TOWARDS DEVELOPMENT OF LIGNIN REINFORCED ELASTOMERIC COMPOUNDS WITH REDUCED ENERGY DISSIPATION

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Kushal Bahl

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Kushal Bahl

Dissertation

Approved:                                   Accepted:

Advisor                                  Department Chair
Dr. Sadhan C. Jana                      Dr. Robert A. Weiss

Committee Member                        Dean of the College
Dr. Avraam Isayev                      Dr. Stephen Z.D. Cheng

Committee Member                        Dean of the Graduate School
Dr. Alamgir Karim                      Dr. George R.Newkome

Committee Member
Dr. Li Jia

Committee Member
Dr. Bi-Min Zhang Newby
ABSTRACT

This research deals with development of lignin as reinforcing filler for elastomeric compounds. Lignins are naturally abundant and cost competitive wood derivatives possessing strong mechanical properties and offering reactive functional groups on their surfaces. The presence of the functional groups imparts polarity to the lignin molecules and makes them incompatible with non-polar elastomers. Also, the large particle size of lignin does not produce desired mechanical reinforcement. The present study deals with solving the outstanding issues associated with the use of lignin as fillers for polymeric compounds. In addition, the work specifically focuses on producing rubber compounds with reduced energy dissipation via partial replacement of carbon black with lignin.

The first part of this study is devoted to suppression of the polarity of lignin and achievement of compatibility with rubber matrix via modification of lignosulfonates (LS) with cyclohexylamine (CA). CA reduces the polarity of lignin via interactions originating from proton transfer and hydrogen bonding. X-ray Photoelectron Spectroscopy (XPS) confirms the attachment of CA on the surfaces of lignin. The mechanical properties of rubber compounds increase substantially along with improvement in cure properties and increase in crosslink density in the presence of LS particles modified with CA. The tensile strength and storage modulus show an increase by 45% and 41% respectively. The values of the 100% modulus and elongation at break also improve by 35% and 60% respectively.
The second part of this study exploits the non-covalent interactions between lignin and carbon black (CB) for the design of novel hybrid filler particles exhibiting lower energy loss in rubber compounds. The hybrid fillers offer unique morphology consisting of coating layers of lignin on carbon black particle aggregates. It is found that such coating layers are formed due to π-π interactions between lignin and carbon black. Raman spectroscopy and $^1$H spin-lattice relaxation times confirm π-π interactions. The hybrid fillers offer reduction of networking of carbon black particles and viscoelastic dissipation in rubber compounds without sacrificing the mechanical performance.

The third part of this study evaluates the performance of polybutadiene-\textit{g}-polypentafluorostyrene (PB-\textit{g}-PPFS) as a coupling agent for promotion of interactions between lignin and rubber and to achieve better overall reinforcing performance. The PB domains of PB-\textit{g}-PPFS are compatible with styrene-butadiene rubber (SBR) while the PPFS segments engage in arene-perfluoroarene interactions with lignin. These interactions are confirmed via UV-vis spectroscopy data. The efficacy of PB-\textit{g}-PPFS as a coupling agent is evaluated for compounds filled with lignin and lignin/carbon black hybrid fillers. The results show that the addition of PB-\textit{g}-PPFS improves the tensile strength by 33% and reduces the viscoelastic loss in filled SBR compounds by improving filler dispersion.

The results presented in this thesis demonstrate that the approaches of surface modification, exploitation of non-covalent interactions, and the use of coupling agents are effective in solving the impending issues associated with the use of lignin, the second most abundant bio-derived material, as effective reinforcing filler for polymer compounds.
DEDICATION

Dedicated to my parents - Vidhi and Mahinderpal Bahl and my brother - Varun Bahl for their everlasting love and support…..
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CHAPTER I
INTRODUCTION

The tire manufacturing industry in America uses about 3 billion pounds of petroleum based carbon black (CB) fillers every year.\(^1\) Although carbon black provides excellent mechanical and electrical properties to the rubber compounds, it is petroleum derived and it contributes adversely to the energy loss or the rolling resistance of tires, thus, reducing the fuel efficiency. Energy dissipation associated with hysteresis loss is directly related to rolling resistance of tires which is a crucial parameter to control in order to achieve greater fuel efficiency. A reduction in rolling resistance by 10% can lead to fuel savings of around 2 billion gallons (115 million tons of CO\(_2\)) per year as predicted by the Transportation Research Board.\(^2\) Thus, significant potential can be tapped to reduce the demand on the non-renewable commodity petroleum if such reduction in rolling resistance is achieved. The U.S. Energy Information Administration predicts that the foreign imports of oil in the USA will increase by 30% by the year 2030 if alternatives to petroleum based products are not identified.\(^3\) In order to derive solutions to this growing problem, it is important to develop inexpensive, easily dispersible, bio-based, and renewable alternatives to carbon black for use in tires and other applications, such that the fuel efficiency of automobiles is significantly increased. The objective of this work is to demonstrate different routes for development of these inexpensive, bio-based renewable alternatives as fillers for rubber compounds and to address some of the
existing issues that have hindered the development and commercialization of these materials.

The aim of this study was to also understand the factors that control the viscous dissipation and rolling resistance in rubber compounds as function of the nature of fillers and the host rubber molecules. Based on the understanding that took shape during the study, we also developed new hybrid fillers with unique properties and morphologies, which can reduce the rolling resistance of rubber compounds. Such hybrid fillers can partially replace carbon black in rubber compounds without detriment and can reduce hysteresis loss.

This study focused on lignin and lignin-derived filler materials. Lignin has received a lot of attention as potential candidate to replace carbon black in rubber compounds. It is a naturally occurring three-dimensional amorphous polymeric material consisting of phenyl propane units along with hydroxyl, methoxyl, carbonyl, and other substitutions. It is one of the main components of woody cell walls in plants along with cellulose and hemicellulose and hence is considered the second most abundant organic material available on earth behind cellulose. It imparts rigidity to the cell walls in plants and is also responsible for their resistance to impact, and bending and compressive deformation. The abundance of functional groups on its surfaces is one of the reasons why it has been widely studied as reinforcing fillers in plastics and rubber industries. The functional groups also provide scopes for chemical modification. Other positive contributors responsible for the widespread work on lignin in plastic and rubber composites are its abundance, cost competitiveness, good inherent mechanical properties, natural stability, and biodegradability. However, there are some issues associated with
the use of lignin as reinforcing fillers. Large particle size, the absence of structural hierarchy, genetic variability, and structural complexities are some of the issues. In addition, polarity of lignin leads to incompatibility with non-polar rubber chains and accounts for suboptimal performance.

Extensive research work was carried out on reinforcing rubber/plastics with different types of lignins.\textsuperscript{9–13} In general, it was observed that lignin by itself gives inferior reinforcement effects especially in comparison to carbon black. Hence, using lignin just as a “drop-in” replacement for carbon black is not sufficient. Note that lignin contains polar functional groups on its surfaces which do not bond well with rubber. This results in poor tensile, tear, and abrasion properties. Thus, in order to take advantage of the promising potential benefits, lignin must be either modified to suppress its polarity and to increase its compatibility with rubber chains, or used along with a coupling agent to increase the bonding with rubber. Also, the functional groups on the surfaces of lignin can be used in chemical modification, so as to optimize the properties such as mechanical reinforcement, rolling resistance, abrasion resistance, and wet traction of rubber compounds.

The primary focus of this study was to demonstrate the different routes by which lignin could be developed as reinforcing filler for polymers. The issues that have hindered the widespread use of lignin thus far were addressed in this work. In addition, several techniques were developed for improving rubber-lignin interactions and for reduction of energy dissipation. The hybrid fillers provide a way of partially replacing the carbon black with lignin.
The first approach focused on polarity of lignin and used surface modification to reduce it. Cyclohexylamine was used to modify the surfaces of lignin and to suppress the polarity of lignin by increasing the number of C-C bonds on the lignin particle surface. This led to improved compatibility with the non-polar rubber matrix resulting in improved mechanical properties and lower hysteresis loss.

Second, the issue of large particle size of lignin was addressed by exploring the non-covalent interactions existing between lignin and carbon black. Unique hybrid filler morphology was obtained due to these interactions. The morphology consisted of lignin layers coated on carbon black particle aggregates. This meant that in the rubber compound, lignin would no longer exist as a set of separate large particles but as a coating on carbon black particles. This alleviated the concerns associated with large size lignin particles. In addition, the unique hybrid particle morphology helped reduce the carbon black filler networking in rubber matrix which is responsible for greater energy dissipation and higher rolling resistance of rubber. The hybrid filler particles also retained the fractal nature of carbon black aggregates which is crucial for achieving good mechanical performance.

In the third part of this dissertation, a new approach was adopted to achieve improvements in compatibility between rubber and lignin. The compound, PB-g-PPFS was considered as a coupling agent for this purpose. The compatibility between PB chains and SBR and between PPFS domains and lignin were exploited via the non-covalent arene-perfluoroarene interactions. PPFS consists of electron-deficient benzene rings whereas lignin consists of electron-rich benzene rings due to presence of hydroxyl groups. This gives rise to a special case of $\pi-\pi$ interactions called the arene-
perfluoroarene interactions. PB-g-PPFS was shown to work well as a coupling agent for rubber compounds of lignin and lignin-carbon black hybrid fillers. The improvements in tensile properties, and dynamic mechanical properties were seen upon incorporation of PB-g-PPFS as the coupling agent.
CHAPTER II
BACKGROUND AND LITERATURE REVIEW

The survey presented in this chapter focuses on the origin, structure, and properties of lignin with special emphasis on kraft lignin and lignosulfonates. Recent literature on unmodified or modified lignin as reinforcing filler in rubber compounds is also discussed. In addition, the chapter covers the concepts and fundamentals behind rolling resistance and viscoelastic damping properties of elastomeric compounds and the material factors that are responsible for controlling it.

2.1 Lignin

Lignin (derived from Latin word “Lignum”) is one of the principal constituents of wood along with cellulose and hemicellulose. The term “Lignin” is generally associated with the lignin extracted from wood, whereas “protolignin” is used for the lignin associated with the cells. When viewed as a natural composite, lignin and hemicellulose form the matrix of wood, and cellulose fibers are present as the reinforcing agent.\(^7\) Lignin is found as a cell wall component in all vascular plants and in the stems of both arborescent angiosperms and gymnosperms.\(^14\) Its total content in the woody stems varies from 15% to 40%. Lignin performs a lot of functions in plants such as controlling the water transport through the cell wall in stems, protecting the plants by hampering enzyme penetration, acting as a UV absorber, flame retardant, and even storing of energy.\(^15\)
Lignin, in fact, is known to give the stems their well-known rigidity and impact resistance.

Since lignin in wood and plants exists as a cross-linked matrix surrounding the cellulosic fibers, its use as a macromolecular material arises from its fragments and oligomers collected after the delignification process. The amount of lignin obtained after delignification has an annual industrial output of 50 million tons. All this lignin generated after the delignification process is just used in the paper mills for energy production by combustion.\(^{16}\) Hence, using this lignin as a macromolecular material or as reinforcing filler in polymers would be a value-addition process for the byproducts of the paper industry.

2.1.1 Delignification

The process of extracting lignin from plant sources is known as delignification. Anselme Payen was the first person who discovered lignin and cellulose in its extracted form after the treatment with nitric acid and alkaline solutions.\(^{17}\) The process involves breaking down the lignocellulosic structure into its fibrous components. Since lignin exists as a crosslinked matrix in its natural form, all delignification processes cause substantial changes to the natural lignin. Hence, the extracted lignin may not resemble the lignin as it occurs in the plant. Therefore, lignins separated by two different methods cannot have the same properties. Hence one of the issues associated with use of lignin is that different sources, and different delignification methods produce different types of lignin, with properties very different from each other.\(^{18}\) The two most widely used processes for delignification are the alkaline pulping process and the sulfite pulping process.
The alkaline pulping process is also known as the kraft process. It results in the formation of alkali or thio-lignin. The liquor used for the pulping consists of sodium hydroxide and sodium sulfide along with minor amounts of other sodium salts such as sodium thiosulfate and sodium carbonate. In the kraft process, the linkages in the protolignin break due to the attack by alkali solutes and other nucleophiles.\textsuperscript{19} The breaking of ether-ether bonds in these conditions results in an increase in the concentration of hydroxyl groups. The cleavage of aryl-alkyl ether bonds increases the amount of aromatic hydroxyl groups in the lignin structure. Lignin is later separated from the kraft liquor due to its decreasing solubility as the pH is lowered. As the pH is lowered, the ionization of lignin is reduced and self-aggregation occurs. The lignin obtained by this method has relatively small quantities of ash and carbohydrates due to their solubility in water even under conditions with low pH. Any acidifying medium can be used to carry out the precipitation.\textsuperscript{20} The kraft process is a very complex delignification process which can result in different lignin structures and different yields based on varying process conditions. The use of different wood species and starting materials for this delignification method adds to the complexity of the pulping process.\textsuperscript{21}

The sulfite process for delignification uses an aqueous solution of sulfite or bisulfite salt of sodium, magnesium, or calcium to digest the wood at 140-170  \degree C. This treatment leads to breaking of linkages between the lignin and carbohydrates, scission of the carbon-oxygen bonds which help lignin form a network, and sulfonation of the lignin chain. In this process, sulfur in the form of sulfonate groups is incorporated in the lignin molecules causing the lignin to be water soluble in the extraction step. Unlike the kraft process, there are fractions of carbohydrates chemically combined with lignosulfonate. It
is difficult to separate the carbohydrates and other chemicals from the lignosulfonate since all are highly soluble in water. In spite of this, lignosulfonates are the most abundant type of lignin available.\textsuperscript{20}

2.1.2 Structure and Properties

As mentioned earlier lignin shows a lot of genetic variability and structural complexity. The structure of extracted lignin not only depends on the wood source but also on the delignification method and the conditions employed in delignification. A representative structure of kraft lignin is depicted in Figure 2.1. As seen, lignin is essentially a polyphenolic compound consisting of phenyl-propane units. A lot of carbon and oxygen based functional groups such as methoxy groups, carbonyl groups, aliphatic hydroxyl groups, are present on the surface. These functional groups are reported for one unit of phenyl-propane unit (PPU) so as to decouple the molecular weight from such data.\textsuperscript{22}

![Figure 2.1: Representative structure of kraft lignin. Re-drawn from Ref.\textsuperscript{23}](image)
Lignins are brown amorphous solids having a glass transition temperature between 70°C and 170°C depending on their structures and molecular weight.\textsuperscript{16} The information on analysis and fundamental characterization of lignin is scarce in spite of modern characterization techniques being available. One possible reason might be increased complexity of the lignosulfonate or kraft lignin. As we know, delignification involves multiple reactions with active species and may also lead to counter ions associated with the delignified molecules. In spite of some of these issues, the basic properties of lignins reported in literature to date are reproduced in Table 2.1.

Table 2.1. Properties of lignosulfonates and kraft lignins\textsuperscript{20}

<table>
<thead>
<tr>
<th>Property</th>
<th>Lignosulfonates</th>
<th>Kraft Lignin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur content</td>
<td>4-8 wt%</td>
<td>1.5-3 wt%</td>
</tr>
<tr>
<td>Sulfur type</td>
<td>Sulfonates, organic</td>
<td>Organically bound and sulfur, sulfite and sulfate</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>1000 – 15000 g/gmol</td>
<td>2500 – 39000 g/gmol</td>
</tr>
<tr>
<td>Tg</td>
<td>No Tg</td>
<td>~140 °C</td>
</tr>
<tr>
<td>Degradation</td>
<td>320 °C (carbohydrates) and 450 °C (lignin)</td>
<td>450 °C (lignin)</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in water, insoluble in organic</td>
<td>Soluble in water under basic conditions solvents</td>
</tr>
</tbody>
</table>
In addition to the properties mentioned in Table 2.1, other properties such as surface energy and water contact angle are also crucial for prediction of the wetting behavior of polymers and lignin. Lignins have surface energies in the range of 52-57 mJ/m$^2$ depending on the type of lignin. Softwood kraft lignins have a higher polar component compared to milled wood lignins since a lot of polar functional groups are introduced in its structure during the kraft pulping process. However, the contribution of the dispersive component to the total surface energy is higher than that of the polar component for all lignins. The water contact angle of lignin is also in the range of 46-52 degrees. This indicates that water partially wets the lignin surface.\textsuperscript{24}

2.2 Lignin as fillers in elastomeric compounds

Lignins are considered promising macromolecular materials due to a variety of reasons e.g. ready availability, cost effectiveness, presence of large number of functional groups which enable chemical modification, and biodegradability as claimed by some researchers.\textsuperscript{8} Along with these advantages, another key reason for the development of lignin as an additive for preparation of polymer composites is its structural versatility. It has polar functional groups capable of forming hydrogen bonds which can dictate the interfacial interactions of ensuing materials. On the other hand, lignin has ether linkages, aromatic rings, and aliphatic sequences which can contribute to hydrophobic properties.\textsuperscript{16} Along with some key benefits, some of the main disadvantages of using lignin are its genetic variability and structural complexity which makes it difficult to predict mechanisms of interaction of lignin when used as a reinforcing agent in polymers. Several researchers have explored the idea of using lignin as reinforcing fillers in elastomers. Some key studies are summarized in Table 2.2.
Table 2.2. Summary of lignin reinforced rubber compounds

<table>
<thead>
<tr>
<th>Rubber /Composite</th>
<th>Amount and type of lignin</th>
<th>Curing behavior</th>
<th>Mechanical properties</th>
<th>Additional comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR*/sulfur-free lignin</td>
<td>Up to 30 phr, MW = 2000 g/gmol, PDI = 1.2</td>
<td>Slight reduction in torque, scorch time, and cure time. Possible interaction of lignin with vulcanization system</td>
<td>Improvement in all tensile properties. Better thermal stability (by 7 °C) upon addition of lignin</td>
<td>Good properties due to lower mass and polydispersity resulting in good miscibility in NR</td>
<td>Kosikova et al.\textsuperscript{25}</td>
</tr>
<tr>
<td>NR/Lignosulfonates and SBR\textsuperscript{/}Lignosulfonates</td>
<td>Up to 40 phr of Ca, Na and Mg lignosulfonate</td>
<td>Reduction in scorch time, optimum cure time and XLD\textsuperscript{**}</td>
<td>Improvement in tensile strength and elongation at break. More pronounced for NR system</td>
<td>Dynamic mechanical properties unchanged. Better mechanical properties obtained by using plasticizer</td>
<td>Alexy et al.\textsuperscript{11}</td>
</tr>
<tr>
<td>Nitrile rubber/Kraft Lignin</td>
<td>50 phr of unmodified and BPO-modified lignin</td>
<td>Inefficient sulfur vulcanization due to acidic nature of lignin</td>
<td>Reduction in tensile strength and elongation at break as compared to control compound</td>
<td>Non-reinforcing effect of lignin seen. 100% modulus and hardness increased due to higher stiffness of lignin</td>
<td>Setua et al.\textsuperscript{26}</td>
</tr>
<tr>
<td>SBR/sulfur-free lignin</td>
<td>Up to 60 phr (Size of lignin particles = 100nm)</td>
<td>Scorch time reduced, optimum cure time increased beyond 20 phr. Lignin interacts with vulcanization system</td>
<td>All mechanical properties including hardness increased.</td>
<td>Lignin shown to be an active filler (positive Wolff activity coefficient)</td>
<td>Kosikova et al\textsuperscript{12}</td>
</tr>
<tr>
<td>SBR/BR/lignosulfonate/CB or lignosulfonate/silica</td>
<td>Up to 15 phr esterified/silylated lignin</td>
<td>Higher torque increment along with lower curing time.</td>
<td>G’ and stiffness comparable to carbon black obtained using esterified lignin</td>
<td>50 phr of CB or silica used along with 15 phr of lignin. Lower tan δ obtained with functionalized lignin.</td>
<td>Benko et al\textsuperscript{27}</td>
</tr>
<tr>
<td>Rubber/Composite</td>
<td>Amount and type of lignin</td>
<td>Curing behavior</td>
<td>Mechanical properties</td>
<td>Additional comments</td>
<td>Reference</td>
</tr>
<tr>
<td>------------------</td>
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<td>-------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>NR/sodium lignosulfonate</td>
<td>Up to 20 phr</td>
<td>Marginal reduction in scorch time. Cure time almost constant. XLD reduced</td>
<td>Tensile strength and modulus decreased, elongation at break increased on adding lignin</td>
<td>Lignin masks the vulcanization sites. All properties showed improvement after aging.</td>
<td>Kumaran. et al 28</td>
</tr>
<tr>
<td>NR/sodalignin, NR/thiolignin</td>
<td>Up to 20 phr, thiolignin – up to 40 phr</td>
<td>Shorter cure times, higher curing rate and higher torque</td>
<td>Reduction in tensile strength and elongation at break, better thermal stability for thiolignin compounds</td>
<td>Thiolignin compounds have higher electrical permittivity which increases orientation polarization</td>
<td>Botros et al. 13</td>
</tr>
<tr>
<td>NR/sodium lignosulfonate</td>
<td>Up to 20 phr</td>
<td>Addition of lignin increased the structural complexity and caused inefficient sulfur based vulcanization.</td>
<td>Lower XLD, tensile strength, and hardness. Lignin inhibited strain induced crystallization</td>
<td>Aging gives improvement in all properties since further crosslinking takes place of the previously masked sites</td>
<td>Kumaran et al. 29</td>
</tr>
<tr>
<td>NR/oxidized alkali lignin co-precipitate</td>
<td>Up to 77 volume %</td>
<td>Delayed vulcanization since lignin reacts with sulfur to form H2S</td>
<td>Better tensile strength, resilience, strain at break. Inferior hardness as compared to CB</td>
<td>Metallic oxides of lead, copper, or bismuth used to control H2S concentration during vulcanization</td>
<td>Griffith and MacGregor 30</td>
</tr>
<tr>
<td>Nitrile rubber/Carbon black/lignin</td>
<td>CB - 50phr, Lignin – 10phr</td>
<td>Lignin blocks active sites on main chain, reduces XLD, scorch time and torque reduced on adding lignin</td>
<td>Tensile strength and resilience decreased, hardness and abrasion loss increased</td>
<td>Lignin gets adsorbed on ZnO surface and hinders formation of sulphurating complexes</td>
<td>Nando et al 31</td>
</tr>
</tbody>
</table>

*NR = Natural Rubber, *SBR = Styrene-Butadiene rubber, **XLD = Crosslink density
From Table 2.2 above, it is clear that lignin shows tremendous promise as reinforcing filler for rubber compounds. Some researchers have reported considerable improvements in mechanical and curing properties. Some other researchers reported deterioration of the properties in the presence of lignin. A few interesting observations are drawn from the studies on the use of lignin in rubber compounds, as summarized below:

- Lignin reduces scorch time during sulfur curing since the hydroxyl groups present on its surface accelerate the vulcanization process.\textsuperscript{25,28}

- Addition of lignin in rubber increased its thermal stability since the phenolic groups in lignin act as radical scavengers and retard the reaction induced by oxygen and oxygen based radicals.\textsuperscript{25,32}

- Upon modification of lignin via esterification or silylation routes, or using coupling agent, it is possible to get a significant increase in the storage modulus along with reduced tan δ (lower rolling resistance). This is possible by improving the polymer-filler interactions by modifying the lignin so that it can covalently bond with the rubber.\textsuperscript{27}

- Lignin causes inefficient vulcanization by blocking sites on rubber main chain and also by getting adsorbed on the surface of curatives and interacting with them due to its polar nature.\textsuperscript{28,31} Inefficient vulcanization also occurs because of higher zinc and hydrogen sulfide formation which dissolves in rubber to retard curing.\textsuperscript{26,30} It basically hinders the formation of sulfurating complexes which are formed during accelerated sulfur vulcanization.\textsuperscript{31}

- The inefficient vulcanization caused by lignin, results in structural complexity and reduction in crosslink density and causes the stiffness and elasticity to go down hence
affecting the mechanical and rheological properties. Higher amounts of sulfur and accelerator can be used to compensate for the inefficient vulcanization and to restore the reduction of crosslink density.

An important source of variability in mechanical properties of lignin-based rubber compounds is the sulfur to accelerator ratio ($\phi$). The sulfur to accelerator ratio determines the type of vulcanization system. This, in turn, controls the length and the distribution of crosslink structures.\textsuperscript{33} In general, the crosslink density\textsuperscript{34,35} and the torque\textsuperscript{36} decreases with an increase of $\phi$. The cure time generally becomes longer with a reduction of the accelerator concentration.\textsuperscript{37} Accordingly, the mechanical properties and rheological behavior are strong functions of $\phi$. This will be studied in detail in Chapter III.

In view of the prior research work surveyed above, it can be inferred that in order to develop lignin as a reinforcing filler for rubber compounds, it is imperative to understand its structure, mechanism of dispersion, and its surface behavior with other compounds. For example, its polar nature and the presence of a large number of functional groups can be disadvantageous for rubber formulations where polar curatives and non-polar rubber are routinely used. In contrast, if exact mechanisms of dispersion and reinforcement are understood, the functional groups on lignin particle surfaces can be functionally modified to improve interactions with carbon black or rubber in the compound. Another approach is to use a coupling agent to bind the lignin to the rubber. In view of the issues mentioned above, it is not sufficient to use lignin simply as a “drop in” replacement for carbon black or other fillers, such as silica, widely used in rubber industry. It is necessary to modify the lignin or to make use of its unique surface properties to exploit the covalent or non-covalent interactions with rubber, filler, or other materials in order to enhance the
mechanical properties and to obtain desired improvements in viscoelastic damping properties.

