with isoL, using a two-roll mill, and the modified lignin rubbers before press plates: 1 NEAT, 2 unmodified, 3 carbon black, 4. butyric, 5. isobutyric, 6. methacrylic and 7 crotonic lignin.*

3. RESULTS

The results will be presented and discussed in the following sections: Characterization of modified lignin, mechanical testing and visual inspection. Totally,

3.1 CHARACTERIZATION OF MODIFIED LIGNIN AND DISCUSSION

The results are shown in figure 23. a-f between 3200-3500 cm^{-1} in figure 23, the unmodified lignin indicates the stretching of different hydroxyl groups. For different modifications in figure 23.b-f (ProL, ButL, IsoL, MetL and CroL) it is possible to see how the region of hydroxyl group fades out, hence an indication of a complete modification. However, some residual hydroxyl group is still observable in CroL (figure 23 f) which is in line with previous studies [12]. The region between 2700-3000 cm^{-1} for modified lignin indicates the presence of C-H stretching of methylene and methyl groups. The signal obtained in this region is slightly dependent upon chain saturation and chain length. For an instance, ButL, IsoL and MetL have higher absorbance in this area than KL, ProL and CroL. According to Li [54] and Thielmans Wool [53], alphatic esterfied lignin is observable between 1700-1800 cm^{-1} which agrees with figure 23 a-c. However, for MetL and CroL double bonds (C=C) peaks are shown in lower wavenumber (1630-1680 cm^{-1}). Furthermore, the region between 1000-1200 cm^{-1} is dominated by ester bonds. For CroL, a new strong peak between 990-960 cm^{-1} is shown and highlights the presence of the alkene. The data for the starting and final masses are presented in table 5. The amount of substance was calculated by the dividing the mass difference in the final and start with the formula weight. Furthermore, the reacted anhydride per gram lignin were calculated by dividing the amount of substance with the start mass of lignin (45 gram)

Table. 5 *The start and- final masses, and formula weight for the lignin samples. The amount of substance (mol) and reacted anhydride per gram lignin (mol/g) are presented*

Modification	Start (g)	Final (g)	Formula weight (g/mol)	Amount of substance $(\frac{Final-start}{Formula\ weight})$ (mol)	Reacted anhydride per gram lignin (mol/g)
ProL	45	52.1	130.14	0.0545566	0.00121237
ButL	45	49.8	158.19	0.0303433	$6.743*10^{-4}$
IsoL	45	53.3	158.19	0.0524686	0.00116597
MetL	45	52.7	154.16	0.0499481	0.00110996
CroL	45	49.6	154.16	0.0298391	$6.631*10^{-4}$

Table 6. *The marked groups (1-4) in the FTIR spectra (figure 23.a-f) for modified lignin*

| Sample	1	2	3	4
ProL	Aromatic C-C stretch	Aromatic C-H stretch	C-O stretch secondary alcohols and aliphatic ethers	C-O stretch primary alcohols, aromatic C-H in plane deformation
ButL	Aromatic C-C stretch	Aromatic C-H stretch	C-O stretch secondary alcohols and aliphatic ethers	C-O stretch primary alcohols, aromatic C-H in plane deformation
IsoL	Aromatic C-C stretch	Aromatic C-H stretch	C-O stretch secondary alcohols and aliphatic ethers	C-O stretch primary alcohols, aromatic C-H in plane deformation
MetL	Aromatic C-C stretch	Aromatic C-H stretch	C-O stretch primary alcohols and Aromatic C-H plane in deformation	C=C stretch methacrylates
CroL	Aromatic C-C	Aromatic C-H	-	C=C stretch crotonic
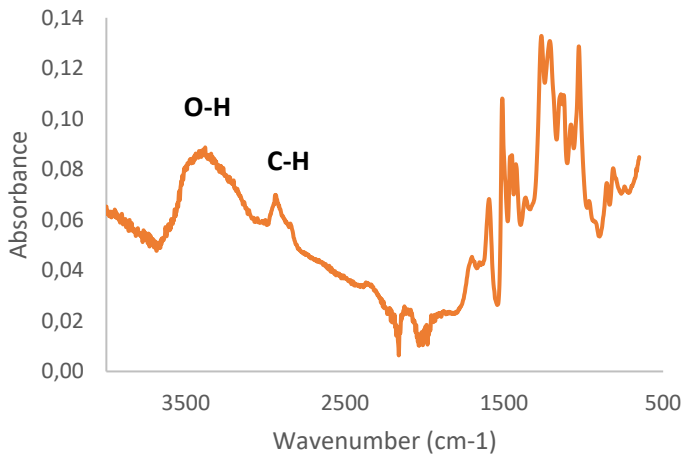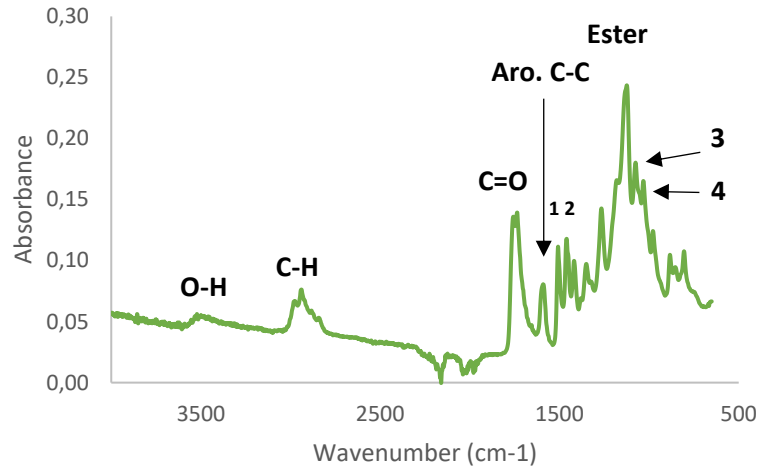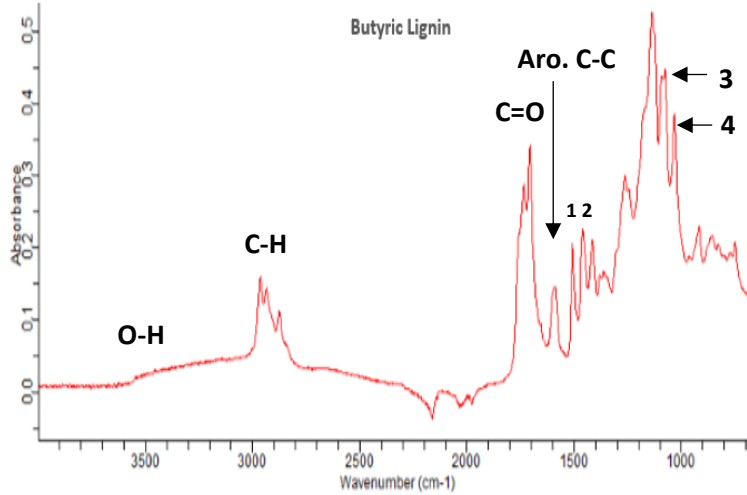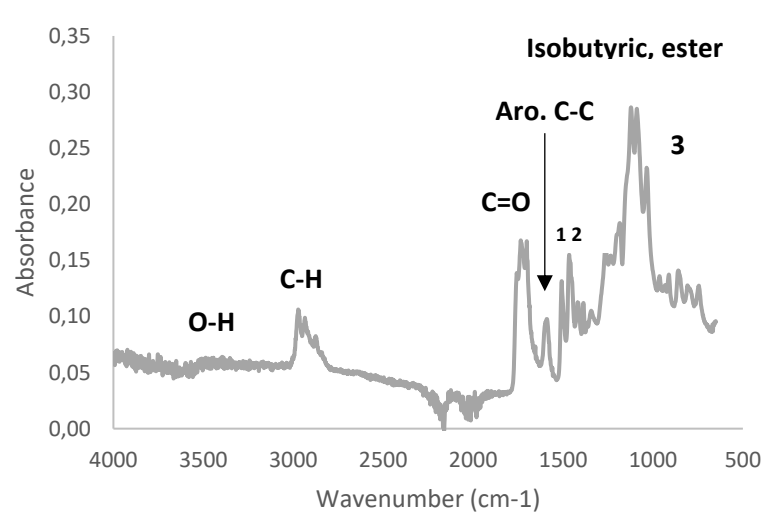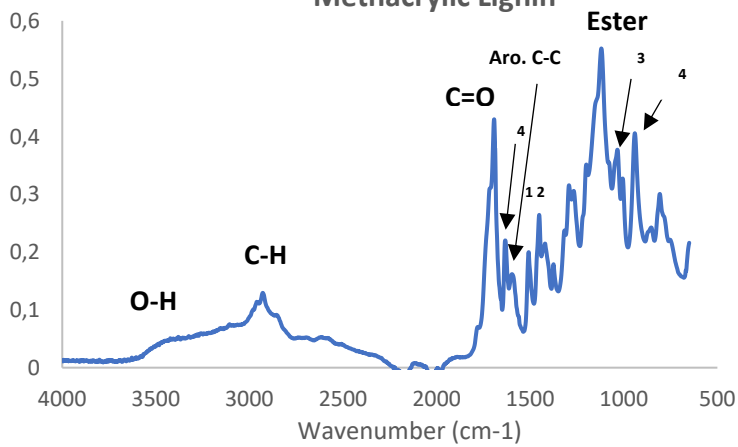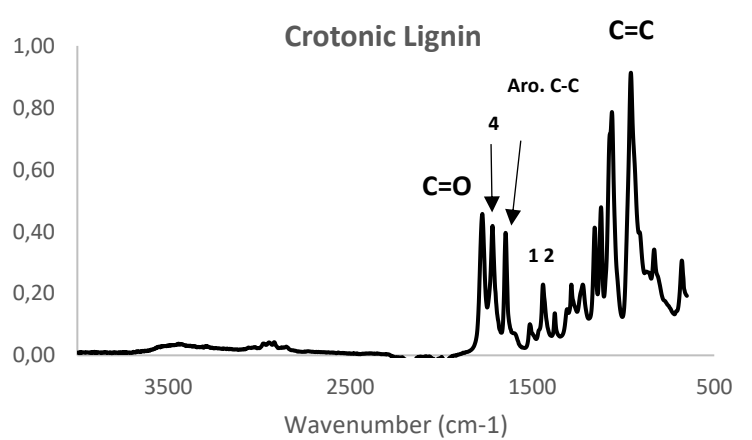
Figure 23.a-f. *FTIR spectra of modified lignin*

