Optimization of agricultural waste derived biochar through physical activation methods for use as reinforcement fillers in rubber composites

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Abstract

Biochar has a variety of applications such as contaminant removal, soil amendment, and general carbon storage. Some recent research has investigated its application as a reinforcing filler for rubber composites. The properties of biochar are influenced by factors such as feedstock composition, pyrolysis conditions, and pre- and post-treatments. The relationship between biochar properties and performance as a reinforcing filler in rubber composites is not yet well understood. This thesis aims to determine the effect of feedstock composition and steam activation on the composition of biochar, and its efficacy as a reinforcing filler.

The first study aimed to determine effective activation methods for the improvement of reinforcement in corn stover biochars. Three steam activation methods, two gaseous and one slurry-based, were performed. The biochars were assessed for their physicochemical properties and then incorporated into styrene-butadiene composites. These composites were then analyzed for their cure performance and mechanical properties in comparison to N772 carbon black-filled composites. The unactivated biochar and gaseous steam-activated biochars demonstrated poor performance as reinforcement fillers. Slurry activation improved reinforcement performance in the rubber composites, comparable to N772. Its improved performance is attributed to increases in mesoporosity, and a correlation between mesoporosity and reinforcement performance is presented.

The second study investigated different feedstocks chosen for suspected valuable properties for reinforcement performance. Two nut shell feedstocks (hazelnut and walnut) and two grain husk feedstocks (oat and rice) were used to produce biochar. These biochars were also subjected to a slurry-based steam activation. The biochar samples were fully characterized, then used in styrene-butadiene rubber composites. The mechanical properties of the resulting composites were analyzed and compared to the N772 filled composite. Nut shell biochars provided very good reinforcement properties with and without activation and met or exceeded the performance of carbon black filled composites, despite having poorer dispersion. High silica content was not found to be beneficial to reinforcement performance. Activation increased mesoporosity and carbon content in all biochars and resulted in various mechanical improvements in formulated

composites. Correlations between low biochar ash content and high feedstock lignin content with favorable composite properties are presented.

It was determined that corn stover is not an effective feedstock for biochar filler. Grain husks showed moderate promise, while nut shell biochars demonstrated excellent reinforcement in composites, meeting or exceeding those of carbon black-filled composites. Across all investigated feedstocks, slurry activation improved the reinforcement effects of biochars. This is theorized to be due to increased mesoporosity from activation, leading to better dispersibility and polymer-filler interactions. These studies also demonstrate that high lignin feedstocks are favorable to develop high reinforcing biochars. Additionally, low ash content in biochars is observed to correlate with better reinforcing effects. These findings will inform future research on biochar-reinforced rubber composites.

Résumé

Le biochar a une variété d'applications telles que l'élimination des contaminants, l'amendement du sol, et le stockage du carbone. L'application du biochar comme charge de renforcement pour les composites de caoutchouc est de plus en plus investiguée. Les propriétés du biochar sont influencées par des facteurs tels que la composition des matières premières, les conditions de pyrolyse, les pré-traitements ainsi que les post-traitements. La relation entre les propriétés de biochar et les performances en tant que charges de renforcement dans les composites en caoutchouc n'est pas encore bien comprise. Ce mémoire vise à déterminer l'effet de la composition de la matière première et de l'activation de la vapeur sur la composition du biochar, et son efficacité en tant que charge de renforcement.

La première étude visait à déterminer des méthodes d'activation efficaces pour améliorer le renforcement des biochar de tige de maïs. Trois méthodes d'activation de la vapeur dont deux gazeuses et une en solution, ont été testées. Les biochars ont été évalués pour leurs propriétés physico-chimiques, puis incorporés dans des composites de styrène-butadiène. Ces composites ont ensuite été analysés pour leurs performances de durcissement et leurs propriétés mécaniques par rapport aux composites chargés de noir de carbone N772. Les biochars non activés et activés à la vapeur gazeuse ont démontré de piètres performances en tant que charges de renforcement. L'activation en solution a améliorée les performances de renforcement dans les composites en caoutchouc, comparables à celles du N772. Ses performances améliorées sont attribuées à des augmentations de la méso-porosité, et une corrélation entre la méso-porosité et la performance de renforcement est présentée.