2.3 Rolling resistance of elastomeric tire compounds

W.M. Hess\textsuperscript{38} defined rolling resistance as “the mechanical energy converted to heat when the tire moved for a unit distance over the road surface”. The mechanical energy is supplied by the engine to the tire in order to maintain the speed. Rolling resistance has received considerable attention from researchers after the oil embargo in the 1970s prompted fuel prices to go up. Since then, a lot of research has been undertaken with focus on reduction of rolling resistance of tires and improvement of the fuel efficiency of cars. Different approaches are employed to reduce the rolling resistance in tires viz. tire construction and dimensions, wheel alignment, inflation and load pressures, temperatures, steering and torque inputs, materials employed, to name a few.\textsuperscript{39} In this research, we are mostly concerned with the material aspects of rolling resistance. For example, what factors of the materials are responsible for determining the rolling resistance of tires. Before we discuss relevant material properties, we first stress on the concept of rolling resistance.

Rolling losses occur when a pneumatic tire continuously deforms and recovers during rotation under the vehicle load. This process leads to dissipation of energy. Rolling resistance encompasses all the tire energy losses under operation. Energy losses of different natures and mechanisms are included in rolling resistance. The four important energy losses associated with the rolling of tire are:\textsuperscript{40}

1. Hysteretic losses within the tire
2. Inertial distortion of the tire
3. Windage losses

4. Friction developed between the tire and the road

Out of the ones mentioned above, hysteretic losses arising from deformation of rubber have the largest contribution to tire rolling resistance.\textsuperscript{41} Sakhnovski et al.\textsuperscript{42} showed that the rolling resistance reduces significantly when the compounds with low hysteresis are used. For example, using a natural rubber and butyl rubber blend as compared to oil extended SBR. The inertial distortions contribute at very high speeds whereas windage losses are dependent on the size of the tire. The frictional losses\textsuperscript{43}, on the other hand, become more dominant under abrasive road conditions. Hence, hysteretic losses will be the subject of our discussion here.

2.3.1 Hysteretic losses

Hysteretic losses are related to the viscoelasticity of the tire compounds. When the load is removed from a viscoelastic material, it recovers some of the stored energy whereas the rest is converted to heat. Each cycle of deformation and recovery results in a mechanical energy loss known as hysteresis.\textsuperscript{39} Hysteresis is therefore relatively independent of the speed since the viscoelastic properties of tire components are independent of the frequency in range of rolling of tires.

Hysteretic losses can be divided into two components viz. energy loss per unit volume under constant strain and energy loss per unit volume under constant stress. The two components can be expressed as follows:\textsuperscript{40}

\[
W \text{ @ constant strain} = \pi \varepsilon_0^2 E''
\]  
\[
W \text{ @ constant stress} = \pi \sigma_0^2 E'' / |E*|^2
\]  

(2.1)  

(2.2)
In equations (2.1) and (2.2), $\varepsilon_0$ and $\sigma_0$ are amplitude of sinusoidal strain and stress cycles respectively, $E''$ is the loss modulus and $|E^*|$ is the absolute value of complex modulus. The energy loss under constant strain represents the deformation due to bending of the tire. The energy loss under constant stress represents the deformation due to compressive effect of the vehicle load. The tread is subjected to both these types of deformations as it passes through the contact patch with the road. Hence, based on equations (2.1) and (2.2) we also infer that the measurement of dynamic properties enables characterization of rolling resistance in tire compounds as it simulates the operating conditions of the tires effectively.\(^{40}\)

Since hysteresis is related to the viscoelastic character of the materials, changes in material formulations can directly affect the rolling resistance. The biggest contributor to hysteresis of tire is the tread component. This is because the tire meets the surface of the road via the tread component.\(^{44}\) Hence, the selection of materials for tread component is extremely important. Rubber and fillers are two most important materials controlling hysteresis and rolling resistance in tread compounds since they account for 40-50% and 30-40% by tread volume and weight of tread component respectively.\(^{45}\) Generally, synthetic rubbers produce higher hysteresis compared to natural rubbers. On the other hand, the particle size, surface topology, dispersion, and adhesion of fillers largely determine its rolling resistance contributions. Carbon black and silica are two of the most widely used fillers for tread compounds of tires. Silica modified with silane coupling agent is known to give lower rolling resistance and better traction compared to carbon black. However, carbon black gives excellent reinforcement of the rubber vulcanizates. Hence, both these fillers are used together with silica to replace more than one-third of
the carbon black in the tread. The effect of the filler characteristics on the overall reinforcement and tire performance will be elucidated in the forthcoming sections.

2.3.2 Measurement of rolling resistance

It is difficult to measure the rolling resistance outdoors under operating conditions of automobiles. Hence, its measurement is carried out using indoor test machines which can simulate operating conditions of an actual automobile. One such instrument is a Schenck dynamometer which measures the energy loss for a range of deflections and inflation pressures. The hysteretic losses can be estimated from the viscoelastic properties of the tires such as loss modulus and tan δ which are measured using a dynamic viscoelastometer which employs strain conditions similar to the ones during operation. Rolling resistance is ideally reported as the rolling resistance coefficient (RRC) obtained by dividing the rolling resistance by the wheel load. The standard tests for measuring rolling resistance in order to calculate RRC are given by the Society of Automotive Engineers (SAE). Procedures J1269 and J2452 are both laboratory procedures which employ a tire as a sample specimen. The main difference between the two methods is that J1269 does the testing at a speed of 50 mph whereas J2452 employs a range of speeds. The standard tests allow reliable comparison between tires.

The above described methods involve the use of a tire as a specimen. It is difficult to prepare tire samples in laboratories for evaluation of materials for tire treads since vulcanization and molding of tire involves a lot of other components and processes. Hence, in order to evaluate the rubber compounds for rolling losses, the use of vulcanized specimen and measurement of dynamic properties are much more convenient. Dynamic properties give an estimate of the viscoelasticity of the compounds which is directly
related to hysteresis as mentioned above. Several research groups\textsuperscript{42,46} have shown that the rolling loss can be directly related to storage modulus (\(E'\)), loss modulus (\(E''\)), and tan \(\delta\). However, as compared to other viscoelastic parameters, tan \(\delta\) is known to give the best relationship with rolling loss.\textsuperscript{47}

The value of tan \(\delta\) at 50-80 °C is known to correlate well with the rolling resistance whereas tan \(\delta\) at 0 °C correlates well with the wet skid resistance and traction. Lower the value of tan \(\delta\) at high temperatures, lower is the viscoelastic loss and lower is the rolling resistance. On the other hand, higher the value of tan \(\delta\) at lower temperatures, better is the wet skid resistance.\textsuperscript{48} This dynamic testing can be done in shear mode using a Rubber Process Analyzer (RPA) or in tension mode using a Dynamic Mechanical Analyzer (DMA). Some studies using a non-resonant dynamic tester have also been reported. It employs Goodrich Flexometer cylinders as the test specimens.\textsuperscript{38} Another novel method for measurement of rolling resistance in elastomeric compounds was invented by Gent et al.\textsuperscript{49,50} The set-up consists of a rigid cylinder which rolls back and forth on a rubber substrate as a result of swinging of a pendulum arm. This device estimates the viscoelastic damping properties by measuring the rate at which the amplitude of pendulum motion of the cylinder decreases. This technique provides a direct estimation of the rolling resistance by measuring the rate of dampening of oscillations. In the current study, the rolling resistance is directly estimated by measuring the tan \(\delta\) values of the compounds using a DMA.

2.3.3 Approaches to produce compounds with low rolling resistance

Different research groups have adopted different approaches to produce tire compounds with reduced rolling resistance. The approaches include synthesizing new
polymers with reduced hysteresis, modification of polymer matrix, modification of fillers, use of hybrid fillers to name a few. Some of the important and relevant work is summarized in Table 2.3:

Table 2.3. Studies on preparation of low rolling resistance rubber compounds.

<table>
<thead>
<tr>
<th>Polymer/ Filler</th>
<th>Filler details</th>
<th>Characterization technique</th>
<th>Dynamic properties</th>
<th>Additional comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/silica</td>
<td>Up to 30 phr loading. Silica dry mixing compared with silica/NR masterbatch</td>
<td>tan δ at 60 ºC used to characterize rolling resistance. Freq = 10 Hz, dynamic strain = 0.1% using DMTA</td>
<td>Lower tan δ for masterbatched silica since it gives better dispersion of silica in NR matrix. Also, on adding coupling agent tan delta reduces further due to improved polymer-filler interaction</td>
<td>Masterbatched silica gave better mechanical, thermal, and aging properties compared with conventional mixing method. Cure retardation of silica also suppressed by masterbatch preparation</td>
<td>Prasertsri et al.⁵¹</td>
</tr>
<tr>
<td>SBR/silica composite</td>
<td>Up to 40 phr. Modified and unmodified silica were compared with CB</td>
<td>Freq = 10 Hz, dynamic strain = 0.5% using DMTA. Work of adhesion was shown to correlate with rolling resistance</td>
<td>Thermodynamic predictors calculated from surface energy. tan δ correlates well with work of adhesion. Lower the adhesion between filler-rubber, higher tan δ</td>
<td>Good correlation obtained between thermodynamic predictors and dynamic properties. Hence, surface energy is important</td>
<td>Stockelhuber et al.⁵²</td>
</tr>
<tr>
<td>Isoprene/ butadiene/ styrene</td>
<td>Terpolymers synthesized to give better tire performance</td>
<td>tan δ @ -20 ºC – wear tan δ @ -0 ºC – traction tan δ @ 60 ºC – rolling resistance</td>
<td>Terpolymers synthesized to give two Tgs, one low and one high for tread wear and traction respectively</td>
<td>Lower the chain end concentration of polymer, lower is RR. Also, tan δ increases with styrene content</td>
<td>Halasa et al.⁴⁸</td>
</tr>
</tbody>
</table>
Table 2.3. Continued

<table>
<thead>
<tr>
<th>Polymer/ Filler</th>
<th>Filler details</th>
<th>Characterization technique</th>
<th>Dynamic properties</th>
<th>Additional comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR/CB/ nanoclay and NR/CB/ CNF ternary composite</td>
<td>50 phr CB, 4-6 phr CNF or nanoclay. Synergistic behavior expected to improve tire performance</td>
<td>Frequency= 1 Hz, strain = 0.01% using a DMTA. Tan δ at 60 ºC related to RR and at 0 ºC related to wet traction</td>
<td>Lower tan δ and higher G’ with addition of nanofillers in addition to CB. Better balance of wet traction and RR with nanoclay</td>
<td>Better tire performance and mechanical properties obtained due to nanofiller-black synergy due to formation of nanochannels and nanoblock morphology</td>
<td>Bhattacharya et al.53</td>
</tr>
<tr>
<td>NR/SBR/I R/BR with TESPT and precipitate silica</td>
<td>60 phr silica. More emphasis on effect of rubber matrix</td>
<td>DMA used with frequencies ranging from 1-100 Hz</td>
<td>Silica filled SBR showed highest tan δ since it had lowest bound rubber and hence higher filler-filler networks</td>
<td>Stronger filler polymer network lowers strain dependency of tan delta</td>
<td>Movahed et al.54</td>
</tr>
<tr>
<td>NR/silica modified with cyclohexyl amine (CA)</td>
<td>Up to 50 phr. CA modification of silica compared with Si69 modification</td>
<td>DMA used with frequency of 11 Hz</td>
<td>Lower tan delta and better traction obtained with CA modified NR as compared to Si69 modified NR</td>
<td>Highest XLD and lower filler networking obtained by using CA. They are responsible for better dynamic properties</td>
<td>Liu et al.55</td>
</tr>
</tbody>
</table>

From Table 2.3, it is clear that the reduction in rolling resistance of tire compounds has received a lot of attention in the recent past due to the emphasis on energy savings. Measurement of tan δ is the most common method for characterizing rolling losses. Also, a lot of research has been conducted on silica and its modification since it gives lower rolling resistance compared to carbon black. Some of the key approaches and concepts behind development of low rolling resistance materials are summarized below:
• Better dispersion and smaller size of filler particles is crucial for increase of polymer-filler contact and hence for reduction of dissipation. Also, it is essential to reduce the surface polarity of fillers so as to match the surface energy of diene rubbers in order to improve their compatibility.

• The performance of filler particles in rubber compounds can be inferred based on their surface energy. The filler surface energy and rubber surface energy can be used to calculate the thermodynamic predictors such as work of adhesion, which help correlate rolling resistance to filler properties. This is extremely helpful since it eliminates the need for preparation of large number of samples and testing on a macro scale.

• The polymer matrix contribution to the bulk properties is also crucial. This contribution can be varied to suit the requirements by mixing rubbers of low $T_g$ with rubber of high $T_g$ rubber in order to achieve optimum wear, traction, and rolling resistance properties.

• In addition to conventional fillers, several nano-fillers can be used to develop optimum tire compounds. The balance in properties of such systems is obtained by the synergistic effects and unique morphologies of the hybrid system.

• One of the most important parameters to control rolling resistance is filler-filler and filler-polymer interactions. Stronger polymer-filler interactions and lower filler agglomeration is important to achieve good balance of tire properties.

2.4 Reinforcement of elastomers

Reinforcement is broadly defined as the modification of the viscoelastic and failure properties of the rubber by a filler to produce intended favorable results.\textsuperscript{56} Effective
reinforcement requires composites to have at least two functional elements. In this literature survey, we consider the elastomer matrix and the filler to play such two elements. The meaning of the term “reinforcement” is very different for elastomers and conventional thermoplastics. Since most thermoplastics are used within their elastic limit i.e. below 10% strain, their elastic behavior is considered more important than their viscoelastic behavior. However, for elastomers, the situation is very different. The performance strain range for rubber materials is considerably higher compared to thermoplastics. Hence, the viscoelastic character controls the rubber performance. This is also the reason why for rubbers, the 100% or 200% modulus is more important than the tensile modulus. Hence, the role played by fillers in reinforcing rubbers and the balance of properties obtained as a result, is very different from the role of fillers in thermoplastics.\(^{57}\)

For tires, the conventional definition of fillers does not hold true. Filler is not used in tire compounds just to increase the volume and to reduce cost. It is also not used just as a reinforcing agent to increase modulus and tensile strength but in fact it should be able to operate as a material to control functional properties of the tire. The filler takes an equally important role alongside the polymer matrix as the material which determines the performance of the tire. Fillers are an extremely crucial component in tires as its type, loading, morphology, and interactions control hysteresis, wet friction, and abrasion resistance.\(^ {58}\)

The controlling factors for filler-induced reinforcement in elastomers are the following interactions - polymer-polymer, filler-polymer, and filler-filler. The important
aspects on which interactions depend are - filler particle size and surface area, structure, surface activity, and surface energy.

2.4.1 Effect of filler particle size and surface area

The most important filler parameter that affects reinforcement is the average particle size. Generally, fillers with particle size > $10^3$ nm do not successfully reinforce rubber and instead may even have detrimental effects on rubber properties. Such fillers increase the compound viscosity and modulus by hydrodynamic effects. Keeping all other factors the same, reinforcement is generally obtained for fillers with particle sizes less than 100 nm. This phenomenon is depicted in Figure 2.2. The reason behind this can be best understood if we take into account the dimension of the filler relative to the polymer chain dimensions. A random coil conformation has a relevant dimension of 50 nm.\textsuperscript{59} Hence, for fillers to be able to successfully reinforce the polymer, their sizes should be comparable to that of the polymer chain. Otherwise, the inclusion of filler particles increases the distance between the polymer chains and produces weak spots in the compound which are susceptible to failure easily.
A more relevant and easy to measure aspect of filler is its surface area. It is closely related to the particle size of the filler. Coarser particles have surface area of less than 1 m²/g whereas certain grades of carbon black and silica have surface areas between 120 – 400 m²/g. The surface area of the filler determines the effective contact area between the filler and the rubber matrix. The higher the contact area better is the reinforcement.

2.4.2 Effect of structure of filler

The primary particles of carbon black do not exist as individual particles. Multiple primary particles are fused together to form the three dimensional branched aggregates. The spatial complexity of carbon black increases with the number of particles. This spatial complexity is known as the “structure” of the filler. It is generally agreed that
higher is the spatial complexity of the aggregate, the higher the structure, and the higher is its ability to reinforce the rubber. Similar particle structures exist for silica with the primary particles linked by chemical bonds to form the aggregates. However, these silica aggregates are strong and do not break down during mixing. They form loose agglomerates due to hydrogen bonding. The “structure” of filler particles is inferred from its void volume.60,61

2.4.3 Effect of surface activity and surface energy of fillers

The rubber-filler interactions, which control the reinforcement of rubber, depend on the surface activity of the fillers. Chemically, surface activity is related to different chemical groups present on the filler surfaces. The surface energy, also strong functions of the chemical nature of the surface groups, determines the energy and the capacity of adsorption. In short, surface activity encompasses a wide range of interactions from van der Waals forces to specific chemical interactions. The presence of oxygen based polar functional groups on the surfaces of the filler leads to higher order interactions with polar rubbers, for example, butyl rubber.59 However, these polar groups on the surfaces do not help in reinforcing conventional hydrocarbon rubbers such as NR or SBR. Thus, in order to increase the interactions between polar fillers and non-polar elastomers, coupling agents have to be added which act as chemical promoters.

The surface activity concept can be explained using the surface energy of the filler particles. For filler-elastomer systems in which no chemical reaction is involved, surface energies determine the interactions between filler and the matrix. It is comprised of cohesive forces such as dispersive, polar, acid-base interactions, and hydrogen bonding.
In general, surface energy ($\gamma^T$) consists of two components viz. dispersive component ($\gamma^d$) and polar component ($\gamma^p$), as presented in equation 2.3

$$\gamma^T = \gamma^d + \gamma^p$$  (2.3)

The conventional elastomers used are either non-polar or they have very low-polarity due to which the interactions between the polymer and the filler are determined by the dispersive component of the surface energy. The dispersive component of surface energy is obtained from the adsorption energies of different standard alkanes on the surface via inverse gas chromatography (IGC). Good filler-polymer interactions and stable dispersions are attained under the following conditions – (1) the surface energy characteristics of filler and matrix are close to each other, (2) the adhesion energies via hydrogen bonding or acid base interactions are high, such that they make the surface energy differences between the filler and matrix irrelevant.\textsuperscript{58}

The significance of the above mentioned concepts will be further elucidated by considering examples of elastomers filled with carbon black and silica, two fillers with demonstrated, significant reinforcing capabilities.

2.5 Mechanism of reinforcement of carbon black in elastomers

The reinforcing effect of carbon black though discovered in early 20\textsuperscript{th} century, became a subject of scientific interest only in 1940s due to the growing use of rubbers in automotive industry and tires. It is the most widely used filler in the rubber industry demonstrating excellent reinforcing behavior. Approximately about 20-30 vol\% of carbon black is used in rubber compounds to give balanced and optimum properties. Carbon black addition in elastomers results in a phenomenal increase in ultimate tensile
properties such as tensile strength and elongation at break. It also results in pronounced
increase in abrasion resistance, elastic modulus, and storage modulus beyond the increase
predicted by Einstein-Guth and Gold theory.\textsuperscript{60,62} This excellent reinforcement is obtained
due to rubber-filler interactions which further enhance the hydrodynamic effects. The
reasons for good rubber-filler interactions from a filler property point of view are
described below.

Carbon black consists of primary particles which are around 10-90 nm in size. These
primary particles come together to form clusters known as aggregates. Several aggregates
together form agglomerates which are weak and break down due to shear in processing
flows. The smallest reinforcing element of carbon black is an aggregate, as break up of an
aggregate into primary particles does not occur due to strong cohesive forces holding the
primary particles.\textsuperscript{59} The small size of the aggregates and the primary particles produce
large surface area potential for interactions with the rubber. The smaller the particle size,
the higher is the surface area available for adsorption of polymer chains. Consequently,
the higher are the interactions and the stronger is the reinforcing character.

The number of primary particles in the aggregates determines the spatial complexity
and the intricacy of the aggregates. This spatial complexity is known as the structure of
carbon black. The higher the structure, greater is the reinforcing behavior. The aggregates
becomes more voluminous and open\textsuperscript{63} with an increase in the number of particles
forming the aggregate. Accordingly, more filler area is available to occlude the polymer
from undergoing bulk deformation. Consequently, the value of modulus and other
fracture properties increases with increase in the reinforcing capability of the aggregate.
The occluded rubber in the aggregates is known as bound rubber.
The schematic structure and surface functional groups of carbon black are depicted in Figure 2.3. As seen in Figure 2.3, the rubber grade carbon black consists of small fractions of oxygen containing functional groups such as carboxyl, hydroxyl, phenols, quinones, and ketones. It has been shown that although the oxygen-based functional groups are responsible for higher order interactions in polar elastomers, they do not play a role in reinforcing conventional non-polar elastomers such as SBR or NR.\textsuperscript{59} Hence, the good filler-rubber interactions are not a result of chemical reactions between the functional groups on the rubber surface and the carbon black surface, but are in fact of physical nature.

![Figure 2.3: Schematic showing chemical groups in particles of carbon black (Reprinted with permission from Ref.\textsuperscript{59})]

From the surface energy perspective, carbon black particles have very high dispersive component and a comparatively low polar component. This high dispersive component
helps the carbon black to disperse well in the rubber and generate large number of sites for interactions between rubber chains and carbon black particles. On the other hand, the low polar component manifests itself in the form of low filler network strength and higher compatibility with conventional non polar rubbers. This weak filler network, however, breaks easily under high strains resulting in dissipation of energy.

The strong reinforcement of rubber by carbon black is a result of favorable filler characteristics of carbon black which result in filler-rubber interactions. The carbon black-rubber interactions are primarily derived from the mobile adsorption of hydrocarbon chains on the surfaces of carbon black particles.\textsuperscript{61} The adsorption sites on carbon black particle surfaces have low energy which results in weak interaction forces, such as London forces, or van der Waal’s forces between the filler and rubber. However, the large number of such sites has a cumulative effect on the reinforcement behavior of carbon black.\textsuperscript{59}

An important ramification of the existence of carbon black-rubber interactions is bound rubber. Bound rubber fills the void spaces between carbon black aggregates.\textsuperscript{64} Due to strong interactions existing between the bound rubber and carbon black, the fraction of bound rubber is inextractable by a solvent of the rubber. Also, since this rubber occupies the void spaces between the aggregates, it is shielded from external deformation and acts as a part of the filler rather than the matrix which is deformable. Hence, this enhances the effective volume of the filler in the matrix resulting in an increase in modulus and other properties.\textsuperscript{60}
2.6 Mechanism of reinforcement by silica in elastomers

Although not directly relevant for this work, this section discusses prior work on reinforcement of rubber by silica. A number of ideas from rubber-silica work were used in this study. One example is the use of cyclohexylamine for treatment of lignin and is discussed in Chapter IV. The driving force for the development of alternative filler for tire compounds is the need for tires with lower rolling resistance. For this purpose, silane treated silica started receiving a lot of attention in the 1980s.

In many ways, silica also demonstrates fractal morphology like carbon black, but its primary particles are linked by chemical bonds to form a “pearl necklace” structure. The dimension of the aggregates is in the range of 50-500 nm which is in correlation with polymer random coil dimensions. Keeping the reinforcing capabilities the same, silica generates higher surface area than carbon black and also has higher specific gravity. The starting material for manufacture of precipitated silica is sand and the process for silica manufacture is a lot more environmentally friendly than carbon black which works in silica’s favor.

The surface functional groups of silica are depicted in Figure 2.4. It is seen that silica particle surfaces contain silanol and siloxane groups which readily form hydrogen bonds with each other to produce a silica particle network throughout the rubber matrix. These strong inter-particle interactions lead to dispersability issues in the rubber. Also, the oxygen rich surface of silica is responsible for adsorbing large quantities of water which affects the curing and rheological properties of silica-filled rubber compounds.
The presence of oxygen containing functional groups on the surface affects the surface energy of silica. Silica has low dispersive component and a high polar component of surface energy. Due to its polar character and low dispersive component of surface energy, it shows poor compatibility with conventional non-polar elastomers. Also, due to its tendency to form hydrogen bonds, it forms filler particle networks in the matrix which are detrimental to reinforcement. Due to this, in order to use silica as filler in diene elastomers, its surface modification is crucial to promote dispersion by reducing inter-particle networks and enhancing its interaction with rubber.

One of the coupling agents widely used to address the above mentioned issues is bis(triethoxysilylpropyl) tetrasulfane (TESPT). TESPT reacts with silanol groups on the silica surface on one side, and forms covalent bond with the rubber chains on the other side i.e. via the tetrasulfane moiety. It interacts with the sulfur based vulcanization system to eventually form covalent bonds with rubber. Hence, adding TESPT promotes rubber-filler interactions which eventually help reduce the particle networks. TESPT reacts with the silanol groups on the silica surface to make it more hydrophobic and more compatible.
with the rubber. The molecular formula of TESPT is \((\text{C}_2\text{H}_5\text{O})_3\text{-Si-}(\text{CH}_2)_3\text{-S}_4(\text{CH}_2)_3\text{-Si-}(\text{OC}_2\text{H}_5)_3\).\(^{67}\)

Thus, adding TESPT along with silica results in the formation of bound rubber via chemical linkages between the silica particles and the rubber matrix. This bound rubber significantly enhances the reinforcement of rubber by giving higher value of complex modulus at high strain and reduced tan \(\delta\) value.