3.2 MECHANICAL TESTING OF THE RUBBER COMPOUNDS AND DISCUSSION

In this section, the mechanical properties of the rubber compounds will be presented. The mechanical testing involves: Rheometer curve, IRHD, shore A, tensile strength, tear resistance and rebound resilience. For the stress-strain and tear resistance curve, three test samples were plotted, and the average data is presented in table 7. The vulcanization curves (rheometer curves) shown in figure 24, slightly differed throughout the samples. As mentioned before, the rheometer curve for vulcanisation can be divided into three stages of vulcanisation mechanism: induction period or scorch time, cross-linking (curing) and over cross-linking, (shown in figure 17). As expected, it was observable that lignin gave an increase in scorch time and interfered with vulcanization compared to the reference sample (CB) and NEAT, hence the delay in crosslinking phase. This mechanism has been reported earlier by [57] Kumaran et.al. and Nando [58]. The addition of lignin (KL in table 6) increased the cure rate. However, poor numbers were obtained for the stiffness of lignin (M_H-maxium torque value, Nm) in the plateau region.

Table 7. *The average value of rheometer data for the rubber compounds, sample size n=3*

| Sample	Scorch time, t_{s2} (s)	Optimum cure time, t_{90} (s)	Cure rate, $100/(t_{90}-t_2)$, (%/min)	Minimum Torque, M_L (dNm)	Maximum Torque, M_H (dNm)	Torque difference, ΔM, $(M_H - M_L)$ (dNm)
Neat	1.29	1.77	208.33	0.227	7.124	6.897
CB	0.84	1.33	204.08	0.137	9.563	9.426
KL	1.00	1.46	217.39	0.117	5.263	5.146
ProL	1.55	2.15	166.66	0.185	4.773	4.588
ButL	1.48	2.29	123.46	0.186	5.867	5.681
IbutL	1.67	2.43	131.58	0.123	5.621	5.498
MetL	1.52	2.74	81.97	0.162	5.586	5.424
CroL	1.60	2.77	85.47	0.114	5.279	5.165
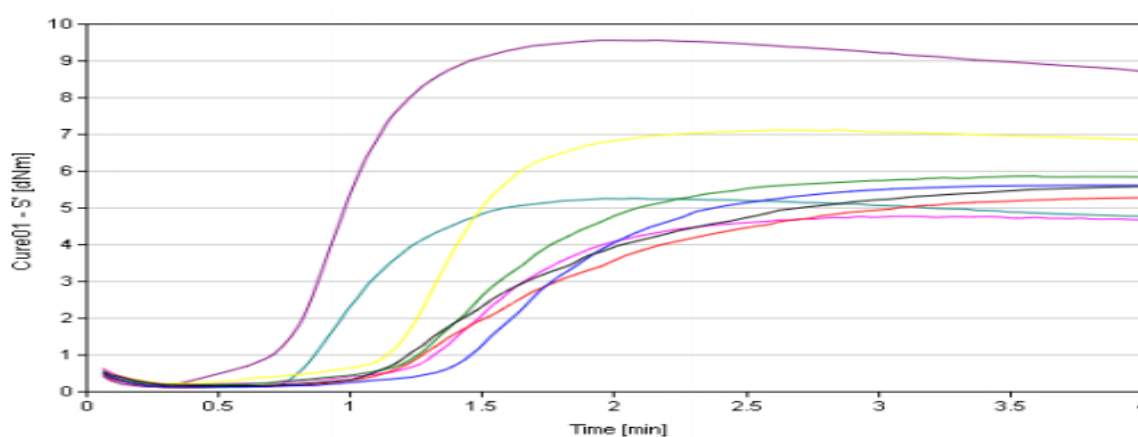
Figure 24. *Rheometer curve compound for the rubber compounds*