La deuxième étude a examiné différentes matières premières choisies pour des propriétés présumées utiles pour la performance de renforcement. Deux coquilles de noix (noisette et noyer) et deux enveloppes de céréales (avoine et riz) ont été utilisées pour produire du biochar. Ces biochars ont également été soumis à une activation de vapeur en solution. Les échantillons de biochar ont été caractérisés puis utilisés dans des composites de caoutchouc styrènebutadiène. Les propriétés mécaniques des composites résultants ont été analysées et comparées à celles d'un composite rempli de N772. Les biochars de coquilles de noix offre de très bonnes propriétés de renforcement avec et sans activation, et ont atteint ou dépassé les performances des

composites chargés de noir de carbone, malgré une dispersion plus faible. Une teneur élevée en silice ne s'est pas avérée bénéfique pour la performance de renforcement. L'activation a augmenté la méso-porosité et la teneur en carbone dans tous les biochars, et a entraîné diverses améliorations mécaniques dans les composites formulés. Des corrélations entre la faible teneur en cendres de biochar et la teneur élevée en lignine des matières première sont présentées.

Il a été déterminé que la tige de maïs n'est pas une matière première efficace pour la charge de biochar. Les cosses de céréales se sont révélées modérément prometteuses, tandis que les biochars de coquilles de noix ont démontré un excellent renforcement dans les composites, atteignant ou dépassant ceux des composites remplis de noir de carbone. Pour toutes les matières premières étudiées, l'activation de la boue a amélioré les effets de renforcement des biochars. On suppose que cela est dû à l'augmentation de la méso-porosité due à l'activation, ce qui améliore la dispersibilité et les interactions polymère-charge. Ces études démontrent également que les matières premières à forte teneur en lignine sont favorables au développement de biochars à fort pouvoir de renforcement. En outre, la faible teneur en cendres des biochars est corrélée à de meilleurs effets de renforcement. Ces résultats éclaireront les recherches futures sur les composites en caoutchouc renforcés par des biochars.

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Abbreviation	Chemical		
BHT	2,6-di- <i>t</i> -butylhydroxytoluene		
DPPD	N,N'-diphenyl-1,4-phenylenediamine		
TMQ	1,2-dihydro-2,2,4-trimethylquinoline		
DAPD	N,N'-diphenyl-p-phenylenediamine		
NPPD	N-phenyl-1,4-phenylenediamine		
TMTD	tetramethyl thiuram disulfide		
DTDM	dithiodimorpholine		
CBS	cyclohexyl benzothiazole sulfenamide		
DPG	diphenyl guanidine		
TESPT	Bis(triethoxysilylpropyl)tetrasulfide		
TESPD	bis-[y-triethoxysilylpropyl]-disulfide		
MEPTS	mercaptopropyltriethoxysilane		
СТР	N-cyclohexylthiophthalimide		

List of Chemical Abbreviations

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Contribution of Authors

This thesis is presented as a manuscript-based thesis. Alexander Bardha, the candidate, designed and conducted biochar production and characterization experiments, performed data analysis on biochar and rubber composite data, and prepared the manuscripts within this thesis. Dr. Marie-Josée Dumont, the candidate's supervisor, contributed throughout the research process including directing experimentation and editing and reviewing manuscripts and the thesis prior to initial submission. Dr. Shiv Prasher, the candidate's co-supervisor, contributed to editing and reviewing the manuscripts and the thesis. Dr. Jiby Kudakasseril Kurian co-authored one of the manuscripts. Dr. Constantine Y. Khirpin and Dr. Jeremy J. Mehlem from Michelin Inc. provided guidance through experimentation and contributed to editing and reviewing manuscripts. Matthew S. Francis, Reyda Lizette Bazan Cornejo, and Julinna Villarta performed rubber work. Details of the manuscripts which have been submitted for publication are below:

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Chapter 1: Introduction

1.1 General introduction

Rubber composite materials are ubiquitous industrial materials and have been for more than a century. These materials are highly engineered and are composed of many additives in addition to raw natural or synthetic rubber. These additives include reinforcing fillers, processing aids, protectants, and the vulcanization system components. The proportion and composition of composite additives varies depending on the intended use of the composite, but generally rubber is composed of roughly 50% additives and 50% rubber [1]. As additives compose half of the rubber composite raw material market, the demand for their production is significant. Many of these additives are petroleum sourced. Petroleum-independence has become an increasingly important objective for many industries as petroleum reserves begin to dwindle and the environmental effects of oil extraction become more prevalent.