Since our study essentially focuses on the dynamic properties such as storage modulus, loss modulus, tan \(\delta\), and hysteresis of filler rubber compounds, it is essential to cover the effect of conventional fillers on the same set of properties. The following section describes the effect of carbon black and silica on the dynamic properties of compounds while focusing on the filler characteristics which dictate the interactions between the filler particles and rubber.

2.7 Effect of fillers on the dynamic viscoelastic properties of elastomers

It is imperative to study the effect of filler characteristics on the dynamic properties of elastomers especially with respect to tire technology. Parts made out of elastomers in tires undergo dynamic deformation and hence some level of optimum dynamic performance is required from the materials. As a result, to develop new materials for tire industry, it is essential to study the mechanisms of dynamic reinforcement in order to develop an understanding of what is exactly needed. Some typical dynamic functions such as storage modulus, loss modulus, and tan \(\delta\) are considered in this section. The dynamic moduli are represented as \(G’\) and \(G”\) when measured in shear mode and as \(E’\) and \(E”\) when measured in tension mode. The variation of these parameters is studied with changing temperature.
and strain for fillers with different loadings, different structures, and different surface activities. In order to discuss the dynamic reinforcement mechanisms, conventional fillers such as carbon black and silica are considered in conjunction with rubber.

The factors which influence the dynamic properties of filled rubber vulcanizates are presented below:

(a) **Rubber network properties**: This contribution arises from the crosslink density and the inherent elastic nature of the polymer matrix.

(b) **Hydrodynamic effect**: Introducing stiffer filler particles in the rubber phase are responsible for the hydrodynamic effect. These stiffer and more rigid filler particles cannot be deformed and hence lead to a strain amplification effect where the local strain on the rubber chains is higher than the overall external strain. On the other hand, since the filler particles cannot be deformed under strain, they impart a strain-independent contribution to the modulus.

(c) **Rubber-filler interactions**: Strong rubber filler interactions further amplify the hydrodynamic effects and hence contribute to the overall storage modulus. These interactions can be physical or chemical nature. The interactions lead to the formation of bound rubber which is shielded from deformation by external strains and hence acts to increase the effective filler content leading to strain-independent contribution to the modulus.\(^{60}\)

2.7.1 Storage modulus and Payne effect in filled rubber compounds

Storage modulus is the in-phase component of the complex dynamic modulus, \(G^*\). It deals with the capacity of the rubber compound to store elastic energy of deformation.
The dependence of dynamic modulus on the strain amplitude is depicted in Figure 2.5. Although the figure depicts the trends in carbon black N234-filled SBR, similar trends are obtained with most conventional fillers. It can be seen that the dynamic modulus increases with the increase in filler loading due to the reasons mentioned above. The modulus of unfilled rubber does not show strain dependence. However, as the filler loading is increased, the non-linearity in the curve increases. This non-linear decrease of the modulus beyond particular strain amplitude is known as the Payne-effect. The Payne effect explains the behavior of dynamic modulus vs. strain amplitude in filled compounds. Payne attributed the higher value of low strain modulus to the filler
network formation in the system and the corresponding increase in effective filler concentration to occlusion of rubber. However, as the strain amplitude increases, the filler network starts to break down. This releases the bound rubber, reducing the effective filler volume fraction, thus resulting in reduction of modulus. The strain amplitude at which $G'$ starts to decrease depends on the strength of the filler network. For carbon black filled compounds, the filler network is formed by weak van Der Waals forces whereas in silica the network, it is formed by hydrogen bonds. Hence, for silica filled compounds, Payne effect is seen at much higher strain amplitudes. When a silane coupling agent is added to silica, the polymer-filler interactions increase which reduces the intra-filler networks and hence the Payne effect is reduced drastically in these systems.

Therefore, Payne effect helps in the measurement of filler-filler interactions and filler-polymer interactions.\textsuperscript{69} It must, however, be noted that filler network does not mean a network of particles which percolates throughout the sample. Filler-filler contact forming local sub-networks are also included in the term “filler network”.\textsuperscript{60}

Hence, according to Payne’s theory, filler–filler and filler-rubber interactions determine the dynamic properties. As explained in detail by Frohlich et. al.\textsuperscript{60,70} these interactions control storage modulus under different strain conditions. The modulus under high strains (>30%) is dependent on the bound rubber which is based on the level of rubber-filler interactions. On the other hand, the modulus under low strain conditions (<5%) is indicative of the degree of the filler networks. Filler networks remain intact under low strains and hence contribute significantly to the strain independent modulus. However, as we enter the high strain conditions, the filler networks break and their
contribution to the modulus becomes insignificant. Hence, in this regime, the strength of the filler-rubber interactions controls the value of modulus.

This concept was reflected in silane coupled silica-rubber systems. On adding silane coupling agent, the rubber-filler interactions increase which results in an increase in the modulus under high strain conditions. However, since filler-filler and filler-polymer interactions are two competitive processes, the filler networking is reduced upon addition of silane and this gives much lower modulus under low strain conditions. The concepts mentioned above are further reinforced by the fact that the filler networks increase with increase in filler loading and surface area. This is because the inter-particle distances become smaller with increasing filler loading and surface area. This in turn, increases the probability of filler particle agglomeration and networking. Hence, with an increase in filler surface area and loading, we see more than a magnitude jump in the low strain modulus. Also, the filler-polymer interactions become worse with decreasing the surface activity of carbon black, which leads to decrease in high strain modulus. One must, however, remember that for these concepts to hold true, the rubber contribution, i.e., the crosslink density and the loading of the filler must be constant. Also, it must be noted that filler networking alone is not effective in explaining the strain dependence of complex modulus. Polymer-filler interactions must also be considered in the network effect. This was elucidated by Movahed et al and Maier et al. who showed that for well bound rubber to the filler, non-linear decrease in $G'$ with strain occurs due to stress which is induced when polymer chains get detached or de-bonded from the filler surface under strain. This is because at >90% bound rubber, filler-filler networking is negligible.
and hence detachment of the polymer chains from filler surface should play a role in reduction of modulus with an increase of strain.

Hence, Payne effect and filler–polymer interactions play a very important role in determining the modulus of filled rubber compounds under dynamic conditions. Its effect on the values of loss modulus and tan δ are discussed below.

2.7.2 Loss modulus of filled rubber compounds

The loss modulus is crucial in determining the change in dissipative properties of compounds as function of strain amplitude and temperature. Unlike $G'$ which decreases with increasing strain beyond a particular strain amplitude (Payne effect), the loss modulus for a filled rubber compound goes through a maximum at moderate strains followed by a rapid decrease with further increments in strain. For an unfilled rubber compound, the loss modulus shows negligible dependence on strain amplitude.

Wang et al.$^{58,70}$ explained this unique strain dependence of $G''$ in terms of filler-networking behavior. They proposed that the variation of $G''$ with strain amplitude depends on the breakdown and reformation of the filler networks. First, the increase of $G''$ with increasing filler loading is a consequence of the hydrodynamic effects which leads to an increase in viscosity. Second, as the filler network breaks down with increasing strains, the reformation of this network becomes increasingly difficult. As the strain reaches a critical level beyond which network reformation is not possible in the time scale of the experiment, $G''$ becomes independent of the filler-network. On the other hand, if the strain level is low enough so that the filler network is intact, the value of $G''$ is largely determined by the hydrodynamic effects and the $G''$ becomes strain
independent. In short, lower the value of $G''$, the lesser the fraction of filler network
broken down and reformed during dynamic testing.

2.7.3 Tangent delta of filled rubber compounds

The value of tangent delta presents the ratio of the loss modulus $G''$ to the storage
modulus $G'$ obtained for a given input during dynamic strain. It represents the ratio of
energy dissipated to energy stored by a compound during dynamic straining. The value of
tan $\delta$ is used as a measure of dynamic hysteresis in rubber compounds. This dynamic
hysteresis is directly related to the rolling resistance and wet skid resistance in tires. As
mentioned before, low tan $\delta$ at high temperatures (50-80°C) and high tan $\delta$ at low
temperature (-20 to 0°C) favors rolling resistance and wet skid resistance respectively.\textsuperscript{46,48,69} The effects of strain amplitude and temperature on the value of loss
tangent along with the factors responsible are described here.

The effect of filler loading on tan $\delta$ depends on the measurement temperature. At low
temperatures, the increase in filler loading reduces the values of tan $\delta$ of the compounds.
At high temperatures, an exactly opposite trend is obtained. Hence, it is safe to assume
that different mechanisms govern the loss tangent value at different temperatures.\textsuperscript{58} The
variation of loss tangent with strain is elucidated below.

At higher temperatures i.e. around 50-80°C, tan $\delta$ of unfilled vulcanizates does not
change much with strain.\textsuperscript{58} However, for filled vulcanizates, the tan $\delta$ is higher and goes
through a maximum at moderate strain levels. The scenario again is different at 0°C i.e.,
at temperature in the transition zone of the vulcanizate. The unfilled vulcanizates do not
show strain dependence, but the filled vulcanizates show hysteresis at low strains with the
loss tangent starting off at a lower value but increasing rapidly with strain and eventually ending at higher tan δ than the unfilled compound. As mentioned before, the tan δ at higher temperatures controls the rolling resistance of rubber compounds. Since we are concerned with rolling resistance property in this work, the tan δ versus strain trend at high temperatures is illustrated in Figure 2.6 for a model compound filled with CB.

Figure 2.6: Dependence of tan δ on strain amplitude for SBR filled with CB – N234  
(Reprinted with permission from Ref.60)

The reason behind such variations in strain dependence at different temperatures can also be explained based on the filler network concept described in the previous section. As we know, tan δ is a ratio of loss modulus to the storage modulus. Hence, as for the moduli, filler-related interactions and structures dominate the tan δ behavior too i.e.
breaking and reformation of the filler networks is responsible for the dependence of \( \tan \delta \) on temperature and strain. Assuming good interactions between filler and the polymer, some bound rubber is trapped between the filler networks which is shielded from deformation and hence acts to increase the filler volume fraction. At \( 0^\circ C \) (transition zone of rubber), the energy dissipation arising due to relative motion between polymer chains dominates the value of \( \tan \delta \). Also, at this temperature, the filler network cannot be broken down easily. This, combined with the fact that some rubber is bound to the filler particles, leads to reduction in effective rubber volume and results in the hysteresis being attenuated at \( 0^\circ C \). Hence, lower \( \tan \delta \) values are obtained at \( 0^\circ C \) upon addition of the filler particles. However, the \( \tan \delta \) value does increase once we reach a certain strain level under which the filler agglomerates are broken down and reformed. Hence, at higher strains, the \( \tan \delta \) of filler compounds surpasses the \( \tan \delta \) of the gum rubber.\(^{70}\)

However, at 50-80\(^\circ\)C (in the rubbery zone, Figure 2.6) the mechanism is different. At this temperature, depending on the strain, the filler network breaks down and reforms. This breaking down and reformation of the filler network results in higher energy dissipation and higher hysteresis. Also, as the network breaks down, the bound rubber is released and further contributes to energy dissipation and \( \tan \delta \). Hence, \( \tan \delta \) at 70\(^\circ\)C is controlled mostly by filler network break down due to strain and dissipation of energy. Denser the filler networks and agglomeration, higher is the dissipation, and higher is the value of \( \tan \delta \) and higher is the rolling resistance. Hence, in order to get compounds with lower rolling resistance in the rubbery region, it is important for the filler networks to be lower and filler-polymer interactions to be higher.\(^{58}\)
The phenomenon described above is shown to be true in the case of silane modified silica filled rubber vulcanizates. Silane coupling agents reduce the polarity of silica particles and increase the polymer-filler interactions. Due to this, filler-filler interactions and network formation goes down and the temperature dependence of tan δ is improved dramatically. This is crucial for production of tires with low rolling resistance.\textsuperscript{72} However, lower tan δ compared to carbon black filled vulcanizates has been reported for unmodified silica filled vulcanizates.\textsuperscript{60} For unmodified silica, the polymer-filler interactions are weak and filler-filler networks are very strong due to hydrogen bonding between silica particles. In spite of this, lower tan δ is obtained which is contrary to the explanation given based on filler network formation. This occurs because the strong filler networks break at much higher strain amplitudes compared to carbon black. Hence, the filler network remains intact at the strain levels employed in the experiment. This reduces the dissipation caused by the breakdown of the filler networks and consequently reduces the value of tan δ.

To conclude, in order to achieve a good balance of tan δ under different conditions, it is important to reduce the extent of filler networking.\textsuperscript{70} From a thermodynamic point of view, in order to suppress filler networking, the following approaches should be applied:

a. Reduce the surface energy differences between the polymer and the filler via modification of polymer, filler, or both.

b. Develop fillers with hybrid surfaces to reduce the probability of filler networking.

c. Increase the compatibility between the filler and the polymer by using coupling agents.\textsuperscript{58}
Rest of this thesis presents our work on how the approaches described in this chapter were adopted for lignin-filled elastomer systems. All the three approaches described above were studied in detail in this work, e.g., surface modification of lignin, formation of hybrid fillers with lignin, and use of coupling agents to improve compatibility between lignin and the host rubber.
CHAPTER III
REINFORCEMENT EFFICACY OF LIGNIN IN RUBBER COMPOUNDS AND ITS
DEPENDENCE ON SULFUR TO ACCELERATOR RATIO

In this chapter, the reinforcement efficacy of unmodified kraft lignin was evaluated as a function of sulfur to accelerator ratio. Kraft lignin at loading levels ranging from 0 to 60 phr was used in isoprene rubber (IR) formulations. The objective of the work was to determine the inherent reinforcing ability of kraft lignin and to study the different reinforcement trends as a function of rubber network properties originating from different values of sulfur to accelerator ratio.

3.1 Introduction

A large body of work exists in the field of lignin-filled rubber compounds due to factors such as abundance, cost competitiveness, bio-derived nature, and inherently good mechanical properties of lignin. The abundance and variety of functional groups on its surfaces is also one of the reasons why lignin is so widely studied as a potential filler in polymeric systems. Some research groups\textsuperscript{10,11,25,27,73} showed that the addition of lignin to natural rubber or styrene butadiene rubber positively impacted the 100% modulus, tensile strength, and elongation at break. Some other positive influences of lignin on rubber compounds include improvement in thermo-oxidative stability\textsuperscript{25,74} and dielectric properties\textsuperscript{13}. On the other hand, lignins were also shown to negatively impact the rubber properties\textsuperscript{13,26,28,75} mainly due to lowering of crosslink density. Hence, a lot of variability
can be seen in the reinforcement efficacy of lignin in rubber compounds. One source of variability in properties of rubber compounds of lignin is the genetic variability of lignin. For example, lignins derived from different sources via different delignification methods produce different sets of properties. Another reason for the variation of properties is different sulfur to accelerator ratio used to cure the rubber compounds containing lignin.

The sulfur to accelerator ratio (φ) in the curative package determines the type of vulcanization system. A conventional system (CV) uses φ = 1.6-10, a semi-efficient system (Semi-EV) uses φ = 0.4-1.6, and an efficient system (EV) uses φ = 0.08-0.4. The value of φ, in turn, controls the length and the distribution of crosslink structures. In general, crosslink density decreases with an increase in φ. The same trend is observed for torque obtained during curing. The cure time, on the other hand, generally increases with a reduction of accelerator concentrations and for higher values of φ.

The sulfur to accelerator ratio (φ) is an important parameter since the type of vulcanization system used for curing of rubber largely controls the curing and performance of the rubber compounds. Prediction of curing and performance characteristics of rubber compounds is extremely important due to ever increasing requirements and challenges for development of new materials for tire and automotive industries. The present study specifically targeted the changes in reinforcing behavior of kraft lignin in compounds of synthetic isoprene rubber (IR) as a function of sulfur to accelerator ratio (φ). The study considered synthetic isoprene rubber as the host material for its relevance in tire compounds that produce reduced rolling resistance. IR is heavily used in tire industries for manufacturing of truck tires, carcass, and side walls of passenger tires, off the road tires, and aircraft tires to name a few.
3.2 Experimental

This section presents detailed information on the materials used in this study, formulations, and the method of preparation of the vulcanizates. The equipment conditions used for characterization and testing of the compounds are also described.

3.2.1 Materials

Kraft lignin was obtained in the form of powder from Weyerhaeuser, \( M_w = 5090; \) polydispersity index = 5.4; \( T_g = 128^\circ C \). Synthetic isoprene rubber used in this study was Natsyn® 2200, obtained from Goodyear Tire and Rubber Co. This grade of rubber had a cis 1,4 – isoprene content of 98.5%, \( M_w \) of 2,490,000 and polydispersity index of 3.07. Natsyn® 2200 has many advantages such as the ease of processing and flow, uniform cure rate, clear light color, and reproducible physical properties.\(^7\)

Several other ingredients were used in preparation of rubber compounds - zinc oxide in powder form and stearic acid in bead form, sulfur curing agent (Rubber Maker), and N-cyclohexylbenzothiazole-2-sulfenamide (CBS) accelerator, all obtained from Akrochem Corporation (Akron, OH).

3.2.2 Compounding

The recipes for rubber compound preparation are given in Table 3.1. Compounding was carried out in two steps. In the first step, rubber was mixed with zinc oxide, stearic acid, and lignin in a Banbury mixer (1.2L Model 86EM9804, Banbury USM Corp., Ansonia, CT) at a rotor speed of 55 rpm and a fill factor of 0.7 at ambient temperature. The rubber was first masticated for 120 s and then the ingredients were added and mixed for 5 minutes.
The compounds obtained from step 1 were then mixed with the accelerator and sulfur using a two-roll mill (Reliable Rubber & Plastic Machinery Co., North Bergen, N.J.) for 5-7 minutes at a speed of 15 rpm under ambient temperature conditions. The rubber compounds were cured in a compression molding press at 150 °C. The time needed to reach 95% of the maximum torque (t_{95}) was taken as the optimum curing time. A sheet mold with dimensions 150 mm x 150 mm and a thickness of 1.5 mm was used for curing. The cured materials were used for evaluation of reinforcement behavior and for characterization of filler dispersion.

Table 3.1. Recipe for formulation of isoprene rubber compounds; phr is parts per hundred parts of rubber.

<table>
<thead>
<tr>
<th>Materials</th>
<th>φ = 1 (phr)</th>
<th>φ = 2 (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene rubber</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td><strong>Sulfur</strong></td>
<td><strong>2.5</strong></td>
<td><strong>2</strong></td>
</tr>
<tr>
<td>CBS</td>
<td><strong>2.5</strong></td>
<td><strong>1</strong></td>
</tr>
<tr>
<td>Lignin</td>
<td>0, 15, 30, 45, and 60</td>
<td>0, 15, 30, 45, and 60</td>
</tr>
</tbody>
</table>

3.2.3 Characterization and Testing

The cure characteristics of the compounds were evaluated using ~ 5 g rubber compounds in a Moving Die Rheometer (MDR 2000) at a temperature of 150 °C, a
frequency of 1.67 Hz, and a strain of 7%. The plots of torque versus time were recorded, and the curing parameters such as scorch time and cure time ($t_{95}$) were calculated.

Dispersion of lignin in isoprene rubber was evaluated using optical microscopy. A small piece of the cured sheet was taken and examined under light microscope to evaluate lignin dispersion.

The crosslink density of cured compounds was determined from swelling test. About 0.3 g vulcanizate was subjected to soxhlet extraction in benzene for 24 h and the weight of the swollen sample was measured. Afterwards, the sample was dried in a vacuum oven for 24 h at 60$^\circ$C and its weight was measured again. The crosslink density ($\nu_e$) of the vulcanizates was calculated in kmol/m$^3$ from the Flory-Rehner equation\textsuperscript{80} given below:

\[ \nu_e = \frac{-\ln(1-\nu_r)+\nu_r+\chi\nu_r^2}{V_t\left(\nu_r^{\frac{1}{2}}-\frac{1}{2}\nu_r\right)} \] (3.1)

In equation (3.1), $V_t$ is the molar volume of benzene (89.37 cm$^3$/mol), $\chi$ is the rubber-solvent interaction parameter, for IR-benzene system, $\chi = 0.42$\textsuperscript{79}, and $\nu_r$ is rubber volume fraction in swollen gel given in equation (3.2).

\[ \nu_r = \frac{W_{dry}}{\rho} + \frac{W_{solvent}}{\rho_{solvent}} \] (3.2)

In equation (3.2), $W_{dry}$ is the dry weight of rubber, $\rho$ is the density of rubber, $W_{solvent}$ is the weight of solvent in the swollen gel, and $\rho_{solvent}$ is the density of the solvent. The Kraus correction factor\textsuperscript{81} for kraft lignin is unknown and was not applied in this work. Consequently, the crosslink data reported in this chapter is termed apparent crosslink density.
The nature of functional groups on kraft lignin particle surface was examined by X-ray photoelectron spectroscopy (XPS) method. The XPS spectra were taken using a Kratos Model ES3000 spectrometer (Manchester, UK) under high vacuum conditions with a pressure of $10^{-8}$ Torr, an aluminum anode, and a resolution of 1 eV. The survey scans were used to evaluate the percentage of different atoms present on the surface of kraft lignin particles. The C1s high resolution scans were used to determine the levels of carbon based functional groups present on the surfaces of kraft lignin.

Dumb-bell shaped specimens for tensile tests (ASTM D412, Type C) were punched out of the cured sheets. However, shorter specimens were used for testing vulcanizates belonging to batch with $\phi =2$ due to elongation test limitations of the machine. Thus, the vulcanizates with $\phi =2$ had a gauge length of 10 mm while the vulcanizates with $\phi =1$ had a gauge length of 25 mm. These tests were carried out at room temperature on an Instron® 5567 tensile tester at a crosshead speed of 500 mm/min. A minimum of 5 specimens were tested per sample.

The dynamic mechanical properties of cured rubber compounds were determined using a TA Q200 instrument and sample of dimension 10 mm $\times$ 4.02 mm $\times$ 1.5 mm were cut from the cured sheets. The temperature sweep tests were performed at 1% strain and 1 Hz frequency. The storage modulus and loss modulus are represented as $E'$ and $E''$ respectively since the measurements were performed in tension mode. The values of $\tan \delta$ were measured specifically at 60 $^\circ$C. The damping factor at 60 $^\circ$C gives a direct indication of the viscous dissipation and rolling resistance in rubber compounds.48
3.3 Results and Discussions

The effect of increasing kraft lignin loadings and the corresponding variations of sulfur to accelerator ratios in synthetic isoprene rubber compounds will be discussed in this section. Results on cure performance, tensile properties, dispersion, and dynamic mechanical properties are presented.

3.3.1 X-ray Photoelectron Spectroscopy (XPS) of kraft lignin

The survey spectrum of kraft lignin is presented in Figure 3.1. The survey spectrum suggests the presence of 76% carbon, 23.4% oxygen, and 0.6% sulfur on the surfaces of kraft lignin particles. These percentages are given as a relative ratio of the number of atoms on the surface and are in agreement with the values seen in literature. A high resolution spectral analysis of C1s peak was carried out. The peak was deconvoluted into four peaks which were assigned to carbon based functional groups as seen in Table 3.2.

(a)
The XPS data clearly indicates the presence of polar functional groups formed by carbon and oxygen atoms on the surfaces of lignin. Approximately 33% of the area under the C1s Hi-Res spectrum belongs to C-O groups on the lignin surface indicating abundance of alcoholic –OH and phenolic -OH groups. These –OH groups in addition to the carbonyl groups present on the surface (Table 3.2), impart polarity to the lignin molecule.

Table 3.2. Peak assignments for C1s Hi-Res XPS spectra of kraft lignin

<table>
<thead>
<tr>
<th>Peak</th>
<th>Binding energy (eV)</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>284.58</td>
<td>Polyaromatic C, C-C, C-H</td>
</tr>
<tr>
<td>C2</td>
<td>285.99</td>
<td>C-O</td>
</tr>
<tr>
<td>C3</td>
<td>287.42</td>
<td>C=O, O-C=O</td>
</tr>
<tr>
<td>C4</td>
<td>288.93</td>
<td>O-C=O</td>
</tr>
</tbody>
</table>
The effects of surface polarity of lignin on curing behavior, crosslink density, and the structural complexity of the IR vulcanizates are presented below.

3.3.2 Cure characteristics

The cure parameters such as scorch time, cure time, and torque difference (ΔM) as a function of lignin loading are presented in Figure 3.2 for sulfur-accelerator ratios, φ=1 and 2. The use of lignin increased the value of ΔM and reduced the optimum cure time to some extent. The increase in value of ΔM is attributed to the hydrodynamic effects, e.g. solid lignin particles increased the viscosity of the compound. The cure time decreased with lignin addition and reached a plateau for lignin loading between 15 phr and 45 phr. Similar effect is seen on the scorch time curve in Figure 3.2(a). A reduction of scorch time is attributed to the hydroxyl groups present on the surfaces of lignin. The XPS data confirmed that lignin particle surfaces contained abundance of –OH groups. The hydroxyl groups are known to accelerate the vulcanization process and to cause increased scorchiness.25,28 The trends observed on cure parameters indicate strong participation by lignin on vulcanization process, as studied previously.25,28,75 An analysis of apparent crosslink density data will reveal more information on the impact of lignin on crosslinking behavior.
Figure 3.2: Vulcanization characteristics of IR-lignin compounds as function of lignin concentration, (a) scorch time, (b) degree of cure, (c) optimum cure time ($t_{95}$).