As for tensile strength test (figure 25 a-h) it was expected that the addition of lignin will have a negative impact on the tensile strength. However, the addition of butyric and isobutyric lignin gave a significant improvement of the tensile strength compared to the other modified samples. All lignin samples (modified and unmodified) gave a higher elongation at break. Compared to the other samples, the addition of protonic obtained the highest elongation at break (650 %). 'Furthermore, it was possible to observe that lignin gave an increase in hardness (Shore A and IRHD) but to a lesser extent than carbon black. For the modified lignin, butyric and isobutyric lignin had a slightly higher hardness than the others. The tear resistance (shown in figure 45-52) gave poor numbers for lignin-based rubber compounds compared to reference sample. On the other hand, crotonic lignin obtained a higher tear resistance compared to the other lignin samples. Furthermore, it was also observable that the addition of lignin gave an increase in the rebound resilience.

Table 7. *The average data of different mechanical properties of the compounds. For tensile strength, elongation at break and tear resistance*

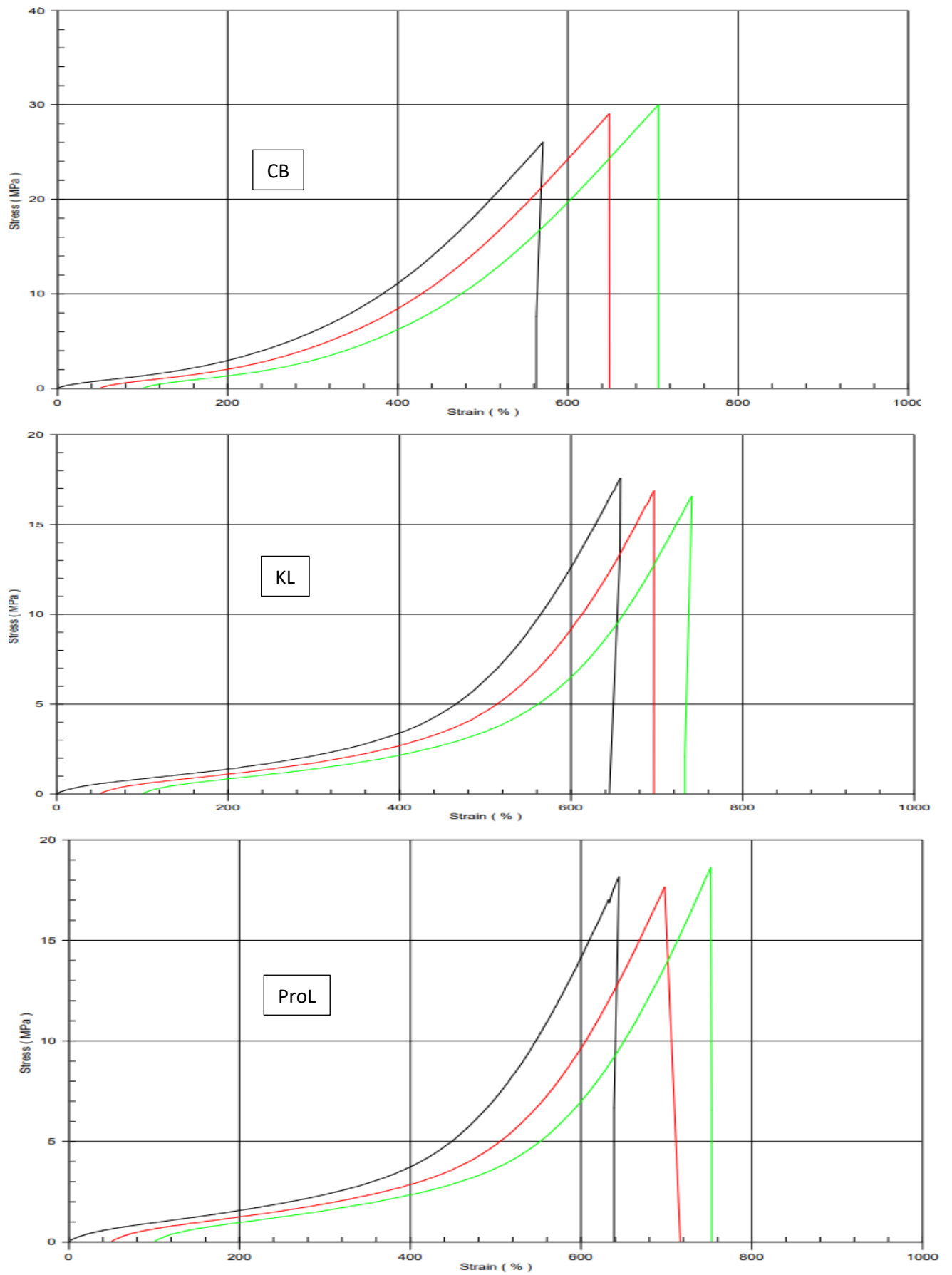| Sample	Tensile strength (MPa)	Elongation at break (%)	IRHD	Shore A	Rebound resilience (%)	Tear resistance (N/mm)
Neat	18.0	604	41	42	80	26.9
CB	28.2	593	48	48	72	77.1
KL	16.8	649	39	40	76	16.3
ProL	18.2	649	43	44	77	14.3
ButL	23.4	640	43	44	78	20.1
IbutL	20.2	635	41	43	77	15.1
MetL	16.3	610	39	41	74	24.2
CroL	13.2	624	38	40	76	26.0
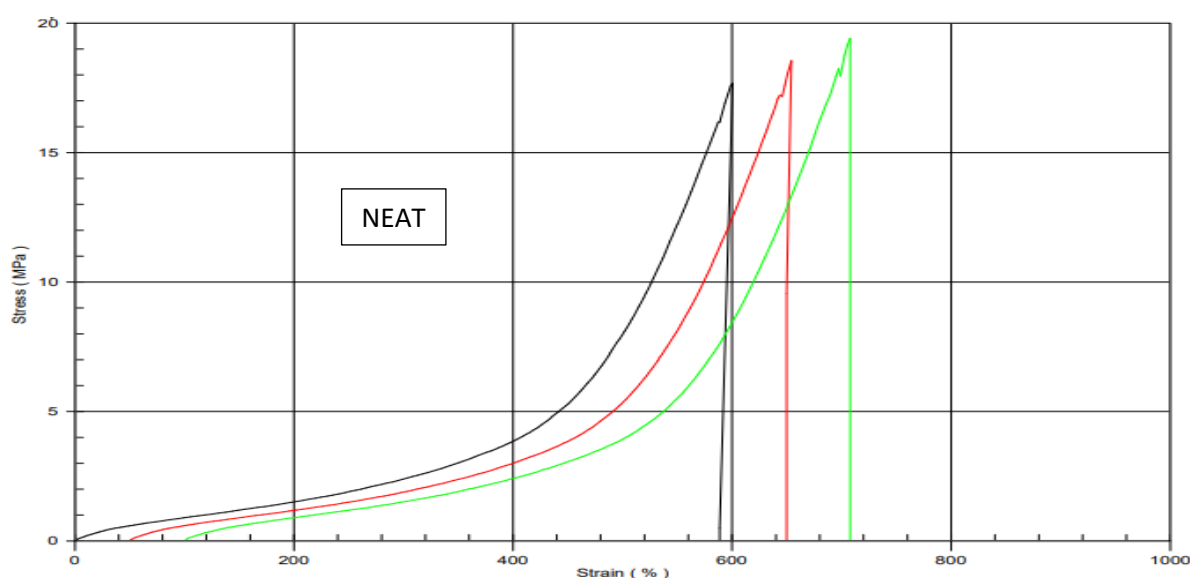
Figure 25 a-d. *The stress-strain curve of Neat, CB, KL and ProL*
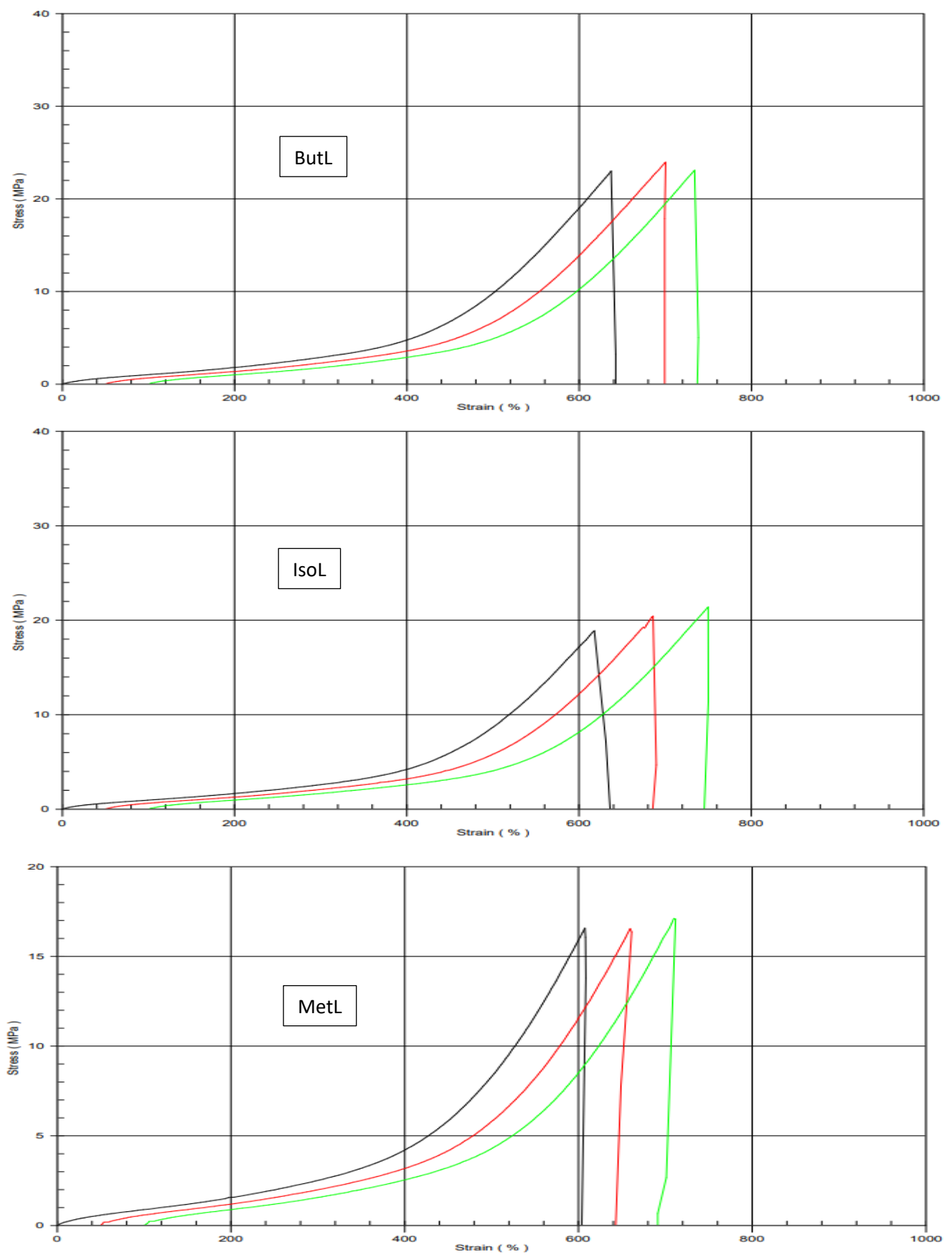
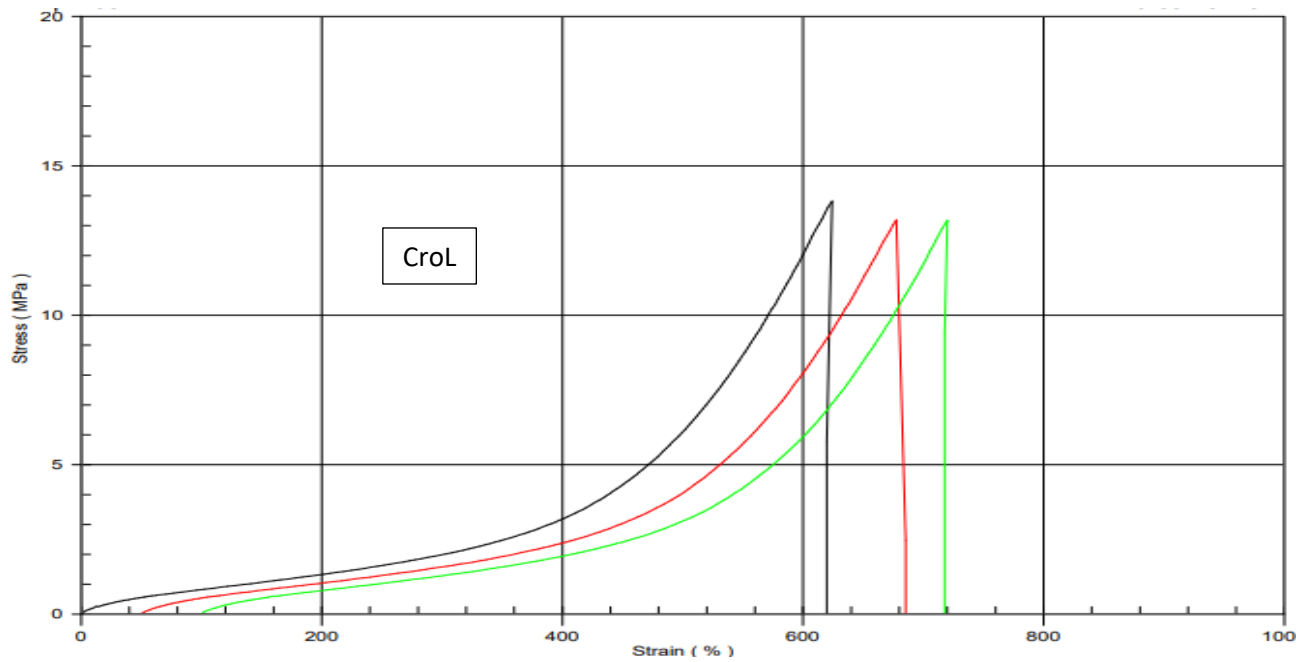**Figure 25 e-g**. *The stress strain curve for ButL, IsoL, and MetL*