We now turn to the influence of $\varphi$ on cure parameters. Figure 3.2 displays a distinct trend of the cure parameters with an increase of $\varphi$. The values of scorch time and optimum cure time decreased with an increase in accelerator concentration as expected. $\Delta M$ decreased with an increase in $\varphi$. The reduction in the value of $\Delta M$ can be interpreted...
as follows. An increase in the value of $\phi$ from 1.0 to 2.0 took the curing system from a semi-efficient system to a conventional system. It is known that the CV system produces more polysulfidic crosslinks$^{76}$ leading to longer length of crosslinks and causing a reduction of stiffness and torque.

3.3.3 Crosslink density of vulcanizates

Figure 3.3 shows apparent crosslink density as a function of lignin loadings for $\phi=1$ and 2. It is apparent that crosslink density (XLD) decreased with an increase in lignin loading for both values of $\phi$. This reduction in XLD can be due to two potential factors. First, some loose bonds between lignin and rubber may block the vulcanization sites in rubber leading to lower XLD.$^{28,84}$ Second, the sulphurating complex formed during vulcanization may be hindered due to adsorption of lignin on active zinc oxide surface.$^{31}$ However, one of the primary reasons for reduction of XLD upon addition of lignin is the presence of polar groups on lignin particle surfaces which promote adsorption of the curatives. Such adsorption disturbs the curing process and results in lower crosslink density values. Similar behavior was also reported and explained for unmodified silica filled rubber compounds.$^{55}$ The presence of polar groups on the surface of lignin was confirmed by X-ray Photoelectron Spectroscopy analysis as presented in Figure 3.1.
Figure 3.3: Apparent crosslink density of IR-lignin vulcanizates as function of lignin concentration.

The crosslink density value obtained from swelling tests also decreased with an increase of $\varphi$. Note that an increase in $\varphi$ also results in an increase in the number of polysulfidic crosslinks. Thus, as the system changes from a CV system ($\varphi=2$) to a semi-EV system ($\varphi=1$), rapid desulfuration of polysulfidic crosslinks takes place. This causes the crosslinks in the semi-EV system to be shorter than CV system. Also, the crosslink density in the semi-EV system becomes greater.

3.3.4 Dispersion analysis of IR-kraft lignin vulcanizates

The analysis of filler dispersion in vulcanizates was carried out using images captured by optical microscope. The optical micrographs in Figure 3.4 reveal the size of lignin particles as received and in the vulcanizate which ranges from 1 $\mu$m to greater than 50 $\mu$m. The lignin particles reveal broad distribution of sizes. Further breakage of lignin particles may take place during compounding. The glass transition temperature of lignin is $130^\circ$C which is well above the room temperature used in rubber compound preparation.
Figure 3.4: Optical micrographs of (a) KL as received, and IR-lignin vulcanizates ($\varphi = 2$).

(a) 15 phr lignin, (b) 30 phr lignin, (c) 45 phr lignin, (d) 60 phr lignin.
At higher loadings, the lignin particles remained as aggregates and formed lignin particle networks. As will be seen later, this might have a negative impact on the failure properties of vulcanizates.

3.3.5 Mechanical properties of IR-kraft lignin vulcanizates

Mechanical properties such as 100% modulus, strain at break and the tensile strength were measured for lignin filled IR compounds (Figure 3.5). The 100% modulus increased with an increase in lignin filler loading. The stiffer lignin particles increased the stiffness of the compounds. The value of 100% modulus however lowered with an increase in φ due to reduction of XLD values on increasing the value of φ.

The strain at break showed completely different trends with an increase in φ. For φ = 1, the strain at break of compound with 60 phr lignin show an increase by about 60% over the unfilled vulcanizate. The reduction in XLD and reduction in elastic nature of the vulcanizates upon addition of lignin also results in an increase in the strain at break. In the case of compounds with φ = 2, the strain at break remained more or less constant with lignin concentration.
Figure 3.5: Mechanical properties of IR-lignin vulcanizates as a function of lignin concentration, (a) 100% modulus, (b) strain at break, (c) tensile strength.

The tensile strength values show the most significant sensitivity to the values of $\phi$. An increase in sulfur-accelerator ratio from 1 to 2, led to a 5-fold increase in tensile strength for unfilled IR vulcanizate. At higher $\phi$, the XLD decreases and the vulcanizate elongate more. This probably results in strain-induced crystallization of IR. It is believed that higher strain at break (~730%) for $\phi = 2$ (Figure 3.5 (b)), compared to ~360% for $\phi=1$ generated more strain induced crystals in the unfilled vulcanizates, which in turn caused much higher stress at break. However, strain induced crystallinity of IR was not experimentally evaluated.

The presence of lignin in the vulcanizates show opposite trends on tensile strength for $\phi=1$ and $\phi=2$. In the case of $\phi = 1$, the tensile strength showed an almost 3 fold increase at 30 phr loading of lignin, beyond which the tensile strength shows reduction although the absolute value of tensile strength is at least 2-fold compared to unfilled system. This
trend is typical of filled rubber vulcanizates. The tensile strength goes through a maximum with increasing filler loading and then decreases beyond a certain concentration due to agglomeration of the filler particles.

For $\phi=2$, however, the tensile strength of IR with 60 phr lignin loading dropped to less than half the value for unfilled rubber. It was already noted that the addition of lignin caused increased structural complexity of the vulcanizate due to inefficient utilization of sulfur. This in turn also led to modifications in the main chain and consequently inhibited the strain-induced crystallization even though the strain at break is unaffected (Figure 3.5 (b)). The inhibition of strain-induced crystallization resulted in lower tensile strength upon addition of lignin. The trends of tensile property reported here are in agreement with the data published in literature. Kosikova et al.$^{25}$ reported an improvement in tensile strength of lignin-filled NR from $\sim 2$ MPa for unfilled NR to $\sim 17$ MPa for NR filled with 30 phr lignin when a value of $\phi$ of 1 was employed. Similar results were reported by Alexy et al.$^{11}$ who saw an increase in tensile strength of NR from $\sim 2$ MPa for the unfilled system to 15 MPa for NR filled with 20 phr lignosulfonate at $\phi=1$. The tensile strength reportedly dropped at filler loadings beyond 20 phr. On the other hand, Kumaran et al.$^{28}$ and Botros et al.$^{13}$ reported using a conventional cure system with $\phi = 1.6 -10$, that the tensile strength of NR upon addition of lignin dropped from 27.5 MPa and 20 MPa for unfilled NR respectively to 10 MPa for NR filled with 20 phr of lignin.

Hence, the sulfur to accelerator ratio is a factor responsible for the variations seen in literature about the reinforcing efficacy of lignin. The data presented in this chapter
endorsed that the value of $\varphi$ must be properly chosen for development of rubber compounds with lignin.

3.3.6 Dynamic mechanical analysis

Dynamic mechanical properties of rubber compounds were evaluated using an oscillatory strain of 1%, at temperatures from -85 to 80 °C. Figure 3.6 shows how the storage modulus, loss modulus, and damping factor evaluated in terms of tan $\delta$ at 60 °C vary with lignin content. The storage modulus of the vulcanizates at both $\varphi=1$ and 2, increased with the filler loading. This can be attributed to the incorporation of stiffer and more rigid lignin particles. The value of storage modulus of the compounds prepared at $\varphi = 1$ was higher than the value of storage modulus of compounds at $\varphi = 2$ due to higher XLD of the compounds prepared at $\varphi = 1$. 

(a)  
(b)
Figure 3.6: (a) Storage modulus, (b) loss modulus, and (c) loss tangent (tan δ) as a function of lignin concentration in IR-lignin compounds.

The loss modulus (E″) is slightly higher for the vulcanizates prepared using φ of 2. In this case, lower elasticity and stiffness caused higher energy dissipation. The loss modulus values increase with an increase in lignin concentration. However, the slope of the enhancement in E″ increases drastically beyond lignin concentrations of 45 phr. It is noted that beyond a threshold concentration, the secondary energy dissipation mechanisms arising from filler networking also contributed to the loss modulus. We conclude from Figure 3.6 that the threshold concentration of lignin in this system is approximately 45 phr.

The values of tan δ correlate the hysteresis loss with the value of rolling resistance of rubber compounds. It is seen that the damping factor value (tan δ) increases with an increase in lignin loading. In this case, the additional dissipation due to filler networking
is captured in the higher values of tan δ beyond approximately 45 phr lignin loading. The
data in Figure 3.6 (c) also shows that the energy dissipation is higher for compounds
prepared with higher sulfur to accelerator ratio (φ). Recall that the compounds with φ = 2
had lower XLD and hence lower elasticity in comparison to compounds with φ =1.

3.4 Conclusions

Several trends emerged on the potential of reinforcement of IR with kraft lignin:

(1) An increase in φ resulted in a reduction of XLD of unfilled IR by 30%. The increase
in the number of polysulfidic crosslinks due to higher value of φ is responsible for the
drop in XLD. The tensile strength of unfilled IR showed a 5-fold increase due to higher
strain-induced crystallization for φ=2. Since the elongation at break doubled upon
increasing the value of φ from 1 to 2, the higher strain-induced crystallization occurred
for φ=2.

(2) The addition of lignin resulted in a reduction of XLD of IR due to the presence of
polar groups on its surfaces which promoted adsorption of curatives. The presence of
polar groups on lignin surfaces was confirmed by XPS analysis.

(3) Lignin showed completely opposite trends on tensile strength with an increase in
sulfur-accelerator ratio. At φ = 1, TS increased by with lignin loading till an optimum at
30 phr was reached. At 30 phr, TS increased by 160% compared to unfilled IR. Beyond
30 phr, the TS reduced due to filler agglomeration. At φ = 2, the TS continuously
decreased due to inhibition of strain-induced crystallization upon addition of lignin.

(4) The storage modulus and loss modulus values increased with an increase in lignin
loading due to the hydrodynamic effect. The slope of the loss modulus vs. lignin content
increased significantly beyond threshold filler loading, indicating filler networking contributions to the dynamic moduli. Similar trends were observed in the value of tan δ.

The results presented in this chapter show that the polar kraft lignin interferes with the rubber curing process resulting in lower degree of cure. The lower degree of cure and crosslink density gives rise to lower elasticity and mechanical performance. The issue of lignin polarity will be addressed in the next chapter where SBR instead of IR will be used. Recall that the reinforcing behavior of lignin in compounds of IR is not very clear due to the self-reinforcing nature of IR. IR and NR are considered self-reinforcing elastomers since they undergo strain-induced crystallization.⁶¹
CHAPTER IV
EFFECT OF SURFACE MODIFICATION OF LIGNOSULFONATES ON
REINFORCEMENT OF STYRENE-BUTADIENE RUBBER

In this chapter, the effects of surface modification of lignosulfonates on potential reinforcement effects of styrene butadiene rubber (SBR) are discussed. Cyclohexylamine was used to modify the lignosulfonate surface since it can interact with lignosulfonate via proton transfer and hydrogen bonding interactions. The objective of this study was to suppress the polarity of lignin in order to enhance its compatibility with rubber matrix and reduce the detrimental effects lignin has on the cure and overall performance of rubber.

4.1 Introduction

Lignin is a naturally occurring three dimensional polymer consisting of phenyl propane units interconnected by a variety of carbon-carbon or ether like carbon-oxygen-carbon bonds. They are polar hydrophilic molecules with surface energies ranging from 53 to 56 mJ/m². The polar component of surface energy varies with the source of lignocellulosic materials or with the delignification process adopted for separation of lignin. For example, the widely used sulfite pulping process for production of lignosulfonates introduces sulfonate groups into the lignin molecules. This makes the lignosulfonates a lot more polar than kraft lignin for example. The increased polarity and the presence of sulfonate groups also make the lignosulfonate water soluble.
representative structure of calcium salt of lignosulfonate (LS) is shown in Figure 4.1 (redrawn from reference 89). Although the abundance of polar functional groups on lignin surfaces and the prospect of their chemical modification by various means make lignins attractive as reinforcing fillers, the presence of polar groups has its set of challenges as well.

![Figure 4.1: Representative structure of calcium lignosulfonate (Redrawn from Ref. 89)](image)

As studied previously, a significant portion of the work on lignin in conjunction with rubber reinforcement reports very little to no reinforcement of mechanical properties. Kumaran et al.\textsuperscript{29} showed that lignin masks certain crosslinking sites in natural rubber (NR) and causes reduction of crosslink density. This leads to lowering of strain induced crystallization, tensile strength, and hardness. Alexy et al.\textsuperscript{11} also reported longer curing
times and lower crosslink density with very little increase in tensile strength upon addition of lignosulfonates to SBR. Poor reinforcement, especially low values of
elasticity, originates from inefficient vulcanization. Due to its acidity and polar nature,
lignin is known to block the vulcanization sites of the polymer chains and to interact with
the molecules of curing agents such as zinc oxide, stearic acid, and amide based curing
agents. The incompatibility of polar LS with non-polar rubber matrix also leads to
inefficient load transfer at the polymer-particle interfaces. The reduction in XLD and
elasticity of the rubber on addition of lignin were discussed in Chapter III. These factors
so far deterred widespread usage of lignin in compounds of commercial thermoplastics
and elastomers. An additional factor, not considered in literature, but important, is the
size of lignin particles.

The results presented in this chapter address the issues associated with polarity of
lignin and demonstrate how surface modification of lignin can produce compatibility
with non-polar rubber and yield reinforcement. Setua et al. modified lignin with benzoyl
peroxide and showed that an increase in polarity of lignin produced superior oil and fuel
resistance in comparison to nitrile rubber compounds filled with carbon black. In this
case, the new functional groups on lignin improved interactions with polar nitrile rubber.

It is apparent that benzoyl peroxide modification is not appropriate for development
of compounds of non-polar rubbers such as natural rubber, synthetic isoprene rubber, and
styrene-butadiene rubber. In this context, Benko et al. functionalized lignin by
esterification and silylation and obtained higher mechanical properties and improved
rolling resistance in compounds of modified lignin, non-polar rubber, and carbon black. It
appears that the functionalization reactions are tedious and involve organic solvents and
catalysts. The study, however, did not present insight on how esterification and silylation of lignin improved its interactions with rubber.

In this work, an easy and environmentally benign process was adopted for lignin modification. Lignosulfonate was modified in water by using cyclohexylamine (CA), a weak base. Lignosulfonates contain the same fundamental lignin structures with the sulfonate groups attached to the backbone. These sulfonate groups assist in water solubility. As lignin surface in LS is acidic the polarity of lignin surface can be suppressed via acid-base reactions with CA. In addition, lignin-CA interactions can also occur via hydrogen bonding; materials with acidic surfaces are known to form strong hydrogen bonds with basic materials as has been reported for silica. These interactions increase the C-C bond concentration on the surfaces of LS particles and can produce compatibility with non-polar rubber molecules. Liu et al. used CA to modify the surfaces of silica particles. They showed that CA modified silica improves dispersion and increases compatibility with rubber matrix.

4.2 Experimental

This section presents detailed information on the materials used in this study, modification techniques and method of preparation of the Vulcanizates. In addition, the equipment used in characterization and testing of the compounds are also discussed.

4.2.1 Materials

Lignin used in this study was a calcium lignosulfonate D618 obtained from Borregaard Lignotech (Rothschild, WI). This grade of LS is a light yellowish brown powder and is soluble in water. Styrene butadiene rubber (SBR) used in this study was obtained from Goodyear Tire and Rubber Co. (Akron, OH) in the form of grade
SLF18B10. The rubber had a bound styrene content of 18.5% by weight. The cyclohexylamine used for modification of lignosulfinate was obtained from Sigma-Aldrich, grade Reagentplus®. Several other ingredients were used - zinc oxide in powder form and stearic acid in bead form, sulfur curing agent (Rubber Maker), and N-cyclohexylbenzothiazole-2-sulfenamide (CBS) accelerator, all obtained from Akrochem Corporation (Akron, OH).

4.2.2 Modification of lignosulfonate

20 g of lignosulfonate was stirred in 100 mL deionized water. The solubility of LS in water at room temperature was found to be ~ 240 mg/mL. A solution of CA in water was added to the solution of LS and stirred for 1 hour. Aqueous solutions of CA at three concentrations were used to modify the LS particles, viz. 0.05, 0.1, and 0.25 g of CA/g of LS. Water from the solution was then evaporated by heating on a hot plate with continuous stirring. The product was dried in vacuum oven overnight at 80 °C to remove residual water. Excess CA was removed from modified LS particles by stirring in toluene for 2 days. The suspension in toluene was filtered and the particles were dried in vacuum oven overnight at 80 °C.

4.2.3 Compounding

The compounds of modified LS particles and rubber were prepared in two steps. In first step, rubber was mixed with zinc oxide, stearic acid, and the fillers in a Brabender Plasticorder internal mixer (80 cm³ internal volume) at a rotor speed of 65 rpm and a fill factor of 0.7 at 80 °C. The rubber was masticated for 60 s and then mixed with the rest of the ingredients for 5 minutes. In second step, the compounds obtained from step 1 were then mixed with sulfur and CBS accelerator using a two roll mill for 5-7 min at a speed of
15 rpm at a roll temperature of 40 °C. The following recipe was used based on 100 parts by weight of SBR - stearic acid (1 phr), zinc oxide (3 phr), sulfur (1.75 phr), CBS (1 phr), and modified LS particles (30 phr). SBR compound without LS particles was also prepared as a control material.

The rubber compounds were cured in a compression molding press at 160 °C. The time needed to reach 95% of the maximum torque (t_{95}) was taken as the optimum curing time. A sheet mold with dimensions 150 mm × 150 mm and a thickness of 1.5 mm was used for curing. The cured materials were used for evaluation of reinforcement behavior and for characterization of filler dispersion.

4.2.4 Characterization

The changes in functional group types and contents on LS particle surfaces due to modification by CA were examined by X-ray photoelectron spectroscopy (XPS) method. Four different powder samples were used for XPS analysis viz. unmodified LS, LS-0.05CA, LS-0.1CA, LS-0.25CA. The powder sample LS-0.25CA represents modified LS particles with 0.25 g CA per gram of LS particles used in modification. The XPS spectra were taken using a PHI 5000 VersaProbe II Scanning XPS microprobe™ under high vacuum conditions with a pressure of 10^{-7} Pa, and an aluminum Kα radiation source. The survey scans were used to evaluate the percentage of different atoms present on the surface of LS particles. The C1s high resolution scans were used to determine the levels of C-C bonds present on the surfaces before and after modification with CA.

TA instrument’s Q500 Thermogravimetric analyzer was used to determine the amount of bound CA on the LS particles. The modified lignin powder after preparation as
described, were dried in vacuum oven for 48 hours before subjecting to TGA analysis. The powders were heated from room temperature to 400 °C using a temperature ramp rate of 20 °C/min. The TGA analysis was carried out in nitrogen environment.

The cure characteristics of the compounds were evaluated using approximately 5 g rubber compounds in a Moving Die Rheometer (MDR 2000) at a temperature of 160 °C, a frequency of 1.67 Hz, and a strain of 7%. The plots of torque vs. time were recorded and the curing parameters such as scorch time and cure time (t95) were calculated.

Dumb-bell shaped specimens (ASTM D412, Type C) for tensile tests were punched out of cured sheets. These tests were carried out at room temperature on an Instron® 5567 tensile tester at a crosshead speed of 500 mm/min. A minimum of 5 specimens were tested per sample.

The crosslink density of cured rubber compounds was determined from swelling test. About 0.5 g vulcanizate was submerged in toluene for 72 h and the weight of the swollen sample was measured. Afterwards, the sample was dried in a vacuum oven for overnight at 60 °C and its weight was measured again. The crosslink density (νe) of the vulcanizates was calculated in kmol/m³ from the Flory-Rehner equation described in Chapter III on page 49. The parameters of equation 3.1 are presented here: Vf the molar volume of toluene is 106.28 cm³/mol, and χ the rubber-solvent interaction parameter, for SBR-toluene system is 0.44692. An apparent crosslink density value is reported since the Kraus correction factor for calcium lignosulfonate is unknown.

The dynamic mechanical properties of cured rubber compounds were determined using a TA Q200 instrument and sample of dimension 10 mm × 4.02 mm × 1.5 mm cut from cured sheets. Strain sweep tests were performed at 60 °C and 1 Hz frequency.
values of storage modulus and loss tangent (tan δ) were recorded at 0.1% strain and 10% strain respectively. The values of tan δ were measured specifically at 60°C. The damping factor at 60°C gives a direct indication of the viscous dissipation and rolling resistance in rubber compounds.

A high resolution scanning electron microscope, JEOL JSM5310 was used to examine the fracture surface of rubber vulcanizates filled with unmodified and modified lignosulfonate molecules. SEM images were also used to obtain particle sizes. The diameter of 40 particles was measured using Image J software for a given specimen. The vulcanizates were cold fractured in liquid nitrogen followed by sputter coating for 1.5 min by a layer of silver under argon gas atmosphere before taking images by SEM. The operating voltage of SEM was 5 kV.

4.3 Results and Discussions

The surface modification of lignosulfonates will be discussed in this section. Results on cure performance, tensile properties, dispersion, and dynamic mechanical properties of SBR compounds filled with unmodified and modified LS are presented.

4.3.1 Evaluation of surface functional groups using XPS

The binding of cyclohexylamine (CA) onto the surface of lignosulfonate was examined using X-ray photoelectron spectroscopy. The survey spectrum was used to identify the relative amounts of carbon and oxygen atoms present on the surface of LS particles. The relative amounts of carbon-based functional groups on the surface were identified from deconvolution of C1s peaks observed in the high resolution spectra. Figure 4.2 presents the survey spectra and the high resolution C1s spectra for unmodified and modified LS. Table 4.1 lists the relative ratio of carbon and oxygen atoms present
and the relative area percentage of C-C bonds present on the LS surface before and after modification with CA.
Figure 4.2: Representative XPS spectra (a) Survey spectra and (b) C1s high resolution spectra for unmodified LS and (c) C1s high resolution spectra for LS modified with 0.1 g of CA/g of LS.

Figure 4.2(a) shows the peaks due to carbon, oxygen, sulfur, and calcium indicating that these detectable atoms were present on the surface of LS particles as is expected from its structure presented in Figure 4.1. Carbon and oxygen atoms constitute the bulk of surface composition with 60% and 35% respectively of the total atoms present on the particle surface (See Table 4.1). In Figure 4.2(b), the C1s high resolution spectrum for LS is deconvoluted into two main peaks corresponding to C-C bonds (284.7 eV) and C-O bonds and C-S bonds (286.3 and 286.2 eV). The peaks corresponding to C-O bonds and C-S bonds overlap with each other, thus the peak in Figure 4.2(b) shows the total contribution of these two functional groups. Figure 4.2(c) presents the C1s high resolution spectrum of LS particles modified with 0.1 g of CA/g of LS. The increase in peak area corresponding to the C-C bonds is clearly evident. The area under the curve of C-C bonds is listed in Table 4.1. The presence of CA in modified LS should change the
relative amounts of carbon and oxygen atoms due to high carbon content in CA molecules.

Table 4.1. Ratio of carbon and oxygen atoms and the % of area under C-C bond peak in XPS spectra obtained for unmodified and modified LS.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>C:O ratio</th>
<th>% Area of C-C bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified LS</td>
<td>1.7</td>
<td>34.4</td>
</tr>
<tr>
<td>LS – 0.05CA</td>
<td>1.9</td>
<td>43.2</td>
</tr>
<tr>
<td>LS – 0.1CA</td>
<td>2.2</td>
<td>53.5</td>
</tr>
<tr>
<td>LS – 0.25 CA</td>
<td>3</td>
<td>67</td>
</tr>
</tbody>
</table>

The C:O ratio and the % area of C-C bonds on the surfaces of LS particles increase with an increase of CA concentration in modification step (Table 4.1). This is not surprising as CA binds onto the LS particle surfaces. Consequently, the number of carbon atoms on the surface increases relative to the number of oxygen atoms. Similar trend is observed for % area of C-C bonds calculated from the area under the curve of the C-C bonds peak and the total area under the curve of the C1s spectra. The quantity of C-N bonds could not be evaluated using XPS due to limited sensitivity of XPS towards nitrogen and smaller amounts of C-N bonds in comparison to C-C bonds on the surfaces of modified lignosulfonate particles. The data presented in Table 4.1 give a clear indication of the presence of CA on the surfaces of modified LS particles. An immediate consequence of the presence of CA on modified LS particle surface is reduction of polarity.
4.3.2 Thermogravimetric analysis (TGA)

The amount of CA bound to LS particle surfaces was determined from TGA data. The difference in weight loss between modified LS particles and unmodified LS particles followed up to 250 °C yielded information on the amount of bound CA. It was perceived that a thermal scan up to 250 °C would allow removal of all bound CA. Note in this context that bound CA would need more thermal energy than needed for boiling of CA at ~ 130 °C. The weight loss at or below 250 °C would also include bound or physically adsorbed water from the LS particle surfaces. We assumed that the amount of water adsorbed was the same in modified and unmodified specimens. Figure 4.3 shows how the amount of CA bound to the LS particle surfaces changes with the concentration of CA in aqueous solution used in the modification step.

![Figure 4.3: Weight percent of CA bound onto the surfaces of LS particles](image)

It is seen in Figure 4.3 that the amount of CA bound onto the LS particle surfaces increases with an increase of the concentration of CA used in the modification process. If
all CA molecules taken in the solution, e.g., 0.05 g CA per g of LS had adsorbed onto the LS particle surfaces, TGA analysis should yield ~ 4.75 wt% CA in modified LS particles. Instead, only 3 wt% CA remained on LS particle surfaces. The amount of CA adsorbed onto LS particles increases to around 6 wt% compared to a possible maximum of ~20 wt% CA when CA concentration was 0.25 g per g of LS. It is apparent from Figure 4.3 that the amount of bound CA would reach a plateau at even higher concentration. However, a concentration higher than 0.25 g CA per g of LS was not tried.

4.3.3 Particle surface morphology

The morphology of particles before and after modification with CA was examined by SEM. Representative SEM images are presented in Figure 4.4. Figure 4.4(a) reveals that unmodified LS powder consists of random shaped particles with sizes in excess of 100 μm. A significant reduction in LS particle size occurred due to modification as seen in Figure 4.4(b). The sizes of 40 representative particles gleaned from SEM images using imageJ software were analyzed for particle size distribution. Such data is presented in Figure 4.5.
Figure 4.4: SEM morphology of (a) unmodified LS, (b) modified LS with 0.1 g of CA/g of LS in modification step.

The reduction in particle size upon modification can be attributed to reduction in polarity of the particles. The particles underwent much less agglomeration during particle isolation compared to unmodified LS particles. The lignin molecules after modification with CA could not form large size agglomerates due to their lowered polarity.
As seen in Figure 4.5, the size distribution shifts to smaller particle sizes with an increase in CA concentration from 0.05 to 0.1 g/g of LS. This is intuitive since higher concentration of CA leads to lower polarity which in turn reduces the agglomeration tendencies of LS particles. However, further increase of the concentration of CA shifts the size distribution to slightly higher particle sizes. Although this was not investigated further, one can hypothesize that excess amine groups on the surfaces of LS particles at 0.25 g of CA per g of LS promote agglomeration via hydrogen bonding among amine groups.

4.3.4 Cure performance of modified LS – SBR vulcanizates

The rubber compounds were cured at 160 °C using moving die rheometer. Cure parameters such as scorch time, cure time, and crosslink density of unmodified and modified LS particles are summarized in Table 4.2. It is apparent from the data presented in Table 4.2 that the scorch time and the cure time of rubber compounds with unmodified LS are much higher compared to those of unfilled rubber. Such an increase in scorch time
and cure time indicates inefficient vulcanization of rubber compounds in the presence of unmodified LS. The polar fillers, such as LS and silica, are known to interact strongly with the curing agents and to adsorb the molecules of accelerator and other curing agents onto their surfaces. In addition, lignin can absorb moisture due to its hydrophilic nature, which in turn, can adversely affect the curing behavior of rubber compounds. These effects hindered the curing process as was reported earlier in the context of curing of rubber in the presence of lignin and silica.  

Table 4.2. Cure parameters for unmodified LS filled and modified LS filled SBR compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Scorch time (min.)</th>
<th>Cure time (min.)</th>
<th>(XLD)\text{app} (kmol/m}^3\text{)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR-0F</td>
<td>5</td>
<td>12</td>
<td>0.08</td>
</tr>
<tr>
<td>SBR-30LS</td>
<td>10</td>
<td>23</td>
<td>0.04</td>
</tr>
<tr>
<td>SBR-30LS-0.05 CA</td>
<td>9</td>
<td>20</td>
<td>0.046</td>
</tr>
<tr>
<td>SBR-30LS-0.1 CA</td>
<td>7</td>
<td>14</td>
<td>0.06</td>
</tr>
<tr>
<td>SBR-30LS-0.25 CA</td>
<td>5</td>
<td>10</td>
<td>0.07</td>
</tr>
</tbody>
</table>

It is also evident from the data presented in Table 4.2 that the modification of LS with CA significantly reduced the scorch time and the cure time in comparison with unmodified LS. In one case – with 0.25 g CA/g LS – the cure time is seen to be lower than the unfilled rubber. The crosslink density also increased with increasing concentration of CA in the modified LS. However, the rate of increase of crosslink density is lower for concentration above 0.1 g of CA/g of LS indicating that the XLD will
reach a plateau at higher CA concentrations. Also, the values of crosslink density obtained with modified LS are lower than that of unfilled SBR (Table 4.2). Kumaran and De\textsuperscript{28} attributed lower and slower crosslinking to masking of cure sites of rubber by lignin particles. In this work, the modified LS particles quite possibly lost some of its masking abilities due to coverage by CA molecules. One can attain additional crosslinking, higher crosslink density, higher mechanical properties by aging the samples for extended periods of time at above the room temperature. This was not investigated in this work.

In addition, the presence of CA in modified LS contributes two effects. First, the CA molecules cover the surfaces of LS particles and reduce their polarity. As a consequence, the modified LS particles can no longer adsorb as many curing agent molecules. Second, amine compounds are known to accelerate the curing process and to produce higher degree of crosslinking.\textsuperscript{94,95}

4.3.5 Tensile properties of cured rubber compounds

The effect of CA modification of LS on tensile strength at break, strain at break, and 100% modulus are presented in Figure 4.6. The tensile strength at break increases significantly upon modification of LS with CA, reaching a 45% increase in strength for compound containing LS particles treated with 0.1 g of CA/g of LS. In comparison, the tensile strength dropped slightly for compound containing LS particles treated with 0.25 g of CA/g of LS. Note that tensile strength is a failure property and is strongly affected by the particle size.\textsuperscript{59} The trend in tensile strength values correlates well with the particle size distribution data presented in Figure 4.5. Recall that particle size distribution moved slightly to higher sizes for LS particles treated with CA of concentration 0.25 g/g of LS. This increase in particle size is quite possibly responsible for lower values of tensile
strength and elongation at the break for compounds containing LS particles treated with 0.25 g CA per g of LS.
The strain at break data follows a trend similar to the tensile stress. The values of strain at break increases gradually to greater than 400% with an increase of CA concentration to 0.1 g of CA/g of LS and then drops to about 300% at CA concentration of 0.25 g of CA/g of LS, which is slightly lower than that of the compound with unmodified LS (Figure 4.6b). It is learned from the data in Table 4.2 that crosslink density increased with an increase of CA concentration in LS modification step. Therefore, one would expect a reduction in elongation at break at higher concentration of CA, as the material cannot elongate much due to increased stiffness in systems with higher crosslink density. The anomalous trend in Figure 4.6(b) can be rationalized based on improved compatibility between rubber and modified LS particles which leads to improved stress transfer between the filler particles and the rubber domains, yielding higher elongation at break. At higher CA concentrations, e.g., at 0.25 g of CA/g of LS, the higher crosslink density and stiffer chains outweigh the effect of stress transfer and
produce lower elongation at break. The increase of chain stiffness due to higher values of crosslink density results in an increase of 100% modulus (Figure 4.6c). The 100% modulus also shows an increase with an increase of CA concentration in modification of LS particles.

4.3.6 Morphology of rubber compounds

The effect of CA modification on morphology of cured compounds was studied using SEM images. The SEM images of representative fracture surfaces of cured compounds with unmodified LS and LS modified with 0.1g of CA/g of LS are presented in Figure 4.7. It is apparent that unmodified LS particles show cracks in Figures 4.7(a) and 4.7(c) which appeared during fracture of samples in liquid nitrogen. On the other hand, the modified LS particles show less cracking since they are much softer and of smaller size due to lower levels of agglomeration.
It is also apparent from SEM images in Figure 4.7(c) and 4.7(d) that the interfaces of LS particles with rubber look much smoother for modified LS particles. The reduced polarity of modified LS particles in this case helped improve the interactions with rubber phase by creating a smooth interface across which stress transfer can occur more efficiently.

4.3.7 Dynamic mechanical analysis

The DMA data obtained from strain sweep experiments at 60 °C is listed in Table 4.3. The storage modulus at 0.1% strain (E’) and tan δ at higher strain level of 10% are reported. As seen from the data, the storage modulus increases with increasing
concentration of CA in modified LS particles and correlates well with the crosslink density data presented in Table 4.2. The reduction in polarity due to modification of LS particles also deterred the interactions between LS particles and the cure components. This in turn helps achieve higher values of crosslink density and higher values of storage modulus for a given amount of curing agent.

Table 4.3. Effect of CA modification on the dynamic properties of LS filled SBR vulcanizates

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>Compound</th>
<th>E’ at 0.1% strain (MPa)</th>
<th>tan δ at 10% strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unfilled SBR</td>
<td>2.9</td>
<td>0.05</td>
</tr>
<tr>
<td>2</td>
<td>SBR-30LS</td>
<td>3.7</td>
<td>0.08</td>
</tr>
<tr>
<td>3</td>
<td>SBR-30LS-0.05 CA</td>
<td>3.9</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>SBR-30LS-0.1 CA</td>
<td>4.1</td>
<td>0.07</td>
</tr>
<tr>
<td>5</td>
<td>SBR-30LS-0.25 CA</td>
<td>4.2</td>
<td>0.065</td>
</tr>
</tbody>
</table>

The higher value of crosslink density in the case of modified LS also plays an important role in reduction of the value of tan δ. An increase in crosslink density value indicates higher elasticity of the vulcanizates and higher values of storage modulus as discussed earlier. This in turn lowers the value of loss tangent. However, tan δ is also dependent on the rubber-filler and filler-filler interactions. As modified LS particles interact better with rubber phase and does not form large size agglomerates due to lower polarity, the filler-filler networking in rubber compound was quite possibly reduced. This, in turn, caused a reduction of the value of tan δ.
4.4 Conclusions

A method was developed to modify the surface of lignin in order to lower its polarity and to increase the concentration of C-C bonds on its surface, so that modified LS particles become more compatible with non-polar rubber matrix such as SBR. The reduced polarity also helped lower the particle size of modified LS particles during isolation from a solution in water. The modification of LS with CA alleviated the concerns of inefficient curing encountered with unmodified LS particles. As a consequence, the cure characteristics improved and higher crosslink density achieved for compounds prepared with modified LS particles. The values of tensile strength and strain at break also improved as a result of better stress transfer across the interface of rubber and LS particles. The values of storage modulus increased and tan δ decreased with increase of CA content on modified LS particle surfaces. The method of modification presented in this work has strong promise in reduction of rolling resistance of filled rubber compounds.

The next chapter presents results on the use of second approach, whereby hybrid fillers were used to reduce filler networking.
CHAPTER V
HYBRID FILLERS FOR RUBBER COMPOUNDS BY NON-COVALENT
INTERACTIONS BETWEEN LIGNIN AND CARBON BLACK

This chapter focuses on the hybrid filler approach towards reducing filler networking in rubber compounds in order to achieve a good balance between energy dissipation and other rubber properties. Hybrid fillers were designed based on the non-covalent interactions between carbon black and lignin. These interactions were confirmed by Raman spectroscopy and measurement of $^1$H spin-lattice relaxation times. The impact of hybrid fillers on the carbon black filler networking and mechanical properties of the rubber compounds were also studied.

5.1 Introduction

As presented in Chapter II, page 6, lignin is an amorphous polymer derived from wood consisting of a phenylpropanoid backbone along with phenolic and benzylic hydroxyl, methoxyl, and carbonyl substitutions. Lignin has an abundance of functional groups on its surface which provide scope for chemical modification and adjustment of polarity to produce compatibility with appropriate matrix polymers. For example, lignosulfonates were shown to be more compatible with SBR matrix upon modification with cyclohexylamine. Other factors such as natural abundance, cost competitiveness, and good intrinsic mechanical properties make lignin attractive for development of plastic and rubber composites.
Nevertheless, large particle size and naturally occurring polarity are two responsible factors against more widespread usage of lignin as filler.\(^9\) The spray drying process limits the particle size of lignin obtained during delignification of cellulose. Commercial lignin shows particle sizes ranging from 10 μm to greater than 100 μm. Such particles are large, increase the viscosity of compounds via hydrodynamic effect\(^5\), and exhibit detrimental effects on mechanical properties. The above factors limit the usage of lignin as “drop in” replacement for conventional fillers in development of compounds of polymers and elastomers.

Some researchers demonstrated several means of reduction of particle size of lignin, for example, by digesting lignin in the presence of protic acid\(^2\), promoting self-assembly of lignin with cationic polyelectrolytes in aqueous solution\(^9\), or by co-precipitation.\(^3\) However, digestion in acid leads to degradation and breakdown of lignin\(^9\) which can also lead to a loss of its reinforcing abilities. On the other hand, the processes of co-precipitation and self-assembly with polyelectrolytes involve the use of aqueous media, which are deterrent to development of rubber compounds. In this work, a new and novel means is examined for alleviating two concerns associated with the use of lignin and carbon black in rubber compounds. The first concern relates to large particle size of lignin and the second concern relates to networking of carbon black particles in rubber compounds and large viscoelastic dissipation. Both these concerns are alleviated in this study by developing hybrid fillers from lignin and carbon black.

Hybrid fillers are vastly useful in rubber compounds for suppression of filler networking whereby the probability of particle-particle contacts and formation of particle networks is greatly reduced.\(^5\) The filler network formation and associated network
breakdown in rubber compounds with strain lead to energy dissipation and conversion of such dissipated energy into heat. A consequence of such energy dissipation is an increase of the rolling resistance of rubber compounds. Thus, efforts to increase the energy efficiency and to reduce the rolling resistance should consider suppression of filler particle networking in carbon black filled rubber compounds.

Ismail et al.\textsuperscript{100} reported improved mechanical and fatigue life performance of compounds of dry mixed, 29:1 by weight, silica and carbon nanotube hybrid filler in comparison with compounds of silica. Sapkota et al.\textsuperscript{101} observed reduction of Payne effect and storage modulus at lower strains by partially substituting carbon black with clay in compounds of natural rubber. These mixed fillers showed reduction of filler networking, although insufficient dispersion of clay particles led to reduction of tensile properties. The synergy between carbon nanotubes and carbon black in their hybrid fillers led not only to increases in storage modulus values but also in the values of loss tangent in compounds with polyisoprene.\textsuperscript{102} It is apparent that the synergy among filler particles does not always produce the desired effects. The most significant work on hybrid fillers was reported by Wang et al.\textsuperscript{103} These authors developed carbon black-silica dual phase filler to obtain better mechanical properties and an optimum balance of tire properties such as rolling resistance, wet traction, and wear resistance. Despite reporting successful implementation of hybrid fillers, fundamental understanding of why particular sets of hybrid fillers work or how research should be guided in the design of new hybrid filler systems is still missing.

The interactions of lignin, specifically sodium lignosulfonates (SLS), with carbon nanotubes have been studied by Liu et al.\textsuperscript{104} These authors obtained stable aqueous
dispersions of multi-walled carbon nanotubes (MWNTs) by grinding the MWNTs with SLS and attributed such stable dispersion to adsorption of SLS on the nanotube surfaces due to \( \pi-\pi \) stacking. However, no studies exist on interactions between lignin and carbon black particles, their unique morphologies, or their applications in development of rubber compounds. As is apparent from the discussion of prior work, research efforts exist on the use of combinations of carbon black, carbon nanotubes, and silica as hybrid fillers. However, very little work exists on development of bio-derived materials from plant sources and agricultural wastes as a component in hybrid filler systems for rubber compounds. Efforts to combine lignocellulosic materials in hybrid fillers for rubber compounds met with limited success. Attarangsan et al.\textsuperscript{105} reported drops in the values of tensile strength, 100\% modulus, and fatigue life in compounds of rubber with hybrid fillers of rice husk powder and carbon black apparently due to poor filler particle adhesion with rubber and large particle size of the rice husk powder (~12 \( \mu \)m).

In this chapter, the interactions between lignin and carbon black are first characterized using electron microscopy and spectroscopic techniques and then exploited in the development of hybrid filler systems.

5.2 Experimental

This section presents detailed information on the materials used in this study, hybrid filler preparation, and characterization techniques. In addition, the equipment and conditions used for characterization and testing of SBR compounds filled with hybrid filler are also described.
5.2.1 Materials

Two types of lignin particles were used in this work - kraft lignin (KL) powder from Weyerhaeuser (Federal Way, Washington) with molecular weight (M<sub>w</sub>) ~5090 g/mol, polydispersity index ~ 5.4, and glass transition temperature (T<sub>g</sub>)~128 °C and calcium lignosulfonate D618 (LS) particles obtained from Borregaard Lignotech (Rothschild, Wisconsin). The generic structure of these lignin molecules is the same. However, the sulfonate groups in LS particles promote its solubility in water. Carbon black grade N330 manufactured by Sid Richardson (Fort Worth, TX) and styrene butadiene rubber (SBR), grade SLF18B10 obtained from Goodyear Tire and Rubber Co were used in preparation of rubber compounds. The SBR contained 18.5 wt% styrene. The rubber curing package included zinc oxide powder, stearic acid in bead form, sulfur curing agent (Rubber Maker), and N-cyclohexylbenzothiazole-2-sulfenamide (CBS) accelerator, all obtained from Akrochem Corporation (Akron, OH).

5.2.2 Preparation of lignin – carbon black hybrid particles

Two types of hybrid fillers were prepared. The first hybrid fillers of KL and CB, designated as KL-CB, were prepared by dissolving KL in solvent (acetone for TEM, 0.5M NH₄OH for surface area measurement) and dispersing CB in the solution using ultrasound. The fillers were recovered by evaporating the solvent and used in characterization work by transmission electron microscopy (TEM) and Brauner-Emmett-Teller (BET) surface area analyzer. KL-CB particles were not used in preparation of rubber compounds. The second type of hybrid fillers, designated as LS-CB particles, was prepared from LS and CB. Carbon black particles were dispersed in solutions of LS in water by ultrasound for 30 minutes. The solid hybrid particles were recovered by slowly
evaporating water and then drying the residue in vacuum oven at 80 °C for 24 hrs. The particle agglomerates were milled to size below 100 micrometer and were used in preparation of rubber compounds. The LS-CB particles in rubber compounds contained LS and CB in the weight ratio 10:90 and 20:80, while LS-CB particles used in characterization by Raman spectroscopy contained LS and CB in weight ratio 3:1 and 1:1.

5.2.3 Rubber compound preparation

Rubber compounds of hybrid fillers were prepared in two steps. In first step, rubber was mixed with zinc oxide, stearic acid, and hybrid filler particles in a Brabender Plasticorder internal mixer of 80 cm³ volume at a rotor speed of 65 rpm and a fill factor of 0.7 at 80 °C. The rubber was masticated for 60 s and mixed with the rest of the ingredients for 5 minutes. The compounds obtained in step 1 were mixed with sulfur and CBS accelerator in a two roll mill for 5-7 min. at a speed of 15 rpm and a roll temperature of 40 °C. The rubber compounds contained the following ingredients based on 100 parts of SBR: 1 phr stearic acid, 3 phr zinc oxide, 1.75 phr sulfur, 1 phr CBS, and 30 phr hybrid filler. A control material was also prepared by compounding SBR and 30 phr of carbon black in the same manner. The flocculation of filler particles was studied using compounds of hybrid fillers and SBR with no curatives.

The rubber compounds for mechanical testing were cured in a compression press at 160 °C. The time needed to reach 95% of the maximum torque ($t_{95}$) was taken as the optimum curing time. A sheet mold with dimensions 150 mm x 150 mm and a thickness of 1.5 mm was used for curing of rubber compounds. The cured compounds or
vulcanizates were then used for determination of tensile and dynamic mechanical properties and morphology.

5.2.4 Characterization

This section gives information on the techniques and conditions used to characterize the lignin – carbon hybrid fillers and their compounds prepared with styrene butadiene rubber. Techniques along with the conditions employed are described in detail.

5.2.4.1 Transmission Electron Microscopy (TEM)

The morphology of KL-CB particles was studied using a TACNAI-12 transmission electron microscope by FEI (Hillsboro, Oregon) at a voltage of 120 kV. A drop of the particle suspension in acetone was cast on a TEM grid and the images were taken.

5.2.4.2 Scanning Electron Microscopy (SEM)

High resolution SEM images of KL-CB particles were taken using JEOL (Peabody, Massachusetts) JSM5310 scanning electron microscope to determine the shape and size of the particle aggregates. The morphology of SBR vulcanizates containing the LS-CB hybrid filler particles was examined using SEM. The vulcanizates were dipped in liquid nitrogen and fractured. All specimens were sputter coated for 1.5 min by a layer of silver under argon gas. The operating voltage of SEM was 5 kV.

5.2.4.3 Raman spectroscopy

Raman spectra of LS-CB hybrid particles were recorded using Horiba Scientific (Edison, New Jersey) LabRAM high resolution Raman spectrometer equipped with a Synapse CCD detector. Laser excitation length of 532.07 nm and 50x objective lens were
used for taking the images. The spectra were analyzed using IGOR pro curve fitting software.

5.2.4.4 Solid state NMR spectroscopy

All experiments were performed on Bruker Avance III 300 NMR spectrometer (Bruker Biospin; Rheinstetten, Germany) equipped with a 4 mm double resonance CP/MAS NMR probe. The $^1$H and $^{13}$C NMR frequencies were 300.1 and 75.5 MHz, respectively. $^{13}$C CP/MAS and $^1$H spin-lattice relaxation time in the laboratory frame ($T_{1H}$) experiments were obtained at a MAS frequency 12 and 4 kHz, respectively. Radio field (rf) strengths of $^1$H and $^{13}$C pulses were 62.5 kHz. The CP and recycle delay time were 1.5 ms and 2 s, respectively. High power $^1$H two pulse phase modulation decoupling with a field strength of 60 kHz was applied during signal acquisition. The $^{13}$C chemical shift was externally referenced to the CH signal of adamantine (29.5 ppm). $T_{1H}$ was obtained by inversion recovery method of $^1$H spins. The $^1$H rf field strength was 80 kHz. The relaxation value was obtained using equation (5.1),

$$\frac{Mz(t)}{Mz(0)}=1-2\exp\left(-t/T_{1H}\right) \quad \text{(5.1)}$$

where $M_z(0)$ and $M_z(t)$ are magnetizations along the longitudinal direction at a relaxation time of 0 and $t$, respectively.

5.2.4.5 Zeta potential measurements

The zeta potential values of carbon black and the LS-CB hybrid particles were obtained using a Zetasizer Nano series (model ZS90) by Malvern Instruments (Westborough, Massachusetts). LS particles were dissolved in deionized water and the insoluble solid was removed using a filter paper. CB particles were then added and stirred
in this solution to allow adsorption of dissolved LS molecules onto the surfaces of carbon black particles. The hybrid particles were recovered by filtering the suspension. The powder hybrid particles were dried and re-dispersed in water to perform zeta potential measurements. A suspension of hybrid particles of concentration 100 ppm was prepared by sonicating the powder in deionized water. In the same manner, a suspension of CB particles was prepared and used as a control. The pH of the suspensions was checked with a pH meter and was found to be the same (7.2) for suspensions of CB particles and the hybrid particles. All measurements were taken at room temperature (25 °C).

5.2.4.6 BET surface area of hybrid fillers

The surface area of hybrid fillers was obtained from nitrogen adsorption-desorption isotherms at room temperature measured using Micromeritics Tristar II 3020 Analyzer and calculated using Brunauer Emmet Teller (BET) method. The powder filler particles were first degassed at 70 °C for 12 h before collecting the data.

5.2.4.7 Filler flocculation experiments

Flocculation of filler particles at rubber curing temperatures may provide an estimate of filler networking that exist in the cured system. An idea about the filler networking can be gleaned from dynamic mechanical properties, such as storage modulus and loss tangent, of uncured compounds containing hybrid fillers. Note that these properties also influence the value of rolling resistance. In this context, the differences in flocculation behavior of hybrid fillers and carbon black were captured from dynamic mechanical properties.

The filler flocculation behavior was studied using an advanced polymer analyzer (APA 2000) based on the procedure described by Stöckelhuber et al.
pre-existing randomly flocculated structures in the rubber compound was eliminated before starting the measurements by subjecting the rubber compounds to 25% strain for 5 minutes. The value of storage modulus at 1% strain was then recorded for two hours. This was followed by a strain-sweep experiment from 1% to 70% strain to evaluate the Payne effect. The measurements were carried out at the curing temperature of the rubber compounds i.e. at 160 °C.

5.2.4.8 Cure analysis of compounds

The cure characteristics of the compounds were evaluated using approximately 5 g rubber compounds in a Moving Die Rheometer (MDR 2000) at a temperature of 160 °C, a frequency of 1.67 Hz, and a strain of 7%. The plots of torque vs. time were recorded and the curing parameters such as scorch time and cure time (t95) were calculated. The crosslink density was measured and calculated as per the method described in section 4.2.4.

5.2.4.9 Measurement of tensile properties

Dumb-bell shaped specimens as per ASTM D412, Type C method were punched out of cured sheets of rubber and tensile tests were conducted. These tests were carried out at room temperature using Instron® 5567 tensile tester at a crosshead speed of 500 mm/min. A minimum of 5 specimens were tested per sample.