Figure 25 h. *The stress strain curve for CroL*

As mentioned before, the average value of the mechanical test was presented in table 7. For further calculation, the confidence intervals were determined for tensile strength (MPa) and elongation at break (%) with the significance level of 0.05 of three specimen. The confidence indicates a large margin of errors. However, only three specimens were used for this experiment. For unmodified lignin (KL) only two specimens were used, hence it is neglected in table 8.

Table 8. *The 95 % confidence interval of the tensile test and elongation at break with the sample size n= 3. Maximum and minimum value of corresponding test are presented in the table.*

Sample	Tensile strength (MPa)	Elongation at break (%)	Tear resistance (N/mm)
NEAT	(13.407, 22.500)	(595.61, 613.26)	(12.583, 41.670)
CB	(23.778, 32.618)	(551.30, 634.64)	(63.283, 90.163)
KL	(14.695, 18.761)	(628.41, 668.79)	-
ProL	(17.255, 19.173)	(639.68, 658.38)	(12.323, 90.163)
ButL	(22.035, 24.681)	(617.71, 662.09)	(7.627, 35.406))
IsoL	(16.841, 23.537)	(596.57, 673.43)	(8.870, 22.103)
MetL	(15.775, 16.770)	(605.82, 614.71)	(14.327, 30.700)
CroL	(11.915, 14.515)	(612.72, 635.82)	(7.871, 38.149)

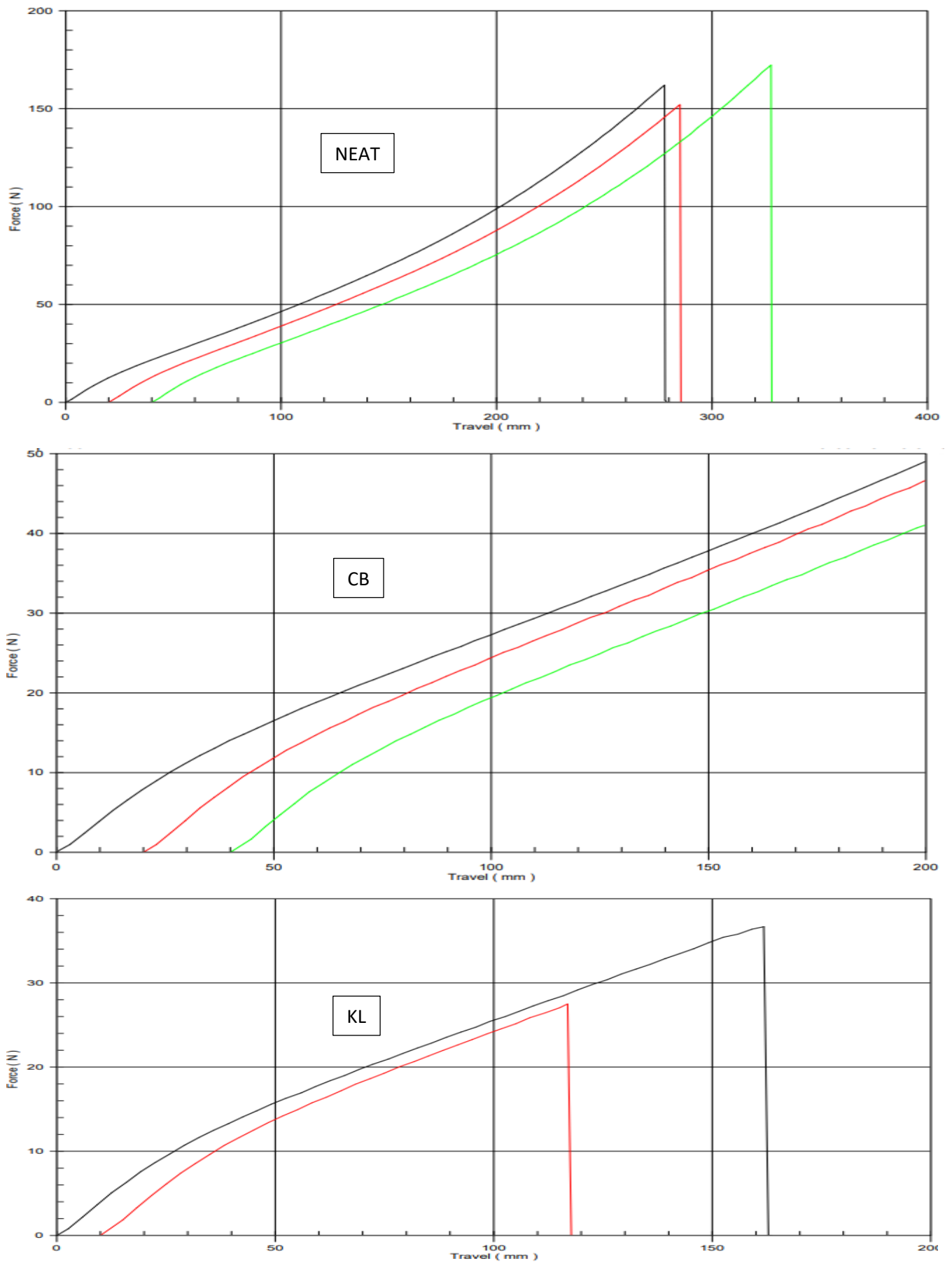In figure 26 a-h, the tear resistance curves of the rubber samples are shown.