5.2.4.10 Dynamic mechanical analysis

Dynamic mechanical properties were measured using TA Q200 (TA Instruments, New Castle, Delaware) dynamical mechanical analyzer. For this purpose, cured samples of dimensions 10 mm x 4.02 mm x 1.5 mm were cut out from cured sheets. The
temperature-sweep experiments were performed at 0.5% strain and 1 Hz frequency at a heating rate of 3 °C/min. The storage modulus is represented as \( E' \) since the measurements were performed in tension mode. The values of storage modulus and loss tangent (\( \tan \delta \)) were obtained at 60 °C. The values of \( \tan \delta \) are reported specifically at 60 °C since the damping factor as reflected from the values of \( \tan \delta \) at 60 °C gives a direct indication of viscous dissipation and rolling resistance in rubber compounds.\(^{48,55}\)

5.3 Results and Discussions

The preparation and characterization of lignin-carbon black hybrid fillers will be discussed in this section. Results on the filler flocculation, tensile properties, and dynamic mechanical properties of SBR compounds are presented.

5.3.1 Morphology of kraft lignin

Kraft lignin particles obtained after delignification process are usually a few hundred micrometer in size as evident from Figure 5.1(a). These particles do not offer much scope for reinforcement of polymers. The size of lignin particles and their morphology can be efficiently designed using proper solvents. KL particles, precipitated from a solution in acetone, appear spherical with diameter varying between 300 nm and 2 μm (Figure 5.1b). The particle size is found to be strongly dependent on the speed of evaporation of acetone – smaller particles result when acetone evaporates more quickly, e.g., from a small volume of stock solution. On the other hand, the platelet-like particle structures of widely varying size (20-100 μm) (Figure 5.1c) are obtained when KL is recovered by evaporation from an aqueous solution in 0.5 M \( \text{NH}_4\OH \).
Figure 5.1: Morphology of kraft lignin particles (a) as received (b) after precipitation from its solution in (b) acetone and (c) aqueous 0.5 M NH₄OH.

The dramatic difference in particle morphology seen in Figure 5.1 is attributed to the difference in solvent evaporation rates. Acetone evaporates quickly due to high vapor pressure, e.g., 180 mm of Hg at 20 °C versus 17.5 mm of Hg for water also at 20 °C. As a consequence, lignin molecules pack in a spherical domain, minimize the surface energy, and promote evaporation of acetone by forming small particles. On the other hand, lignin precipitates as soon as ammonia molecules leave the aqueous solution and random micrometer size particles are obtained as in the case depicted in Figure 5.1(c). The spherical nanomorphology of kraft lignin in thin films was reported in the literature²⁴,¹⁰⁷, although the bulk morphology seen in Figure 5.1(b) was not reported in literature to the best of our knowledge.

The spherical nanometer size kraft lignin particles in Figure 5.1(b), although look attractive, were not used in preparation of rubber compounds in this work as acetone
must be used as the solvent. Our approach to obtain “green” filler materials for rubber compounds calls for the usage of more innocuous solvents, such as water. Nevertheless, the interactions between lignin and carbon black particles were studied using these spherical kraft lignin nanodomains. The nanometer size of these spheres can easily help identify the changes in the morphology as a result of any non-covalent interactions with carbon black particles.

5.3.2 Morphological evidence of interaction between lignin and carbon black

KL molecules consist of phenylpropane units and hydroxyl groups attached to the aromatic and aliphatic carbon atoms. A representative structure of lignin is shown in Figure 2.1. It is apparent that lignin molecules can undergo π–π interactions with other molecules of similar structures. The ability of lignin to interact with carbon black particles via non-covalent π–π interactions was explored by considering solution of KL molecules in acetone and the results are presented in this section.
The spherical nano-domains of kraft lignin molecules organized due to evaporation of acetone from its 0.2 wt% solution are presented as TEM images in Figure 5.2(a). Carbon black primary particles (~30 nm) form non-spherical aggregates of typical size ~100 nm as revealed from the TEM image shown in Figure 5.2(b). The KL-CB hybrid particles are also non-spherical (Figures 5.2c and 5.2d). In this case a drop of suspension of CB in KL
solution in acetone was allowed to evaporate on a copper grid for TEM. Figures 5.2c and 5.2d reveal that carbon black particles are coated by layers of lignin.

Figure 5.3: SEM images of (a) as-received CB-N330 particles, (b) hybrid particles with 1:1 wt ratio of KL and CB obtained from evaporation of aqueous solution of ammonium hydroxide.

The morphology of bulk KL-CB hybrid particles isolated from a dispersion of carbon black in 1 M ammonium hydroxide solution of KL is apparent from the SEM images in Figure 5.3(b). The carbon black particles are found coated by KL molecules similar to what is seen in TEM images in Figure 5.2(c-d). However, it is seen in Figure 5.3(b) that not all CB particles were coated by lignin even when 1:1 weight ratio of KL and CB was used. Similar images were obtained for LS-CB particles, indicating that the basic structural units of lignin drive its interactions with carbon black particles.

Some of the advantages of particle morphology seen in Figure 5.2(c-d) and Figure 5.3(b) are presented as follows:
(1) Figure 5.2(c) confirms that the fractal structure of carbon black is retained in the hybrid fillers.

(2) In KL-CB hybrid fillers, lignin is now present as coating layers of CB particles, instead of large, micrometer size particles of lignin seen in Figure 5.1(a).

(3) Lignin coating on CB particles should reduce the filler networking of CB since it reduces the probability of one CB particle to come in contact with another CB particle. Thus, it is anticipated from the fractal nature of KL-CB particles that these hybrid fillers present promise for reinforcement of rubber as with CB, while a part of CB can be substituted for by the naturally occurring lignin particles.

We now recall from Figure 2.3 that carbon black particles also contain aromatic groups and are capable of π-π stacking with lignin. Such interactions occur while CB particles are in dispersion in acetone and water. Consequently, carbon black particles can act as nucleating sites on which lignin molecules precipitate during solvent evaporation and form the coating layers. In the following section, the results of Raman and solid state NMR spectroscopy are presented for evaluation of the nature of such interactions.

5.3.3 Characterization of lignin carbon black hybrid fillers

Having seen the morphological evidence of existence of interactions between lignin and carbon black, this section now presents the Raman and solid state NMR spectroscopic evidences of interactions between lignin and carbon black.

5.3.3.1 Raman Spectroscopy of lignin – carbon black hybrid particles

The Raman spectra of carbon black and lignosulfonate-carbon black hybrid fillers are presented in Figure 5.4. The LS-CB hybrid particles were prepared by dispersing CB in solution of LS in deionized water followed by evaporation of water. The spectra were de-
convoluted into three peaks\textsuperscript{108–110} to produce a composite curve that fit well with the experimental curve as shown in Figure 5.4(b). The graphitic crystal structures and the amorphous carbon in carbon black particles contribute to the Raman intensity. The first high intensity peak at 1580-1600 cm\textsuperscript{-1} is attributed to the G-band arising from graphitic crystal lattice vibrations in carbon black. The second high intensity peak (D-band) is located at \( \sim 1350 \text{ cm}^{-1} \) and is obtained due to the defects/disorders in graphitic crystal lattices. The third peak seen at \( \sim 1500 \text{ cm}^{-1} \) is obtained due to the presence of amorphous carbon in carbon black.\textsuperscript{108,111}
Figure 5.4: (a) Raman spectra. Curves (1) CB N330 particles, (2) LS-CB 1:1 ratio by weight, and (3) LS-CB 3:1 ratio by weight, (b) representative curve fitting of Raman spectrum of CB N 330 (actual spectrum (red), fitted curve (blue), peak assignments (green)).

The relative intensity of the D-band ($I_D$) to the G-band ($I_G$), designated as $I_D/I_G$ in Figure 5.4a is seen reduced in hybrid particles (curves 2 and 3); the reduction is greater at higher content of lignin. It is noted that the D-band or the defect band appears due to the presence of defects or disorder in the graphitic crystal structures in carbon black. These defects or disorders in carbon black mostly occur at the edges of the graphitic crystallites. The edges of the crystallites are regarded as the highest energy sites in carbon black due to high concentration of $\pi$ electrons. Thus, a reduction in intensity of the D-band relative to the G-band in hybrid particles can be attributed to the interactions
between lignin molecules and carbon black particles via π–π stacking. Similar conclusions were drawn for interactions of CNTs with sodium lignosulfonate.\textsuperscript{104}

Another indication of strong interactions between lignosulfonate molecules and carbon black particles is the shift of D- and G-band peaks to higher wavenumbers with an increase of the concentration of lignosulfonate in hybrid particles. The D-band shifts from 1343 cm\(^{-1}\) for CB particles to 1361 cm\(^{-1}\) and 1367 cm\(^{-1}\) respectively for the 1:1 and 3:1 weight ratio of lignin – carbon black hybrids. The G-band, however, shows a slightly smaller shift from 1586 cm\(^{-1}\) to ~ 1590 cm\(^{-1}\) for the hybrid particle system. The much larger peak shift in the D-band is again an indication that lignin interacts with carbon black particles at the edges of the crystallites where the concentration of π bonds is high. Also, the D-peak shift by almost 20 wavenumbers is an indication that the interactions between lignin and carbon black are very strong, requiring an increase in the energy for sustaining vibrations. Although π–π interactions are considered weaker than some other non-covalent interactions, such as hydrogen bonding, the greater numbers of sites in lignin and carbon black particles promote π – π stacking and contribute to the strength of these interactions.

5.3.3.2 Solid state NMR of lignin – carbon black hybrid particles

Figure 5.5(a) shows $^{13}$C CPMAS NMR spectra of lignin and the hybrid filler with a weight ratio of 1. The OCH\(_3\) and OCH\(_2\) groups appear at 55 and 60 - 80 ppm, respectively. The aromatic and C=\(\text{C}\) carbons appear at 110 – 130 ppm and CO carbon appears at 147 ppm.\textsuperscript{113} Individual peaks are quite broad, thus it is difficult to draw specific intermolecular interactions between lignin and carbon black from the chemical shift values. Only the aromatic signals at around 110 - 130 ppm in the hybrid filler is
slightly enhanced compared to the lignin spectrum, which is attributed to aromatic components in carbon black.

![Figure 5.5](image)

**Figure 5.5:** (a) $\text{^{13}C}$ CPMAS NMR spectra and (b) $T_{1H}$ relaxations of lignosulfonate (blue) and lignosulfonate-carbon black hybrid particles (red) with a weight ratio of 1.

The $T_{1H}$ measurement is an alternative means to investigate the intimate mixing of heterogeneous components. If two components have different relaxation values in pure states, $^1\text{H}$ relaxation values are utilized to investigate the degree of mixing of the two components. When two components are miscible on certain nanoscales, effective spin diffusion between the two components leads to the averaged relaxation value. On the other hand, if two components have heterogeneous domain structure at scales more than the nanoscale, spin diffusion process does not average out $T_{1H}$ values of the two components.

Figure 5.5(b) depicts $T_{1H}$ relaxation behaviors of the hybrid films (red filled circles) and lignin (blue filled circles) at room temperature. The relaxation process is analyzed in terms of single exponential behavior. Using equation 5.1, the solid curves give best fit
values of 80 and 21 ms for the lignin and the hybrid film respectively. The observed single component for the hybrid system indicates that $^1$H spin diffusion effectively occurs between lignin and carbon black within $T_{1H} = 21$ ms. Under the assumptions of stacked sandwich structures of lignin and carbon black (one dimensional spin diffusion), the average heterogeneous length scale $<r>$ can be expressed in terms $<r> = (4/3*D*T_{1H})^{1/2}$,\textsuperscript{114} where $D$ is spin-diffusion constant and $D = 0.8$ nm$^2$/ms of glassy polymers\textsuperscript{115} is used for the hybrid system whose $^1$H line width at half height is ca. 30 kHz. Simple spin-diffusion equation roughly indicates that heterogeneous length scale of the hybrid film is less than ca. 5 nm.

5.3.4 Zeta potential measurements

The changes in the values of zeta potential also provide evidence of adsorption of lignin molecules on the surfaces of CB particles. Suspensions of CB particles before and after adsorption of LS at the same pH (7.2) and the same level of solids at 100 ppm were used for such measurements. The values of zeta potential were measured at 25°C. The average values of zeta potential from 10 experimental runs are reported in Table 5.1.

Table 5.1. Zeta potential values of carbon black before and after adsorption of lignin at 25°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zeta potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CB N330 in water</td>
<td>-32 ± 1.4</td>
</tr>
<tr>
<td>CB N330 in solution of LS in water</td>
<td>-40.8 ± 2.4</td>
</tr>
</tbody>
</table>

It is seen from the data in Table 5.1 that the value of zeta potential of carbon black reduced significantly from -32 ± 1.4 mV to -40.8 ± 2.4 mV when dispersed in solution of lignosulfonate. This is due to adsorption of LS molecules onto the surfaces of carbon
black particles. The adsorbed molecules of lignosulfonate contribute anionic groups such as sulfonate, phenoxide, and carboxylate groups\textsuperscript{116} on the surface of hybrid particles leading to higher net negative change and smaller value of zeta potential.

5.3.5 BET surface area of hybrid fillers

The surface area of hybrid particles was first measured and compared with that of carbon black particles. Note that favorable carbon black-rubber interactions are promoted by high surface areas. The surface area of KL-CB hybrid filler particles determined from BET measurements are listed in Table 5.2.

Table 5.2. BET surface area of lignin-carbon black hybrid filler particles.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>KL:CB wt. ratio in hybrid filler</th>
<th>BET surface area (m\textsuperscript{2}/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Carbon black N330</td>
<td>72.7</td>
</tr>
<tr>
<td>2</td>
<td>10:90</td>
<td>66.9</td>
</tr>
<tr>
<td>3</td>
<td>20:80</td>
<td>60.9</td>
</tr>
<tr>
<td>4</td>
<td>50:50</td>
<td>30.8</td>
</tr>
</tbody>
</table>

It is evident that BET surface area dropped as the concentration of lignin in the hybrid filler was increased. This implies greater coverage of carbon black surfaces by lignin molecules. Among the three hybrid fillers, the most significant drop in surface area occurred in the case of 50:50 weight ratio of KL to CB. Hence, anticipating poor reinforcement, the 50:50 weight ratio of lignin to CB in hybrid fillers, was not considered
for rubber property evaluations. The BET surface area of hybrid fillers with 10:90 KL to CB shows less than 10% reduction.

5.3.6 Filler flocculation test

The flocculation experiments were carried out using uncured rubber compounds containing 30 phr filler. The values of storage modulus ($G'$) as functions of time and percent strain are presented respectively in Figures 5.6(a) and 5.6(b). The data in Figure 5.6(a) give an indication of the flocculation behavior of the filler particles, e.g., a growing value of storage modulus with time implies gradual filler network formation or flocculation of filler particles in the compound. The values of storage modulus with breakdown of flocculated structures in response to implied strain are presented in Figure 5.6(b). Such behavior is reminiscent of the Payne effect observed in cured rubber compounds. Payne effect describes the non-linear decrease in storage modulus with strain\cite{68}; greater reduction in storage modulus is associated with greater energy release upon application of strain.

The following trends are evident from the data presented in Figure 5.6. First, carbon black shows much higher flocculation tendency compared to hybrid fillers. Second, the slope of the flocculation curve decreases with increasing lignin concentration in the hybrid filler. Third, the reduction of storage modulus values with strain is much less severe for hybrid filler indicating lower energy dissipation.
Figure 5.6: Storage modulus values as function of time (a) and as function of strain (b).

The trends in Figure 5.6 can be rationalized using the following arguments. The solid-state NMR, Raman spectroscopy, and zeta potential data conclusively presented evidence for close association between lignin molecules and carbon black particles in hybrid fillers. Consequently, the flocculation of carbon black particles due to van der Waals
interactions is significantly subdued. Thus, the hybrid fillers present strong potential for reduction of filler networking and lower rolling resistance in rubber compounds, provided the cured rubber compounds of hybrid fillers also meet the desired tensile property targets.

5.3.7 Rubber compound properties and morphology of hybrid filler particles

The rubber compounds evaluated for property evaluations were: (1) SBR-0F i.e. unfilled SBR, (2) SBR-30CB i.e. SBR filled with 30 phr of carbon black, (3) SBR-30LSCB1090 i.e. SBR filled with 30 phr of LS-CB hybrid filler consisting of LS and CB in 10:90 ratio by weight, and (4) SBR-30LSCB2080 i.e. SBR filled with 30 phr of LS-CB 20:80 hybrid filler consisting of LS and CB in 20:80 ratio by weight.

The tensile strength at failure of the rubber vulcanizates reflects the true reinforcement behavior of the hybrid fillers. The values of tensile strength of cured compounds of carbon black and hybrid filler particles are presented in Figure 5.7.

![Figure 5.7: Tensile strength of SBR vulcanizates filled with 30 phr filler.](image-url)
As seen in Figure 5.7, the tensile strength of the LS-CB hybrid filler with 10:90 LS:CB by weight is close to the values obtained with only carbon black. This closeness in values can be attributed to the remnant fractal morphology of the hybrid filler particles. However, the tensile strength drops dramatically for the compound with 20:80 weight ratio of LS to carbon black. The SEM images in Figure 5.8 present some valuable insights.

Figures 5.8 (a) and (b) show that carbon black aggregates dispersed very well in the rubber compound. The CB particle aggregates visible in the images show size of about 100 nm. The SEM image of the compound of 10:90 hybrid filler (Figure 5.8c-d) shows 100 nm carbon black aggregates dispersed in rubber matrix in addition to hybrid filler domains consisting of carbon black particles separated by lignin. The concentration of lignin in this hybrid filler was much smaller than the concentration of carbon black. Thus, as supported by SEM image in Figure 5.3(b), not enough lignin was present to completely coat all carbon black particles. Instead, it quite possibly entered the space between the primary particles and prevented the carbon black particles from forming a network of its own. The presence of large particle aggregates in SEM images in Figure 5.8(e) also provides evidence of strong interactions between lignin and carbon black, which resist breakage of the networks and dispersion by shear forces during compounding.
Figure 5.8: SEM images of fracture surfaces of SBR vulcanizates containing 30 phr of CB (a,b), 10:90 LS:CB (c,d), and 20:80 LS:CB (e)

The SEM images of compounds containing LS and carbon black in the ratio of 20:80 show large number of particles of size 20-50 μm. Note in this case that greater number of CB particles were coated and became stiffer in this case than in the case of LS:CB ratio of 10:90. These aggregates could not break and easily disperse in the rubber. This is
reflected in low values of tensile strength in Figure 5.7. Thus, it is critical to use enough lignin in the design of hybrid fillers. The lignin to carbon black ratio should be enough to prevent carbon black filler networking and at the same time not affect the reinforcing behavior of carbon black. As is evident from the tensile strength and filler flocculation data, the 10:90 weight ratio of lignin to carbon black is acceptable as it provides a balance between reinforcement and suppression of flocculation.

Table 5.3. Comparison of properties of carbon black filled and hybrid filler filled SBR vulcanizates

<table>
<thead>
<tr>
<th>Property</th>
<th>SBR-OF</th>
<th>SBR – 30CB</th>
<th>SBR – 30LSCB 10:90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apparent XLD (kmol/m³)</td>
<td>0.08</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>Elongation at Break (%)</td>
<td>247.2 ± 22.7</td>
<td>408.1 ± 29.7</td>
<td>724.7 ± 13.1</td>
</tr>
<tr>
<td>100% Modulus (MPa)</td>
<td>1 ± 0.02</td>
<td>2.09 ± 0.04</td>
<td>1.59 ± 0.07</td>
</tr>
<tr>
<td>Storage Modulus E’ (MPa)</td>
<td>2.5</td>
<td>6.0</td>
<td>5.4</td>
</tr>
<tr>
<td>Tan Delta</td>
<td>0.04</td>
<td>0.10</td>
<td>0.132</td>
</tr>
</tbody>
</table>

The values of representative mechanical and dynamic mechanical properties of carbon black and hybrid filler with 10:90 LS:CB ratio are listed in Table 5.3. The method of measurement of apparent crosslink density is reported elsewhere. The apparent crosslink density of the compounds of hybrid filler was much lower than the compound of CB. This can be attributed to the polarity of lignin, which essentially can cause insufficient vulcanization due to interactions with other polar curing ingredients such as stearic acid and the amide accelerator. The reduction in crosslink density also leads to a drop in 100% modulus and an increase in elongation at break and the loss tangent.
values. However, the issue of lowered XLD upon addition of lignin can be solved by surface modification as will be demonstrated in the next section.

As seen in Table 5.3, the loss tangent of the compounds of hybrid filler at 60 °C is higher than that of the compounds of carbon black, indicating greater viscoelastic loss in the former compounds. This contradicts the results obtained from the filler flocculation experiments. The loss tangent of compounds is dependent on a number of factors such as filler networking in the rubber, the filler-rubber interactions, and the contribution of the polymer matrix. In view of the different crosslink density values reported in Table 5.3, the rubber contribution to the loss tangent was not the same in compounds of only carbon black and the hybrid filler. This quite possibly masked the positive effect of reduced filler networking in compounds of hybrid fillers. In view of this, compounds of hybrid filler were prepared using greater amounts of curative to match the apparent rubber crosslink density value of the compound of carbon black. The loss tangent value of the new compound is compared in Table 5.4.

Table 5.4. Tan delta values for carbon black and 10:90 lignin carbon black filled SBR with similar apparent XLD

<table>
<thead>
<tr>
<th>Property</th>
<th>SBR – 30CB</th>
<th>SBR – 30LSCB 10:90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tan Delta</td>
<td>0.10</td>
<td>0.089</td>
</tr>
</tbody>
</table>

Now that the rubber contribution was the same, the loss tangent of the compound of hybrid filler is lowered by 10%. The results correlate well with the filler flocculation experiments showing that LS-CB hybrid fillers can reduce carbon black network formation leading to lower energy dissipation.
5.3.8 Cyclohexylamine (CA) modification of lignosulfonate – carbon black hybrid fillers

This section examines the effects of surface modification of lignosulfonate – carbon black hybrid fillers using CA and the effects of surface modification on the reinforcing behavior of SBR compounds. As seen in Chapter IV, CA helps suppress the polarity of lignin to derive compatibility with non-polar rubber matrix. This compatibility manifests itself in the form of improved cure performance, tensile properties, and dynamic mechanical performance. In addition, the modified lignin-rubber interface also allows efficient stress transfer across the interfaces. The hybrid particles alleviated the concerns associated with large particle size (~ 100 µm) of LS when they are used as drop-in fillers. In LS-CB hybrid particles, lignin exists as coating layers on carbon black particles.

LS-CB hybrid particles modified with CA were prepared as follows. First, a 10:90 ratio of LS-CB hybrid particles were prepared as highlighted in section 5.2.2 on page 92. These hybrid particles were then modified with 0.1 g of CA/g of LS, following a process described in section 4.2.2 on page 69. The procedure for compound preparation, curing, and characterization are discussed in detail in section 5.2.3 and 5.2.4. The compounds evaluated in this study are: (1) SBR-0F i.e. unfilled SBR, (2) SBR-30CB i.e. SBR filled with 30 phr of carbon black, (3) SBR-30LSCB1090 i.e. SBR filled with 30 phr of LS-CB hybrid filler consisting of LS and CB in 10:90 ratio by weight, and (4) SBR-30LSCB1090-CA i.e. SBR filled with 30 phr of LS-CB 10:90 hybrid filler modified with CA.

5.3.8.1 Cure analysis of compounds of surface modified hybrid particles.

Figure 5.9 shows the cure parameters of rubber compounds cured at 160 °C in a moving die rheometer. It is apparent from the data that the scorch time and the cure time
of unmodified hybrid fillers are much longer than the compounds of carbon black. As stated before, this is due to inefficient vulcanization caused by interactions of lignin with the curing agents. This was already discussed in Chapter IV, section 4.3.4, page 79.
However, the scorch time and the cure time of compounds of modified hybrid fillers are reduced by 6% and 30% respectively and are comparable to the scorch time and cure time of the compound of carbon black. The torque difference values are an indication of the crosslink density. It is seen that the torque difference improved significantly upon modification with CA. The CA molecules helped suppress the polarity of the LS coating layers on CB and hence reduced its interaction with the curatives used. Also, the amines are known to accelerate the curing and to produce higher degree of crosslinking.\textsuperscript{94,95}

5.3.8.2 Tensile properties of compounds of CA modified hybrid fillers

The values of tensile strength, strain at break, and 100% modulus are presented in Table 5.5. The tensile strength of compounds of hybrid fillers is seen to be comparable to the value obtained with carbon black. The tensile strength does not show an increase for CA-modified hybrid fillers within an experimental error range. As the tensile strength of compounds of unmodified hybrid filler is comparable to the tensile strength of the
compounds of carbon black, the surface modification of hybrid fillers with CA was not anticipated to improve the tensile strength significantly.

Table 5.5. Comparison of the properties of SBR vulcanizates filled with modified and unmodified hybrid fillers based on LS and CB.

<table>
<thead>
<tr>
<th>Property</th>
<th>SBR – 30LSCB</th>
<th>SBR-30LSCB1090-1090</th>
<th>SBR-30CB-CA</th>
</tr>
</thead>
<tbody>
<tr>
<td>XLD (kmol/m³)</td>
<td>0.06</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>12.5 ± 0.7</td>
<td>12.6 ± 1.34</td>
<td>12.8 ± 1.54</td>
</tr>
<tr>
<td>Strain at Break (%)</td>
<td>724.7 ± 13.1</td>
<td>636 ± 27</td>
<td>408.1 ± 29.7</td>
</tr>
<tr>
<td>100% Modulus (MPa)</td>
<td>1.59 ± 0.07</td>
<td>1.75 ± 0.03</td>
<td>2.09 ± 0.04</td>
</tr>
</tbody>
</table>

On the other hand, the crosslink density and the 100% modulus showed 30% and 10% increase respectively with modification by CA. The improvement in crosslink density and 100% modulus can be attributed to reduced polarity of LS after modification with CA. The reduced polarity also causes a reduction in interactions of lignin with the curing agent molecules and helps in attaining additional crosslinking. The stiffness achieved upon additional crosslinking is responsible for the increase in 100% modulus. It is also responsible for the 12% reduction seen for strain at break for the modified hybrid filler compound.

5.3.8.3 Morphology and dynamic mechanical properties of SBR compounds filled with CA-modified hybrid filler.

SEM images of fractured surfaces of SBR compounds filled with unmodified and CA-modified hybrid particles were used to infer dispersion of the fillers in rubber compounds. These SEM images are presented in Figure 5.10. The images 5.10 (b) and (d)
are enhanced versions of (a) and (c) respectively and show the hybrid filler domains highlighted. It is evident from Figure 5.10 (a) and (b) that the strong interactions between LS and CB make the breakdown of the hybrid domains below sizes of 20 \( \mu \text{m} \), difficult. However, the SEM images of SBR compounds with CA-modified hybrid fillers at roughly the same magnification (Figure 5.10 (c) and (d)), show the absence of domains of size 20 \( \mu \text{m} \) or larger.

![Figure 5.10: Morphology of fractured surface of SBR compounds filled with (a) (b) unmodified and (c) (d) CA-modified LS-CB hybrid particles. The images (b) and (d) are enhanced versions of (a) and (c) respectively with hybrid filler domains outlined.](image)
The reduction in the filler domain size upon CA modification can be attributed to the improved interactions between the lignin coating layers on CB and the rubber matrix which led to enhanced hybrid filler dispersion in SBR.

![Graph showing storage modulus and tan δ](image)

Figure 5.11: Dynamic mechanical properties (a) storage modulus (b) tan δ of SBR compounds filled with CA modified and unmodified LS-CB hybrids at 0.5% strain.

The storage modulus of the compounds show small drop from 5.4 MPa for unmodified LS-CB hybrid to 5.25 MPa for LS-CB hybrid modified with CA, as seen in Figure 5.11. This is counter-intuitive since the crosslink density increased upon modification of the hybrid filler with CA. An increase in XLD generally results in higher elasticity and hence, higher value of storage modulus. However, the storage modulus at low strains (e.g. 0.5%) is heavily dependent on the state of rubber-filler and filler-filler interactions. As seen from the SEM images in Figure 5.10 (c) and (d), the CA modification of hybrid filler led to enhanced dispersion due to improved polymer-filler
interactions. These improved polymer-filler interactions cause a further reduction of filler networking and hence are responsible for the lowered values of storage modulus at low strains.

The drop in the value of tan δ (E''/E') in spite of a drop in E' can also be attributed to the improved polymer-filler interactions upon CA modification of the hybrid filler. The results presented in this section show that CA modification is effective in improving the reinforcing performance of LS in SBR as seen in Chapter IV, as well as in enhancing the properties of SBR filled with LS-CB hybrid fillers.

5.4 Conclusions

The study demonstrates how the π-π interactions between two seemingly incompatible filler materials - lignin and carbon black - can be used to create novel hybrid filler particles for rubber compounds. The study shows that the surface characteristics and the morphology of the hybrid particles can be controlled by the ratio of the two materials in the hybrid. It is seen that both kraft lignin and lignosulfonate molecules are capable of forming coating layers on CB particle aggregates and that the coating layers maintain the fractal nature of CB particles. Raman spectroscopy analysis and solid state NMR confirmed that the interactions between lignin and CB occur due to π stacking over length scales of several nanometers. These results are further confirmed by zeta potential measurements.

The hybridization of lignin and carbon black is shown to be advantageous on a number of accounts. First, it alleviates the concerns associated with the detrimental effects of large particle size of lignin on mechanical properties of rubber compounds; the hybridization process renders lignin coatings on CB particles and that lignin does not
appear as separate particles in rubber compounds. Second, the process subdues networking of carbon black in rubber compounds by the dual action of lignin coating layers and the filling of the space between carbon black primary particles; both these effects make the hybrid particle aggregates stiffer. Accordingly, the hybrid particles do not undergo as much flocculation as CB. This is reflected in the lowering of loss tangent values of rubber compounds of hybrid fillers for rubber networks of a given crosslink density. The study provides data in support of partial replacement (up to 10 wt%) of CB in rubber formulations with bio-derived, energy efficient, and less expensive lignin. A reduction in the amount of CB by 10 wt% would lead to annual savings of approximately 300 million pounds of carbon black just for the tire industry.

However, one of the drawbacks of using hybrid fillers is the poor cure performance obtained due to the presence of lignin. This drawback was shown to be resolved by CA modification of LS-CB hybrid fillers. The CA modification not only improved the cure performance, but further enhanced the dispersion and dynamic mechanical performance of SBR compounds filled with LS-CB hybrid fillers.
CHAPTER VI
POLYBUTADIENE-g-POLYPENTAFLUOROSTYRENE AS A COUPLING AGENT FOR LIGNIN FILLED RUBBER COMPOUNDS

This chapter explores the coupling agent approach to increase polymer–filler interactions in order to improve the reinforcing behavior of lignin in addition to reducing the energy dissipation of the rubber compounds. A coupling agent was synthesized and designed to explore the non-covalent interaction as a route of coupling. These interactions were confirmed by UV-vis spectroscopy and morphological evidence was obtained from SEM images. The efficacy of PB-g-PPFS as a coupling agent was evaluated based on the improvements in tensile properties, dynamic mechanical properties, and dispersion of the filler.

6.1 Introduction

Lignin is an amorphous, polyphenolic material and is one of the main components of vascular plants and a by-product of the pulp and paper industry. It is second only to cellulose in natural abundance as an organic polymer. The main function of lignin in wood and other vascular plants is to mechanically strengthen the cell walls. This natural polymer is a complex, three-dimensional structure that lacks the regular and ordered repeat units typically found in other natural polymers such as cellulose. Three alcoholic monomers form the basic building blocks of lignin polymer: coniferyl alcohol (1), sinapyl alcohol (2), and p-coumaryl alcohol (3); Their structures are presented in
Figure 6.1. In view of the generic lignin building blocks depicted in Figure 6.1, and the representative structure of kraft lignin in Figure 2.1, one can deduce that the chemical make-up of lignin consists of benzene rings containing alkyl, alkoxy, and hydroxyl substituents. The substituents make lignin molecules electron-rich. The types of substituents vary based on the delignification methods employed. For example, kraft lignins are more electron-rich than lignosulfonates since the sulfonate groups on the benzene rings in lignosulfonate are electron withdrawing in nature.

The presence of hydroxyl, carbonyl, and carboxyl substituents in lignin makes lignin polar, hence, incompatible with non-polar polymers such as rubber. As a consequence, lignin does not show good reinforcement of the rubber if mixed without chemical modification. One way to derive compatibility of lignin is chemical surface modification. Another way is to use a coupling agent. This study is focused on the coupling agent approach for improvement of rubber-filler interactions and for enhancement of mechanical and viscoelastic properties of rubber compounds.

Coupling agents are used in rubber compounding to provide a bridge or a link between the filler and the rubber matrix. These bridges or links can be physical or
chemical in nature. The high surface area and the propensity of chemical activity on the filler surfaces due to the presence of functional groups on the filler surfaces provide latitude for an array of coupling agents provided some elementary requirements are met. The coupling agent should not exert negative influence on rubber properties. Examples can be reduction of mechanical properties, higher swelling, high volatility and loss during compound preparation, and health hazards. If these requirements are met, the coupling agent designs should allow the following attributes: The coupling agent (a) aids processing of rubber, (b) increases the stiffness of the vulcanizate, (c) reduces energy dissipation, and (d) improves the failure properties of the vulcanizates due to enhanced dispersion.\textsuperscript{120} An example of chemical coupling agents are silanes for silica-rubber compounds, known since the 1970s.\textsuperscript{121,122} Silane coupling agents such as bis(triethoxysilylpropyl) tetrasulfane (TESPT), react with the silica surfaces via hydrolysis and condensation reactions and form Si-O-Si linkages. Another part of the coupling agent molecules, the tetrasulfane groups, break down and release sulfur, which in turn, participates in curing reactions to form the covalent bonds between the coupling agent and the rubber.\textsuperscript{123}

A number of studies reported the use of coupling agents to derive compatibility between lignin and the polymer. Kharade et al.\textsuperscript{124} showed that the addition of ethylene acrylic acid copolymer or a titanate based coupling agent improves the mechanical properties of compounds of lignin and polyolefins. Luo et al.\textsuperscript{125} reported that the use of ethylene vinyl acetate (EVA) copolymer and polyethylene grafted maleic anhydride (PE-g-MA) as coupling agents for LDPE/lignin systems improved the toughness and elongation, and the tensile strength and modulus respectively aided by much improved...
dispersion of lignin in LDPE. Similar results were reported by Toriz et al.\textsuperscript{126} for PP/lignin systems compatibilized with PP-g-MA. Mohanty et al.\textsuperscript{127} reported the use of polymeric methylene diphenyl isocyanate (PMDI) as a coupling agent for lignin - switchgrass hybrid fillers for development of poly(butylene succinate) (PBS) compounds. These authors showed that PMDI, acted as a compatibilizer via mechanical interlocking or via the formation of urethane linkages by reactions between the –OH group of lignin and the –NCO group of PMDI. These compounds showed improvements in mechanical and heat deflection properties. Not much work is reported on the use of coupling agents for lignin-rubber compounds with the exception of Benko et al.\textsuperscript{27} These authors showed that functionalized lignins, when used with TESPT type coupling agents, impart higher stiffness and lower energy dissipation compared to the compounds with no coupling agent.

6.1.1 Polybutadiene-g-polypentafluorostyrene (PB-g-PPFS)

The current study focuses on non-covalent coupling between lignin and rubber and uses a PB-g-PPFS graft copolymer as the coupling agent. The structure of PB-g-PPFS is presented in Figure 6.2. The graft copolymer consists of PPFS homopolymer grafted onto the main chain of PB. The PB-g-PPFS graft copolymers were first investigated by Paz-Pazos et al.\textsuperscript{128} The PPFS homopolymers are more thermally stable and are resistant to photo-oxidation than PS and can be readily polymerized under milder conditions than the pressurized conditions necessary for aliphatic fluoropolymers.\textsuperscript{128} These graft copolymers combine the elastomeric properties of PB with the low surface energy and high UV, chemical, and thermal stabilities of PPFS.\textsuperscript{128}
The rationale for using PB-g-PPFS graft copolymers as a non-covalent coupling agent in compounds of rubber and lignin are presented as follows. First, the pentafluorostyrene contains electron-deficient π-ring system whereas lignin has phenolic structures (Figure 2.1) which also contain electron-rich π-ring system. Thus, the aromatic fluorocarbons in PPFS can interact with the aromatic hydrocarbons in lignin by π–π stacking via arene-perfluoroarene interactions. The proposed π–π stacking is demonstrated in Figure 6.3(a).

Second, the PPFS grafts are attached to the PB backbone, which in turn, is compatible with SBR rubber. It is known that SBR and PB are blended together to obtain better balance of tire properties as PB improves the wear and rolling resistance in the compounds. Consequently, PB and SBR compatibility is brought by one end of the compatibilizers, while PPFS and lignin interact via π–π stacking.
6.1.2 Arene – perfluoroarene interactions

A vast assortment of stacking phenomena in chemistry and biology are attributed to non-covalent interactions or intermolecular forces between the aromatic groups. The double helix of a DNA strand is an evidence for these types of stacking interactions.\textsuperscript{130} Considerable work is devoted to arene-arene (π-π) interactions, but interest has grown recently on study of the interactions between arene-perfluoroarene groups.\textsuperscript{130–143} Patrick and Prosser first documented a new crystalline solid formed from a 1:1 mixture of benzene (m.p. = 5.5 °C) and hexafluorobenzene (m.p. = 5 °C) with a melting temperature of 24 °C.\textsuperscript{139} The higher melting point of the crystal clearly demonstrated the formation of a stable complex from the π-π stacking between the electron-rich benzene π-system and electron-deficient hexafluorobenzene π-system (Figure 6.3(b)).\textsuperscript{139} Patrick and Prosser also studied a 1:1 mixture of methylnaphthalene (m.p. = 35°C) and hexafluorobenzene which gave rise to a crystalline solid with melting point of 56°C.\textsuperscript{139}

![Chemical structures](image)

Figure 6.3: (a) Proposed π-π stacking between lignin and PB-g-PPFS. (R = H or alkyl group depending on the source and type of lignin) (b) Face-to-face π-π stacking between benzene and hexafluorobenzene.\textsuperscript{139}
The arene-perfluoroarene complexes are a special case of π-π stacking phenomenon between electron-rich and electron-deficient π-ring systems. In this work, electron rich lignins were compounded with electron deficient PB-g-PPFS copolymer. PB-g-PPFS is evaluated as a coupling agent for both compounds of lignin, and lignin-carbon black hybrid fillers.

6.2 Experimental

This section presents detailed information on the materials used in this study, synthesis, and characterization of the graft copolymer. In addition, the equipments and conditions used for characterization and testing of the SBR compounds with and without coupling agent are also described.

6.2.1 Materials

The graft copolymer was synthesized from 2,6-di-t-butyl-p-cresol (butylated hydroxytoluene, BHT, Polymer Sciences) and polybutadiene (Goodyear, $M_n = 1.25 \times 10^5$, PDI = 4.6, 97.7% 1,4-cis, 0.8% 1,4-trans, 1.5% 1,2-vinyl content according to supplier; GPC$_{PSM}$ $M_n = 1.11 \times 10^5$, PDI = 3.55, RI detector), used as received. Benzoyl peroxide (BPO, Aldrich, 97%) was recrystallized from chloroform and methanol (1:3 v/v) below 25 °C and stored in a freezer at < -10 °C. The 2,3,4,5,6-pentafluorostyrene monomer (PFS) (Apollo Scientific) was passed through a short column of basic activated alumina to remove the inhibitor immediately before each use. Reagent grade tetrahydrofuran (THF, Aldrich) was dried by distillation from purple sodium benzophenone ketyl under N$_2$ when used in polymerizations and from LiAlH$_4$ when used in GPC measurements, GPC sample preparations and UV-vis measurements. All other reagents and solvents were commercially available and used as received.
Lignin used in this study was kraft lignin (KL) powder from Weyerhaeuser (Federal Way, Washington) with molecular weight ($M_W$) = 5090 g/mol, polydispersity index ~ 5.4, and glass transition temperature ($T_g$) ~ 128 °C. KL was ball-milled to particle sizes of less than 100 micrometers before use. The carbon black used in preparation of hybrid kraft lignin – carbon black particles was grade N330 manufactured by Sid Richardson (Fort Worth, TX). Styrene butadiene rubber (SBR), grade SLF18B10 obtained from Goodyear Tire and Rubber Co. was used as the primary rubber material. The rubber had a styrene content of 18.5% by weight. The ingredients used for curing of rubber include zinc oxide powder, stearic acid in bead form, sulfur curing agent (Rubber Maker), and N-cyclohexylbenzothiazole-2-sulfenamide (CBS) accelerator, all obtained from Akrochem Corporation (Akron, OH).

The hybrid fillers were prepared as per the method described in section 5.2.2 on page 92. However, instead of water, 0.5 M NH$_4$OH was used to dissolve the kraft lignin since KL is not soluble in water. A 10:90 ratio by weight of KL:CB was used to prepare the hybrid fillers.

6.2.2 Synthesis of PB-g-PPFS graft copolymer

The PB-g-PPFS graft copolymer was synthesized following a procedure previously reported.$^{128}$ PFS and PB were used in the molar ratio of 2:1 in synthesis. A dry round bottom flask equipped with a stir bar, high vacuum joint, and perfluoro o-ring was used. A solution of PB (1.36 g, 25.2 mmol repeat units) in dry THF (75 mL) was degassed by five freeze-pump-thaw cycles and stirred at 50 °C under N$_2$ overnight (13.5 h) to dissolve PB. PFS (9.79 g, 50.4 mmol) and BPO (0.31 g, 1.3 mmol) were added to the PB solution and degassed by five freeze-pump-thaw cycles. The flask was then sealed under vacuum.
(0.3 mm Hg) and immersed in 60°C oil bath with constant stirring. After 48 hours, the polymerization was quenched by immersing the flask in an ice water bath and by exposing to atmosphere. A GPC aliquot (0.5 mL) was removed prior to precipitation and diluted with 0.5% w/v solution of BHT in dry THF (9 mL). The remaining solution was precipitated in a 1% w/v N₂ saturated solution of BHT in methanol (1% w/v, 500 mL) to obtain a white precipitate. The precipitate was collected in a glass frit and dried in vacuo overnight at room temperature to yield 6.83 g crude polymer (61.3% yield) containing the graft copolymer, PPFS homopolymer, and up to a trace amount of unreacted PB homopolymer. The crude polymer is a mixture of the graft copolymer, and PPFS homopolymer and was used as the coupling agent in SBR compounds filled with lignin and lignin-carbon black hybrid particles. The crude polymer will be referred to as PB-g-PPFS in the rest of the chapter.

6.2.3 SBR compound preparation

Before compounding, the lignin specimens and the coupling agent were mixed in THF to generate intimate contact between the two materials. For this purpose, PB-g-PPFS coupling agent was first dissolved in THF, and lignin was then added to this solution and the solution was stirred until all THF evaporated. The precipitated material contained an intimate mixture of lignin and PB-g-PPFS. The hybrid filler/coupling agent mixtures were prepared by replacing lignin in the above procedure with KL-CB hybrid fillers.
Table 6.1. Compounding recipe of filled SBR compounds

<table>
<thead>
<tr>
<th>Materials</th>
<th>SBR-0F (phr)</th>
<th>SBR-30KL (phr)</th>
<th>SBR-30KL w/copolymer</th>
<th>SBR-30KLCB1090 w/copolymer</th>
<th>SBR-30KLCB1090 w/copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>CBS</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Lignin</td>
<td>-</td>
<td>30</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>KLCB 1090</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>PB-g-PPFS</td>
<td>-</td>
<td>3.3</td>
<td>3.3</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

The compounds of SBR with KL and KL-CB hybrids with and without the coupling agent were prepared in two steps. In the first step, rubber was mixed with zinc oxide, stearic acid, and the treated filler in a Brabender Plasticorder internal mixer (80 cm³ volume) at a rotor speed of 65 rpm and a fill factor of 0.7 at 80 °C. The rubber was masticated for 60 s and mixed with the rest of the ingredients for 5 minutes. The compounds obtained in step 1 were mixed with sulfur and CBS accelerator in a two roll mill for 5-7 min. at a speed of 15 rpm and a roll temperature of 40 °C. The compounds were prepared following the recipe given in Table 6.1.
The rubber compounds were cured in a compression molding press at 160 °C. The time needed to reach 95% of the maximum torque (t\textsubscript{95}) was used as the optimum curing time. A sheet mold with dimensions 150 mm × 150 mm and a thickness of 1.5 mm was used for curing. The cured materials were used for evaluation of reinforcement behavior and for characterization of filler dispersion.

6.2.4 Characterization

This section gives information on the techniques and conditions used to characterize the graft copolymer and its interactions with kraft lignin. Details on testing and characterization of rubber compounds along with the conditions employed are described in detail.

6.2.4.1 \textsuperscript{1}H NMR spectroscopy

Proton NMR spectroscopy method was used to characterize the grafting reaction. \textsuperscript{1}H (300 MHz) NMR spectra (δ, ppm) were recorded on a Varian Mercury 300 spectrometer. All \textsuperscript{1}H NMR spectra were recorded in CDCl\textsubscript{3}, and the resonances were measured relative to residual solvent resonances and referenced to tetramethylsilane (TMS, 0.00 ppm).

6.2.4.2 Gel permeation chromatography (GPC)

Molecular weights of the PB-g-PPFS graft copolymers relative to linear polystyrene (Aldrich) were determined by gel permeation chromatography (GPC\textsubscript{PSi}) at 35 °C using THF as solvent (1.0 mL/min), a guard column and a set of 50, 100, 500, 10\textsuperscript{4} Å and linear (50-10\textsuperscript{4} Å) Styrage columns, a Waters 410 differential refractometer (RI), and/or a Waters 486 tunable UV/Vis detector set at 254 nm and Millenium Empower 3 software.
6.2.4.3 UV-vis spectroscopy

UV-vis spectroscopy was performed to confirm the presence of arene-perfluoroarene interactions between kraft lignin and PB-g-PPFS copolymer. UV-vis measurements were made using the Hewlett Packard Model 8453 using THF as the solvent and the reference. KL and PB-g-PPFS were used at concentration 0.02 g/L and 0.1 g/L in THF respectively. These concentrations were chosen since they gave optimum absorbance values. The UV-vis absorbance study was carried out at wavelengths of 200 to 400 nm with samples kept in quartz cuvette cells.

6.2.4.4 Characterization of rubber compounds

The cure characteristics of the compounds were evaluated using approximately 5 g rubber compounds in a Moving Die Rheometer (MDR 2000) at a temperature of 160 °C, a frequency of 1.67 Hz, and a strain of 7%. The plots of torque vs. time were recorded and the curing parameters such as scorch time, torque difference, and cure time (t95) were calculated. The crosslink density was calculated as per the method described in section 4.2.4 on page 71.

Dumb-bell shaped specimens as per ASTM D412, Type C method were punched out of cured sheets of rubber for tensile tests. These tests were carried out at room temperature using Instron® 5567 tensile tester at a crosshead speed of 500 mm/min. A minimum of 5 specimens were tested per sample.

Dynamic mechanical properties were measured using TA Q200 (TA Instruments, New Castle, Delaware) dynamical mechanical analyzer. For this purpose, the samples of dimensions 10 mm x 4.02 mm x 1.5 mm were cut from the cured sheets. The temperature-sweep experiments were performed at 0.5% strain and 1 Hz frequency at a
heating rate of 3 °C/min. The values of storage modulus and tan δ were obtained at 60 °C. The values of tan δ were determined specifically at 60 °C since the damping factor (tan δ) at 60 °C gives a direct indication of viscous dissipation and rolling resistance in rubber compounds.

A high resolution scanning electron microscope, JEOL JSM5310 was used to examine the fracture surface of rubber vulcanizates filled with KL-CB hybrids with and without the coupling agent. The vulcanizates were cold fractured in liquid nitrogen followed by sputter coating for 1.5 min by a layer of silver under argon gas atmosphere before taking images by SEM. The operating voltage of SEM was 5 kV. SEM images were also used to study the morphology of mixtures of KL and PB-g-PPFS.

6.3 Results and Discussions

The characterization of the graft polymer and its interactions with kraft lignin will be described in this section. In addition, its effect on the cure performance, tensile properties, dispersion, and dynamic mechanical properties of filled SBR compounds will also be explained in detail.

6.3.1 Characterization of grafting reaction by 1H NMR spectroscopy

The proton NMR of PB-g-PPFS was obtained using the 300 MHz Varian Mercury spectrometer. CDCl3 was used as the solvent and the resonances were referenced to residual solvent and TMS. The proton NMR spectrum is shown in Figure 6.4. Although the PB resonances are present, the spectrum is dominated by the PPFS homopolymer resonances. This is because PPFS homopolymer is the major product of the reaction.
Figure 6.4: $^1$H NMR spectrum of crude PB-g-PPFS used as the coupling agent.

The resonances and the groups to which the protons belong to are as follows; CH$_2$ of PPFS (2.00 ppm), cis-CH$_2$-CH= of PB backbone (2.08 ppm), mr + rr CH of PPFS (2.39 ppm), mm CH of PPFS (2.74 ppm), cis-CH$_2$-CH= of PB backbone (5.38 ppm).$^{128}$

6.3.2 GPC analysis of PB-g-PPFS graft copolymer

The UV detector trace of the crude copolymer taken at the end of the reaction is depicted in Figure 6.5. Two peaks are seen in the chromatogram. The first peak at lower retention time, corresponding to the higher molecular weight polymer, is attributed to the graft copolymer PB-g-PPFS. The second peak corresponding to the lower molecular weight polymer is attributed to the ungrafted PPFS homopolymer.
Figure 6.5: GPC UV detector (254 nm) trace of PB-\textit{g}-PPFS graft copolymer sample taken after 48h.