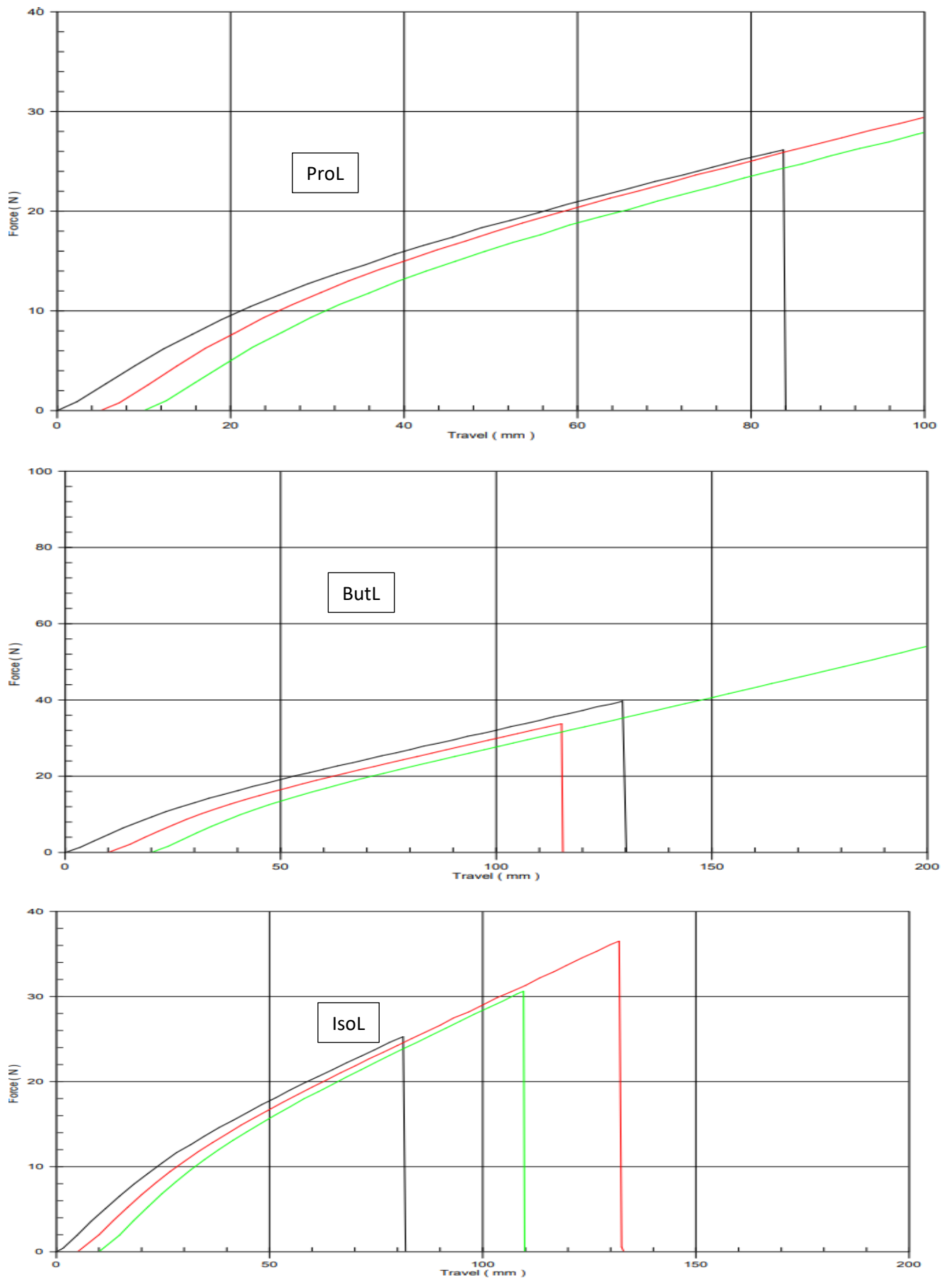**Figure 26 a-c**. *The tear resistance curve for Neat, CB and KL*

Figure 26 d-f. *The tear resistance curve for ProL, ButL and IsoL*
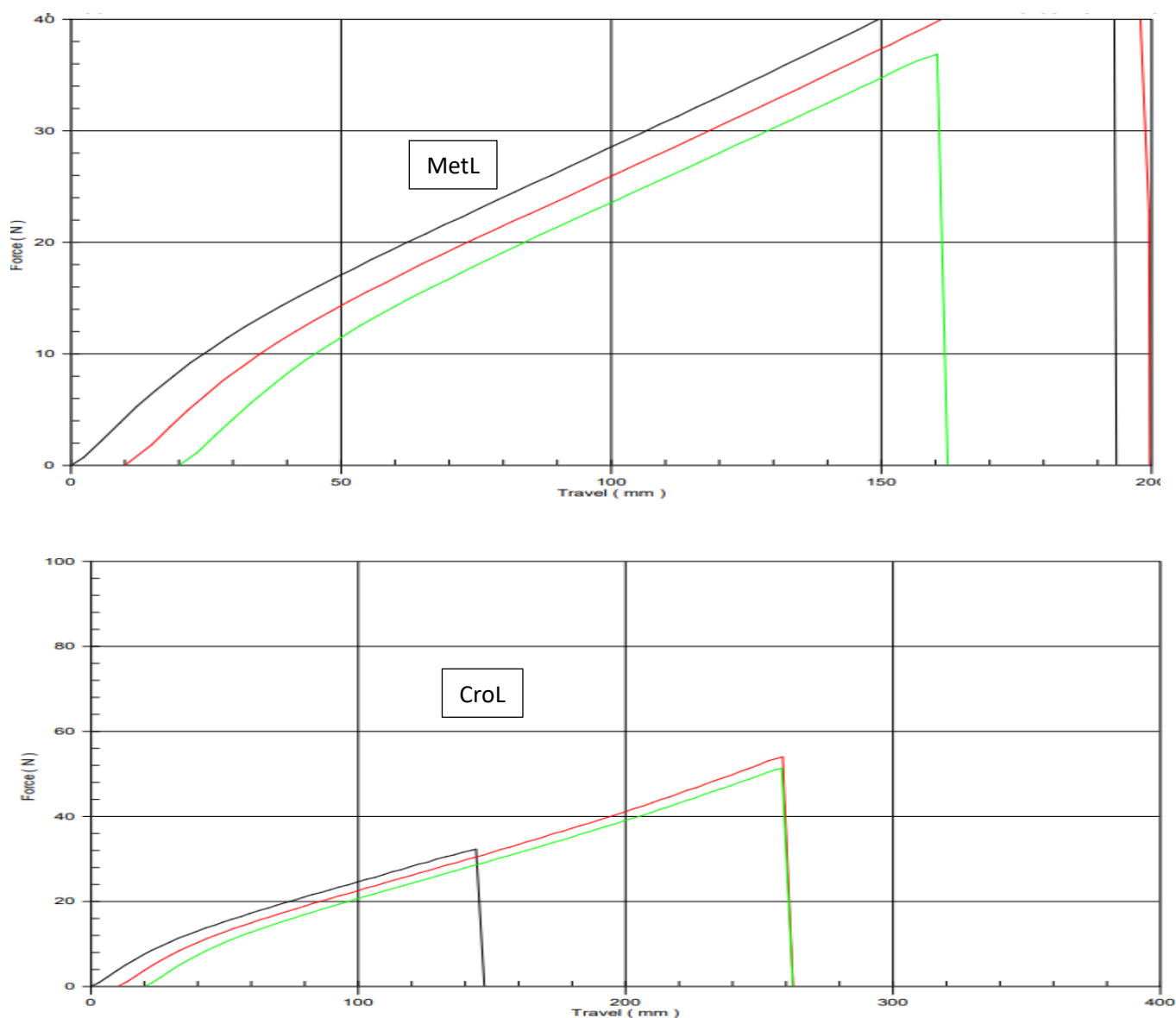
Figure 26 g and h. *The tear-resistance curve of MetL and CroL*