The amount of PPFS which homopolymerizes and the amount which is grafted on PB can be determined by resolving the peaks from the GPC chromatogram. The grafting parameters summarized in Table 6.2 are calculated based on the amounts of grafted and ungrafted PPFS determined from the GPC chromatogram. The grafting ratio is defined as the ratio of the mass of the PPFS grafts to the mass of the PB backbone. Grafting efficiency is the percentage of the polymerized monomer grafted on the PB backbone whereas the grafting frequency is defined as the number of PB repeat units present between two successive PPFS grafts.\textsuperscript{128}
Table 6.2. Molecular weight and grafting parameters for crude PB-g-PPFS

<table>
<thead>
<tr>
<th>PFS:PB mole ratio</th>
<th>( M_n \times 10^{-5} ) (g/mol)</th>
<th>( M_w \times 10^{-5} ) (g/mol)</th>
<th>PPFS ( M_n \times 10^{-4} ) (g/mol)</th>
<th>Grafting ratio</th>
<th>Grafting efficiency</th>
<th>Grafting frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>4.85</td>
<td>7.27</td>
<td>1.5</td>
<td>0.23</td>
<td>0.08</td>
<td>1452</td>
</tr>
</tbody>
</table>

The grafting ratio value indicates that, on an average, 0.23 g of PPFS grafts are present per gram of PB backbone. An average grafting efficiency of 0.08 is achieved, i.e. 8% of the reacted PPFS is actually grafted on the PB chain. The rest of PPFS homopolymerizes to produce ungrafted PPFS. Thus, the intensity of the PPFS homopolymer is much higher in the UV detector trace in GPC shown in Figure 6.5. A grafting frequency of 1452 is obtained under the given reaction conditions, i.e., around 1452 repeat units of PB are present between two successive graft points.

6.3.3 UV-vis spectroscopy of KL and PB-g-PPFS mixtures

UV-vis spectroscopy was performed in order to verify the arene-perfluoroarene interactions between kraft lignin and PB-g-PPFS graft copolymer. The UV-vis spectra of the mixtures are presented in Figure 6.6. Four spectra are presented in Figure 6.6 of KL, PB-g-PPFS (2:1 PFS:PB), KL and PB-g-PPFS mixed together, and the spectra obtained from the addition of the absorbance of the KL and PB-g-PPFS spectra.
Figure 6.6: UV-vis spectra of KL and PB-g-PPFS mixtures in THF.

The spectrum of KL solution in THF shows two main peaks. A broad peak is seen at around 210 nm followed by a second peak at ~ 280 nm. The spectrum is similar to what was reported by Deng et al.\textsuperscript{144} for sodium lignosulfonates at concentrations lower than 0.1 g/L. Bolker and Somerville\textsuperscript{145} also reported a strong absorbance peak at ~ 210 nm and a weaker absorbance peak at ~ 280 nm for a number of isolated lignins. The PB-g-PPFS graft copolymer also shows two peaks, one at ~213 nm and other at ~261 nm. The additive spectrum (green curve) represents the added absorbance of both the spectrum of KL and spectrum of PB-g-PPFS. The absorbance of the additive spectrum was compared to the absorbance of the mixture of KL and graft copolymer. If no interactions exist between KL and PB-g-PPFS, the absorbance of the mixture should be same as the absorbance of the additive spectrum.
In UV-vis spectroscopy, benzene shows an absorption peak at ~ 203 nm which is called the first primary absorption band of benzene. The presence of substituents on the benzene ring pushes the primary absorption peak of benzene to higher wavelengths since the substituents stabilize the polar excited states. For example, the presence of –OH substitution on benzene pushes the primary absorption peak from 203.5 nm to 210.5 nm. Hence, the peaks around ~ 210 nm seen in the spectrum of KL and PPFS can be attributed to the aromatic building units in lignin and/or substituted benzenes. On the other hand, the peak at ~ 280 nm in lignins is mostly due to the presence of free hydroxyl and ether groups. Pew showed that the absorption spectra of almost 14 model compounds of lignin, e.g., unconjugated guaiacyl and methoxy phenyl compounds lies in the region from 277 nm to 282 nm. Hence, the peak at ~ 280 nm belongs to the non-conjugate groups including the phenolic group structure of lignin.

The UV-vis absorbance spectrum of the mixture KL and PB-g-PPFS gives us valuable insight on the interactions existing between KL and PB-g-PPFS molecules. The absorbance of the peaks at ~ 210 nm is much lower for the mixture than for the additive spectra of KL and PB-g-PPFS. Also, a slight shift in the peak is obtained for the mixture since the \( \lambda_{\text{max}} \) (wavelength corresponding to the peak) moves from 210 nm for KL and 213 nm for PB-g-PPFS to 222 nm for the mixture. The absorbance intensity reduced in a comparison of the KL+PB-g-PPFS mixture curve and the KL + PB-g-PPFS additive curve with the same concentration of the species. Also, red shift in the \( \lambda_{\text{max}} \) occurred from 210-213 nm to 222 nm. These two are indicators of \( \pi-\pi \) stacking. Note that the peaks at these wavelengths are associated with the aromatic groups and the substituted benzenes which engage in \( \pi-\pi \) interactions. The \( \pi-\pi \) stacking is attributed to the arene-
perfluoroarene interactions between KL and PB-g-PPFS molecules. Also, no reduction in absorbance nor a shift in the peak are seen for the absorbance peak at 280 nm for KL or at 261 nm for PB-g-PPFS. The peak at 280 nm belongs to the non-conjugate groups in lignin and hence cannot contribute to π–π stacking.

6.3.4 Morphology of KL and PB-g-PPFS mixtures

The particles of KL and PB-g-PPFS mixtures were examined by SEM. A set of representative SEM images are presented in Figure 6.7. The KL agglomerates were broken down into sizes smaller than 100 µm (Figure 6.7 (a) and (b)) before mixing with PB-g-PPFS and compounding with rubber. Hence, KL shows a bimodal particle size distribution with larger particles of 30-60 µm in size and smaller particles with size of less than 5 µm. The representative image of PB-g-PPFS precipitated from its solution in THF is also presented in Figure 6.7 (c) for comparative purposes.
Figure 6.7: SEM images of (a) and (b) KL milled to particle sizes less than 100 µm, (c) PB-g-PPFS precipitated from THF (d) and (e) KL, PB-g-PPFS mixture precipitated from THF.

Figures 6.7 (d) and (e) show no change in morphology of KL particles due to treatment with PB-g-PPFS. The surface of a representative PB-g-PPFS particle shows a
large number of KL particles adhering to it. To study the adhered KL particles in detail, the surface of the PB-g-PPFS from Figure 6.7(d) is magnified and presented in Figure 6.7(e). We attribute this adherence to arene-perfluoroarene interactions between KL and PB-g-PPFS molecules. It is apparent from Figure 6.7(d) that not all KL particles are associated or attached to the graft copolymer. This is due to large excess of KL compared to the amount of PB-g-PPFS in the mixture with 90:10 ratio by weight of KL and PB-g-PPFS.

6.3.5 Cure characteristic of compounds

The rubber compounds with and without the coupling agent were cured at 160 °C using a moving die rheometer to study the effects of coupling agent on the cure parameters such as scorch time, cure time, and difference in torque (ΔM). The cure parameters of the compounds of KL and KL-CB hybrid filler are presented in Figure 6.8. The scorch time and the ΔM values show very little to no change upon addition of the coupling agents. This is not surprising since the coupling agent is primarily a grafted rubber molecule and does not consist of any reactive moieties to enhance the onset of cure or to increase the torque generated upon curing of rubber.

![Graph showing scorch time for different compounds](image)
Figure 6.8: Cure parameters of SBR compounds of KL and KLCB hybrid filler with and without the coupling agent.

On the other hand, some differences are seen with the cure time data upon addition of the coupling agent. The differences are more apparent in the compounds of KL as the amount of lignin was higher than in the hybrid filler. An increase in cure time or a slowdown of the curing reactions in system with large quantities of lignin can be attributed to the interaction of polar lignin with the compounds used in rubber curing. In this context, a steep drop in cure time for compounds containing the coupling agent
indicates much reduced interaction of the lignin molecules with the compounds used in curing of rubber. It was seen earlier that PB-g-PPFS and lignin engage in π-π interactions. We believe that these preferential interactions of lignin molecules with PB-g-PPFS molecules reduce the ease with which lignin can interact with the compounds used in rubber curing.

6.3.6 Tensile properties of vulcanizates

The effects of coupling agent addition on tensile strength at break, strain at break, and 100% modulus (M100) are seen from the data presented in Table 6.3. The tensile strength at break increased by 20% upon addition of coupling agent to compounds of KL while the presence of PB-g-PPFS in the compounds of KLCB hybrid filler shows an increase of 10% in comparison to compounds with no coupling agent. The improvement in tensile properties indicates an efficient coupling between rubber and lignin upon addition of PB-g-PPFS graft copolymer. The filler particles are now linked to the rubber matrix via non-covalent interactions existing between KL and PB-g-PPFS. The addition of the coupling agent makes the tensile strength of hybrid fillers comparable to the tensile strength of carbon black filled compounds reported in section 5.3.7 on page 113. Hence, although the increase in strength is only 10%, it is very significant in the context that lignin can substitute some CB in the formulation.
Table 6.3. Comparison of the properties of SBR compounds of KL and KL-CB hybrid fillers with and without coupling agent

<table>
<thead>
<tr>
<th>Property</th>
<th>SBR-0F</th>
<th>SBR-30KL</th>
<th>SBR-30KL</th>
<th>SBR-30KLCB1090</th>
<th>SBR-30KLCB1090</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>w/copolymer</td>
<td>w/copolymer</td>
<td>w/copolymer</td>
<td>w/copolymer</td>
<td>w/copolymer</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>1.51 ± 0.08</td>
<td>1.67 ± 0.14</td>
<td>2 ± 0.08</td>
<td>11.06 ± 0.78</td>
<td>12.12 ± 1.41</td>
</tr>
<tr>
<td>Strain at Break (%)</td>
<td>247.17 ± 22.7</td>
<td>431.65 ± 57.9</td>
<td>373.7 ± 19.5</td>
<td>545.5 ± 30.2</td>
<td>556.8 ± 35.3</td>
</tr>
<tr>
<td>M100 (MPa)</td>
<td>1 ± 0.02</td>
<td>1.14 ± 0.02</td>
<td>1.3 ± 0.03</td>
<td>1.88 ± 0.04</td>
<td>1.88 ± 0.03</td>
</tr>
<tr>
<td>(XLD)_{app} (kmol/m^3)</td>
<td>0.08</td>
<td>0.04</td>
<td>0.044</td>
<td>0.08</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The strain at break decreased slightly and the 100% modulus increased upon addition of the coupling agent to KL. An increase in 100% modulus may be attributed to the improved stiffness upon addition of the coupling agent. The improved stiffness is confirmed by a slight increase in the crosslink density of the vulcanizate upon addition of the coupling agent. On the other hand, the strain at break, 100% modulus, and crosslink density did not show an appreciable difference upon addition of the coupling agent in compounds of KL-CB hybrid fillers. The effect of lignin-PB-g-PPFS coupling is subdued.
in the hybrid filler systems due to much lower amount of lignin in them as compared to carbon black since a 10:90 KL:CB weight ratio was used in the hybrid filler.

6.3.7 Dynamic mechanical analysis

The DMA data for compounds of KL and KL-CB hybrid fillers was obtained at 1 Hz frequency, 0.5% strain, and 60°C to obtain an estimate of how the PB-g-PPFS coupling agent influenced the viscoelastic properties of the compounds. The graphs of storage modulus and tan δ are presented in Figure 6.9. In compounds of KL, the storage modulus increased upon addition of the coupling agent. This was accompanied by a reduction in the value of tan δ. We already learned in the previous section that the addition of coupling agent to lignin resulted in an increased stiffness. This increased stiffness is responsible for higher storage modulus and lower value of tan δ. In addition, the improved rubber-filler interactions promoted by the coupling agent, contributed to a reduction of the tan δ value.

The observations are slightly different for the compounds of KLCB hybrid fillers. In this case, no increase in stiffness and crosslink density was observed for these systems upon addition of the coupling agent. Thus, the dynamic mechanical properties of these compounds are dominated by the filler-filler and filler-polymer interactions. The filler networking plays a more important role in the case of hybrid fillers in comparison to lignin-only systems because the particle sizes of hybrid fillers are more than an order of magnitude smaller than lignin powders.
Figure 6.9: Effect of coupling agent on (a) storage modulus, (b) tan δ of KL filled and KLCB hybrid filled SBR compounds.

The KL-CB hybrid filler compound showed a slight reduction in the storage modulus and tan δ upon addition of the coupling agent. The reduction in storage modulus at low strains (0.5%) is associated with lower filler networking and improved filler-polymer interactions. The loss tangent also reduced upon the addition of the coupling agent. The fact that the value of tan δ reduced in spite of the drop in storage modulus reinforces
our theory that the trends in hybrid fillers are stiffness independent and vary with the state of filler-filler and filler-polymer interactions in this case. The reduction in tan δ can be attributed to improved filler-polymer interactions due to the addition of the coupling agent. The improved filler-polymer interactions should result in improved filler dispersion. This will be analyzed in the next section.

6.3.8 Effect of coupling agent on dispersion of SBR compounds filled with hybrid filler

The SEM images of the fracture surfaces of SBR vulcanizate filled with hybrid filler with and without the coupling agent are shown in Figure 6.10. The dispersion of the hybrid filler domains was evaluated based on the fracture surface morphology. The hybrid filler domains are highlighted in Figures 6.10 (b) and (d). The fracture surface of the compound of KL-CB hybrid (Figure 6.10 (b)) shows hybrid filler domains of 30-50 μm in size. The large size of domains results from the strong interactions that exist between KL and CB as a result of π–π stacking as demonstrated in Chapter V. The strong interactions prevent the breaking of the hybrid domains in shear which results in its large particle size.

Upon addition of the coupling agent, the size of the hybrid filler domains drops drastically. Figure 6.10 (d) shows that 30-50 μm sized hybrid filled domains are rare. This can be attributed to improved interactions between the lignin coating on the hybrid fillers and the rubber due to addition of the PB-g-PPFS graft copolymer.
Figure 6.10: Dispersion analysis of SBR – KLCB hybrid fracture surface (a) and (b) without coupling agent, (c) and (d) with coupling agent. The images (b) and (d) are same as (a) and (c) respectively, except with the hybrid filler domains outlined.

Hence, the SEM images correlate well with the tensile and dynamic mechanical data. The addition of the coupling agent does improve the dispersion of filler in the rubber. The improvement in dispersion manifests itself in the form of reduced filler domain sizes.

6.4 Conclusions

A PB-g-PPFS graft copolymer was developed to increase the interactions between lignin to the SBR rubber matrix via arene-perfluoroarene interactions. Coupling occurred because SBR and PB are compatible on one side whereas the PPFS grafts on the copolymer interact with lignin via arene-perfluoroarene interactions on the other side.
UV-vis spectroscopy confirmed the formation of π–π stacks since the absorbance of the mixture was subdued and a spectral red shift was obtained.

The addition of PB-g-PPFS to kraft lignin filled SBR resulted in increased stiffness, reduced energy dissipation, and improved failure properties all of which are expected upon enhanced coupling between rubber and the filler. In KL-CB hybrid filled systems, the tensile strength of the hybrid filler compounds improved by 10% upon addition of PB-g-PPFS and reached the value comparable to that of CB filled SBR compounds. However, not much difference was obtained in the stiffness of the vulcanizates. As a result, the slight decrease in storage modulus and the loss tangent is attributed to the improved filler-polymer interactions upon coupling. This improvement in filler-polymer interactions was confirmed by improved dispersion of the hybrid filler domains as seen via SEM analysis.

Hence, the “non-covalent” approach towards establishing coupling of lignin filler to rubber was successfully demonstrated in this study. The trends clearly showed improvement in failure properties, reduction in energy dissipation, and improvement of dispersion of fillers. However, the improvements were not as drastic as seen for a covalently coupled system (e.g. TESPT and silica) because of the lower strength of π–π stacking as compared to the covalent bonds. The strength of the interactions can be controlled by increasing the number of sites at which the interactions takes place, i.e., by increasing the grafting frequency of PPFS grafts on the PB main chains.
CHAPTER VII

OVERALL SUMMARY AND RECOMMENDATIONS FOR FURTHER STUDY

This thesis deals with development of lignins as a reinforcing filler for elastomers to produce compounds with low energy dissipation or rolling resistance. The development of lignin reinforced elastomers was achieved by first outlining and establishing the issues associated with the use of lignin, simply as a “drop-in” replacement for current commercially used fillers such as carbon black and silica. Three different approaches were followed in detail to solve the problems associated with lignins, and to produce more energy efficient compounds by partially replacing the carbon black with lignin. These approaches are surface modification of lignin, development of lignin–carbon black hybrid fillers, and development of coupling agent to couple the lignin with the rubber matrix. Two of the approaches were also used in conjunction.

In the first part of this thesis, lignin was directly used as filler in synthetic isoprene rubber compounds (IR) to establish the efficacy of untreated lignin as the reinforcing filler. It was seen that lignin had a negative effect on the crosslink density of rubber compounds. For example, XLD went down with an increase in lignin concentration. This was attributed to the polarity of lignin, which in turn, led to its interaction with the curatives, thereby reducing the efficiency of vulcanization. The lower density and lower degree of cure resulted in poor elasticity and mechanical performance which is
detrimental to producing compounds with low rolling resistance and strong reinforcement. Also, the large size of lignin particles (20-100 μm) was seen as a detriment to the reinforcing effect of lignin. It was observed that the degree of reinforcement by lignin varied with the amount of sulfur to accelerator ratio. The strain induced crystallization of IR masked the effects of lignin on the values of tensile strength and elongation at break. Except for lignin interfering with the curatives and the degree of cure, the use of IR did not yield clearer image of the potential of lignin as reinforcing filler. To circumvent this issue, a non-self-reinforcing elastomer, SBR was used as the rubber matrix in the rest of the work.

The first approach studied to produce lignin reinforced SBR compounds with low energy dissipation is based on surface modification of lignin. This approach successfully alleviated the concerns associated with the polarity of lignin. Cyclohexylamine (CA) was used to modify the surface of lignin via hydrogen bonding and proton transfer interactions. The CA modification helped to increase the C-C bond concentration on the surface and as a result suppressed the polarity of lignosulfonates (LS) to make them more compatible with the non-polar rubber matrix. The reduced polarity manifested itself in the form of lower LS particle sizes due to reduced agglomeration. The cure performance and XLD of the rubber compounds improved dramatically upon modification with CA. A significant increase in mechanical properties was observed due to improved stress transfer across the rubber-filler interface due to modification by CA. The method of CA modification shows strong promise in reduction of rolling resistance since it resulted in a decrease in the value of loss tangent of LS filled SBR compounds. The CA surface
modification method is very attractive since it is a green technique and uses no organic solvents or catalysts. Instead, the modifications are carried out in water.

The second approach used hybrid filler to produce rubber compounds with low energy dissipation by partially replacing CB with lignin. This approach successfully solved the large particle size issue of lignin e.g. lignin could now be placed in the compounds as coating layers instead of particles of 10-100 µm. Novel hybrid fillers consisting of lignin coating on carbon black particles were prepared by exploiting the π–π interactions between the two materials. Raman spectroscopy and solid state NMR studies were used to confirm the π–π interactions between lignin and carbon black. The hybridization of lignin and carbon black was shown to be advantageous in many ways. First, it solved the particle size issue of lignin and the poor reinforcement obtained due to large lignin particle size. The lignin was present as coating layers and not as separate particles. Second, it was shown via filler flocculation experiments that the lignin coating layers reduced the filler networking of carbon black by occupying the spaces between carbon black primary particles. Hence, it reduced the probability of a carbon black particle to come in contact with another carbon black particle. The reduction of filler networking resulted in a reduction in the Payne effect and reduction in the value of loss tangent, i.e., it reduced the energy dissipation of rubber compounds. It was shown that a 10:90 ratio by weight of lignin to carbon black in the hybrid filler was the optimum. It gave lower filler flocculation without sacrificing the mechanical performance.

The third approach taken to produce lignin reinforced SBR compounds with low energy dissipation was the use of a coupling agent with lignin. A non-covalent coupling approach was used in this work instead of the coupling via covalent bonding which has
been widely established for silica filled systems. A PB-g-PPFS graft copolymer synthesized in laboratory was evaluated as a coupling agent. The graft polymer consisted of electron-deficient benzene rings in the PPFS grafts which interacted with the electron-rich benzene rings present in lignin via arene-perfluoroarene interactions i.e. $\pi-\pi$ stacking. On the other end, the PB main chains of the graft copolymer are compatible with the SBR rubber and hence, the PB-g-PPFS can act as a coupling agent for lignin filled SBR systems. The arene-perfluoroarene interactions between lignin and the copolymer were established by UV-vis studies. The addition of PB-g-PPFS resulted in increased stiffness, reduced energy dissipation, and improved failure properties in lignin filled systems, all of which are expected due to enhanced coupling between rubber and the filler. In KL-CB hybrid filled systems, the addition of coupling agent improved the filler-polymer interactions which resulted in improved tensile strength, reduction in storage modulus at lower strains, and reduction in loss tangent.

The research results described in this dissertation have made several new contributions to the literature. These contributions are highlighted as follows:

(1) For the first time, the reinforcing potential of lignin in IR was examined by relating it to sulfur to accelerator ratio. The finds helped understand why there is so much variability in the data reported in literature on the reinforcing efficacy of lignin in rubber compounds. This work highlighted the problems associated with the use of lignin and presented the steps needed to solve the problems.

(2) A new, clean, green, and environmentally friendly surface modification technique was developed to suppress the polarity of lignin and to improve the compatibility between lignin and the rubber matrix. The rationale, scope, methods, and results
were described in detail so as to enable the extrapolation of this work for researchers seeking material solutions to develop other polar, bio-derived materials for application in non-polar polymers.

(3) A new approach was developed towards producing hybrid fillers capable of reducing energy dissipation in rubber compounds. The existing literature of hybrid fillers mostly focuses on dry mixing of two different fillers without exploring the interactions between them or rendering them into unique morphological forms. This work established the π–π interactions between CB and bio-derived lignin and used such knowledge to produce hybrid fillers with morphologies that could be tuned by controlling the ratio of lignin to CB. It was established that the 10:90 ratio of lignin to carbon black would give the best combination of low value of tan δ and good mechanical performance. The hybrid fillers were prepared in water. Thus, the approach utilized a green method in filler preparation. In addition, the potential for 10wt % reduction of CB by using a hybrid filler is worth yearly CB savings of 300 million pounds only in tire industry.

(4) A new coupling agent was developed for lignin-filled rubber compounds based on a new mechanism of coupling. The PB-g-PPFS compound showed all the improvements expected from coupling of the filler with the rubber. This study helped to demonstrate the proof of concept of a new mechanism of coupling - via non-covalent interactions between filler and rubber. The advantage of this method is that the strength of interactions can be tuned based on the grafting frequency of
PPFS domains on PB. As a result, the effect of coupling on the macro-properties can be controlled.

Despite demonstrating new, novel, and green routes towards development of bio-derived materials to produce sustainable products for the future, some of the outstanding issues are provided as recommendations for future work.

- The right formulations and recipes for SBR compounds filled with hybrid filler should be determined such that rubber crosslink density effects are taken care of to obtain lowered rolling resistance without sacrificing the mechanical performance.

- This study was mainly focused on reduction of rolling resistance of rubber compounds. However, further work must be done on evaluation and optimization of wet skid resistance and abrasion resistance for the hybrid filler compounds.

- This study used only one grafting level of PPFS. However, further work must be done on improvement of the extent of non-covalent coupling of lignin by increasing the grafting level of PPFS domains on PB using controlled free radical polymerization.

- This study demonstrated improved hybrid filler dispersion and performance with addition of PB-g-PPFS coupling agent. However, further work must be done to understand the mechanism of interactions between hybrid fillers and PB-g-PPFS since both, CB in the hybrid filler and PB-g-PPFS coupling agent interact with lignin via π-π stacking.
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(102) Galimberti, M.; Coombs, M.; Riccio, P.; Riccò, T.; Passera, S.; Pandini, S.; Conzatti, L.; Ravasio, A.; Tritto, I. The Role of CNTs in Promoting Hybrid Filler


This chapter contains the cure curves and stress-strain curves of various vulcanizates evaluated in this dissertation. The cure parameters reported in the dissertation were calculated from the cure curves presented in Figures A.1 - A.5. The stress-strain curves for the vulcanizates are presented in Figure A.6 – A.10. The tensile properties were reported by averaging the values obtained from at least five specimens per sample.

Figure A.1: Cure curves for IR - lignin compounds prepared using sulfur to accelerator ratio ($\varphi$) = 1.
Figure A.2: Cure curves for IR - lignin compounds prepared using sulfur to accelerator ratio ($\phi$) = 2.

Figure A.3: Cure curves for unmodified and modified lignosulfonate filled SBR compounds.
Figure A.4: Cure curves for SBR compounds with unmodified and modified LS-CB hybrid filler.

Figure A.5: Cure curves for SBR compounds of KL and KLCB hybrid filler with and without the coupling agent.
Figure A.6: Stress-strain curves of IR - lignin compounds prepared using sulfur to accelerator ratio ($\varphi$) = 1.

Figure A.7: Stress-strain curves of IR - lignin compounds prepared using sulfur to accelerator ratio ($\varphi$) = 2.
Figure A.8: Stress-strain curves for unmodified and modified lignosulfonate filled SBR compounds.

Figure A.9: Stress-strain curves for SBR compounds with unmodified and modified LS-CB hybrid filler.
Figure A.10: Stress-strain curves for SBR compounds of KL and KLCB hybrid filler with and without the coupling agent.