3.3 VISUAL INSPECTION OF THE RUBBER COMPOUND

For this experiment, a two- roll mill was directly used for the rubber compound and this might
have an impact on the dispersion of the compound. Thus, the discussion of visual inspection
of the rubber compound is essential. In figure 27.b , it is visible that the rubber compounds
obtained different dispersion and homogeneity. For an instance, propionic lignin (number 4)
had small undispersed corns that were spread out to the sample. Crotonic (number 8) did not
obtained a good dispersion however it was better than propionic. Methacrylic (number 7)
caused some difficulties during the modification of lignin. It was hard to separate the product
from the aluminium form and it is believed that small aluminium fragment was present in the
rubber compounding. On the contrary, butyric and isobutyric achieved a good dispersion and

no visible corns were visible. For unmodified lignin, a better dispersion than propionic was observable but to a lesser extent than isobutyric and butyric. Furthermore, the carbon black based obtained the best dispersion and no corns were visible. The NEAT sample was used as a reference. Figure 27.a illustrates the different form the modified lignin obtained after esterification. As mentioned before propionic and crotonic were in powder form and underwent a repeat centrifugation after the modification process. However, for isobutyric and butyric a butter consistency was formed during the experiment and it could be further separated by decantation. Even though the samples were left to dry under fume hood for several days, isobutyric and butyric did not obtain powder form. In figure 27.a, it is visible that the particle size of propionic are small. The crotonic sample obtained larger particle size. The form of methacrylic and isobutyric resembled the form of butyric in figure 27.a.
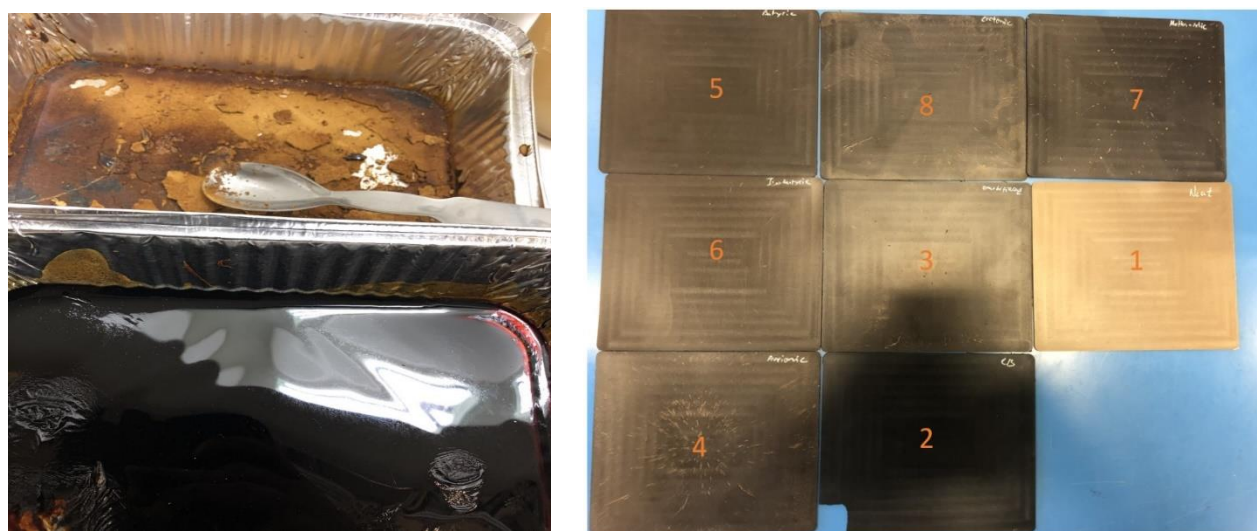
Figure 27 a and b. a: *The rubber compounds after press plate, 1 Neat, 2 CB, 3 Unmodifed, 4 Propionic, 5 Butyric, 6 Isobutyric, 7 Methacrylic and 8 Crotonic, b: Dried Propionic (brown powder) and Butyric lignin (black butter*

The conclusion of the visual inspection and dispersion of the rubber compound is presented in table 9. This was made to differentiate the dispersion and particle size of the samples. No data of the particle size were obtained. However, in order to differ the sizes, , sugar grains were used as a reference and the particle size of CB and modified lignin particles were ranked as (1, 2 ,3 and 4) With the same concept, the dispersion of the rubber compounds is ranked as "bad and good dispersion". Due to the consistency and form of ButL, IsoL and MetL, the average particle size could not be estimated. However, it was visible after drying the samples that they differed. MetL obtained larger "clumps" than butL and isoL Furthermore, ButL formed smaller clumps than IbutL.

Table 9. *Visual inspection of the rubber compounds, (forms, particle size and dispersion)*

Sample	Form	Average particle size	Dispersion
Sugar grain	Reference	2	Reference
KL	Powder	1	Bad
CB	Powder	3	Very good
ProL	Powder	1	Very bad
ButL	Butter/Elastomer	-	Good
IsoL	Butter/Elastomer	-	Good
MetL	Butter/Elastomer	-	Good
CroL	Powder	4	Bad

4. DISCUSSION

The replacement of carbon black with modified lignin had been earlier investigated by [10] D. Barana and [51] Frigerio. However, the rubber compounding and ingredients followed the same procedure as [10] Barana with some marginal adjustment. As mentioned before, the FTIR-spectra of modified lignin indicates a complete and successful modification. It is visible how the region of hydroxyl group fades out in the FTIR-spectra (figure 23.a-f). Despite the lack of theoretical mass, it was possible to further analyse the samples. Instead, the reacted anhydride per gram lignin were calculated. To a certain extent, it is reasonable to say that the obtained data in table 5 indicates a complete modification of lignin. It should be noted that that some samples after the modification were easily separated from the supernatant and others required a two-step centrifugation, which could have an impact on the final mass. Furthermore, it was reported by [58] Vila, that the crotonic lignin left 25 % of aliphatic hydroxyls and 22 % of phenolic hydroxyls unmodified and in the same conditions, esterification with butyric and isobutyric were reported to give complete esterification. It is observable in table 5 that butyric and isobutyric gave high yields which is in line with the results of [58] Vila .

As for the mechanical testing of the rubber compounds it is seen that the fully replacement of carbon black with modified lignin did not give a significantly improve the rubber material. However, the various esterification of lignin gave a significant change on the mechanical properties of the rubber compounds. As mentioned before, the obtained rheomoeter data for the lignin-based rubber compounds (unmodified and modified) in table 7 gave an indication of an increase in scorch and that lignin interfered with vulcanization, thus the delay in

crosslinking phase. This mechanism was supported by [55] Kumaran et.al and Nando [56] .However, compared to KL, the modified lignin gave a significant higher scorch and optimum cure time, especially isobutyric lignin which directly had an impact on the cure rate. Subsequently, it is possible to conclude that the esterification of lignin improves the dispersion of lignin in natural rubber. In this experiment, isobutyric lignin (which had a scorch time of 1,67 seconds) gave a good dispersion and interaction with natural rubber. The reason behind this phenomenon is unknown due to the complex structure of lignin and its end groups. However, one hypothesis could be that the esterfied lignin plays an extensive roll in decreasing the cross-link density and the number of polysulfidic cross-links. Furthermore, it is possible to see the correlation between the structure of the aldehyde (i.e configuration and double bounds/ methyl group) and the obtained data. Therefore, based on the collected rheometer data in table 6 and the analysis of the aldehyde structures it is possible to say that the configuration and double bonds of the aldehydes takes part in the vulcanisation process of the rubber compounds. This correlation and mechanism can be further analysed by a systematic investigation on the network structure of lignin-modified rubber by determining the chemical crosslink densities and varying the amount of sulfur in the rubber compound.

As mentioned before, it was also expected that the addition of lignin would have a negative impact on the tensile strength. However, as for the rheometer data, similar results were obtained for the stress-strain curves. It is noticed that the addition of ButL and IsoL gave a significant improvement of the tensile strength compared to the neat sample (reference) but to a lesser extent than carbon black. Xiao et.al [59] and Kosikova and- Gregorova [60] reported that the addition of lignin in rubber compounds caused low mechanical properties of the blends. The reason behind this was reported to be the presence of significant amounts of highly polarized hydroxyl groups. The statement is in line with the obtained data in table 7 in general. However, the lignin samples had superior rebound resilience and elongation at break compared to carbon black as mentioned above. ButL and IsoL differed from the other samples and similar to the obtained results the configuration of the aldehydes affects the mechanical properties of the rubber compounds. However, it is still unknown how the double bonds and isomer of the aldehydes affects the mechanical properties. Another hypothesis could be that the presence of double bonds and isomer decreases the impact of the polarized hydroxyls by slightly interfering with the vulcanisation in the rubber compound which is in line with the FTIR spectra of (ButL, IbutL, MetL and CrotL), where the hydroxyl group clearly fades out between 3200-3500 cm^{-1}. As for the confidence intervals in table 8 and 9, one can believe that

larger errors were obtained. However, only three samples were analysed, hence the large standard deviation

In order to assess more aspects the of rubber blends and its interaction, a visual inspection of the rubber compounds was essential. Normally, this is further analysed with scanning electron microscopy (SEM) which produce a magnified image of the rubber compound. However, in this experiment only a normal visual inspection was conducted by using a simple camera and the dispersion of the rubber compounds were compared by the "presence of undispersed corns". As stated above, butyric and isobutyric lignin gave by far best dispersion compared to the other lignin samples. No undispersed corns were visible; however, CB obtained a slightly better dispersion than isobutyric and butyric. It is interesting to see how the configuration also impacts the dispersion of the rubber compounds which is in line whit the first hypothesis above. As mentioned before, IbutL gave the highest scorch time which indicated that it interfered and dispersed well with natural rubber. In this visual inspection it is clearly seen that IbutL and ButL obtained the best dispersion of the modified samples which directly is related to the consistency and grain size of the lignins. In **1.5.2 Materials** (*Fillers:Carbon black*), the particle size of the carbon black is further discussed and its roll in compounding. Although no data for the average particle size of the different modified lignin were obtained, an estimation by visual inspection could be done. It is clearly observable in table 10 that too big or to small corns were unfavourable. However, as mentioned before ButL, IbutL and partially MetL formed a butter consistency (elastomeric materials after drying). Thus, this could be the reason why ButL and IbutL interacted and dispersed well with. This hypothesis is supported by the [9] Barana where he investigated the Hansens Solubility Parameters of the esterfied lignin samples Barana concluded that in overall, all modified lignin was at least partially miscible with natural rubber with the increasing order: crotonic lignin < propionic lignin < butyric lignin < methacrylic lignin < isobutyric lignin.

Despite the poor numbers of the mechanical properties of the rubber compounds, interesting data was obtained in overall. The successful and complete modification of the samples was a vast achievement for this experiment. It was clearly observable that the different aldehydes had an impact and played an extensive roll in the vulcanisation process. In general, it is possible to conclude that the addition of isobutyric and butyric lignin were the better choices than the other lignin samples.

Another important parameter that needs to be discussed is the bad odour of lignin. Even though the small quantities, the strong odour of lignin caused major problems when processing the samples. Furthermore, the hydrophobicity of lignin also caused difficulties while washing the equipment, acetone and other solvents were used in the cleaning part. For the odour part, a new initiative by Valmet and RISE [61] have managed to produce an odour free lignin without changing its properties. This opens the doors for the utilization of lignin in many areas.

Lignin has a potential future in the rubber industry. However, a fully replacement of carbon black is difficult. For further studies, it would be interesting to see how the mechanical properties of the rubber compounds would behave with the mixing of varying amount of lignin (i.e modified and unmodified lignin) with carbon black, for an instance (5-10, 10-5, 7,5;7,5 PHR). This would give a significant increase in scorch time, and optimum cure time than conventional carbon black. Furthermore, the elongation break would also increase. Another interesting study could be varying the pH of the lignin samples in the modification. For further research, it would be of value to further investigate the possibility of integrating a paper and pulp with rubber industry and if lignin could be use as another element in the rubber compound, namely stabilizer or antioxidant.

Various complex parameters such as dispersion, cross-linking phase and molecular structure affects the rubber compounds. In this thesis, I had difficult time to fully comprehend the parameters involved in lignin-based rubber compounding. For a better understanding, a P-NMR- 31 could be used to calculate the yield of the reaction and a scanning electron microscopy (SEM) for production of a magnified image of the rubber compound. This could give a better results and comprehension of the lignin-based rubber compound and its characteristics.

5. CONCLUSSION

In this study, the replacement of carbon black with modified lignin in rubber materials intended for tyre use, was studied. To summarize, the research question for this thesis were formulated accordingly:

- How does lignin (unmodified and modified) structure affect the mechanical properties in the rubber compound?
- How does lignin affect the cross-link and vulcanisation in the rubber compound?
- How does lignin affect the dispersion of the rubber compound?
- Which modification of lignin is more compatible with the rubber compound?

It was observable that the addition of lignin in rubber compounds did not significantly improved the mechanical properties of the rubber compound as for carbon black. However, compared to unmodified lignin, it was seen that the esterification of lignin improved the mechanical properties but to a lesser extent than carbon black. According to the rheometer curve, it was shown that the addition of lignin delayed the crosslinking phase and lignin took part in the vulcanisation process. Furthermore, interesting correlation between the configuration and double bonds of the aldehydes and the vulcanisation process were observable. It was also evident (visibly and odourwise) that choice of aldehyde affected the consistency of lignin samples and mechanical properties of the rubber compounds. The modified samples obtained different dispersion of the rubber compounds. It was possible to conclude that the modification of lignin dispersed well with natural rubber, but to a lesser extent than carbon black. It was clear that the addition of isobutyric lignin were the best choice and gave the best properties of lignin. Furthermore, the FTIR spectra of the modified lignin indicated a successful esterification.

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