In recent years, proponents of the development of a bioeconomy have conducted much research on biological sources for a variety of industrial products and chemicals. Research into biosourced rubber composite materials is ongoing, with some products being commercialized, such as rice husk ash. There is great focus on utilizing available biowaste for these product sources. The most significant rubber composite additive by mass is the reinforcing filler. Research has noted biochar to be a very promising candidate that can be derived from biowaste. The properties and composition of biochar vary greatly depending on numerous factors such as pyrolysis conditions, treatment methods, and feedstock choice. Previous studies have developed biochars which are capable of partial replacement of carbon black in rubber composites. However, complete replacement of carbon black without sacrifice of mechanical properties has yet to be realized. More sample data is necessary to understand the workings of biochar reinforcement performance more completely.

1.2 Objectives

This study intended to develop and characterize biochar from feedstocks yet to be used as reinforcing fillers and subject them to steam activation and analyze their performance in rubber composites. The objectives of each chapter herein are as follows:

- I. Review literature on the current and future state of biowaste alternatives to traditional rubber composite additives. Describe and discuss the mechanisms of each class of additive, the current commercial additives used, and the biowaste candidates for replacement.
- II. Report physicochemical properties of biochar produced from corn stover both unactivated and subjected to three different methods of steam activation. Analyze their mechanical performance in styrene-butadiene rubber composites as compared to traditional N772 carbon black-filled composites. Determine the efficacy of biochars as reinforcing fillers. Assess the effects of the three steam activation methods on biochar properties and rubber composite performance and determine the most effective for future studies. Attempt to draw correlation between biochar properties and mechanical performance of rubber composite.
- III. Report physicochemical properties of unactivated biochar produced from two grain husks (rice and oat) and two nut shells (hazelnut and walnut) and those subjected to slurry-based steam activation. Analyze their mechanical performance in styrene-butadiene rubber composites as compared to traditional N772 carbon black-filled composites. Determine the efficacy of biochars as reinforcing fillers. Assess the effects of slurry-based activation on biochar properties and rubber composite performance. Correlate feedstock composition and biochar composition to mechanical properties of rubber composites.

Chapter 2: Current and future research into biowaste candidates for rubber composite additives

Abstract

Rubber composites are highly engineered materials composed of a multitude of additives in addition to natural and/or synthetic rubber. These additives range from reinforcing fillers, to processing aids, to protectants, to cross-linking systems. Current commercial additives are generally sourced from petroleum sources, including carbon black and various petrochemicals. As research into more sustainable production practices has increased considerably in recent years, identifying and developing effective bio-sourced alternatives to these components of rubber composites warrants investigation. Waste biomass is an attractive raw material source as it is readily abundant and cost-effective. Current research has shown that waste biomass can be used to produce compounds that have similar physical and chemical properties to many rubber additives. Some have demonstrated efficacy in polymer formulations, while others have developed these components for entirely different applications. This review overviews additive types in rubber composites, their function, the current commercial fillers used, discusses current novel biowaste alternatives, and develops hypothetical candidates for future investigation.

2.1 Introduction

Rubber tires have been an essential industrial product for the last century, with no indication of slowing. Tire production has increased almost linearly from just under 1.5 billion units in 2007 to over 3 billion in 2020 [1]. This growth in the tire production sector will therefore increase the demand for the various materials and compounds used for production, including those for the complex rubber chemical compounds. Generally, tires are built of a highly engineered composite of fabric and/or steel and formulated rubber [1]. The rubber formulations themselves contain a multitude of chemicals to achieve specific optimal properties depending on the intended use of the tire, such as the type of vehicle it will support and the environmental and surface conditions it is designed to handle. The properties of the tire materials, in tandem with the composite structure and the tread design, determine the efficacy of the tire in various conditions.

The formulated rubber of a tire is composed approximately of: 50% natural and/or synthetic rubber, 25% reinforcing fillers such as carbon black and silica, 20% processing aids such as plasticizers and peptizers, 1-2% protectants such as antioxidants and antiozonants, and 3-4% cross-linking systems [2]. The exact formulation depends on the desired properties of the tire (such as all-season versus winter tires) and the vehicle it supports (such as passenger versus truck tires).

Many of the components of the traditional tires are petroleum-sourced, from the synthetic rubbers used to mineral oils, to carbon black, and other compounding additives. The impacts of climate change, dissipating oil reserves, and general societal pushes to sustainable development have created a need for tire manufacture that shifts away from traditional petroleum-based rubber tire formulations. Tire manufacturers have already begun tackling this issue and have commercialized tires that are less reliant on petroleum products. In the early 1990s, Michelin initiated the Green Tire Technology initiative to begin shifting focus away from petroleumdependent tire ingredients. In 2008, Dunlop commercialized the ENASAVE97 which increased the amount of non-petroleum materials from 44% to 97% through use of natural rubber, silica instead of carbon black, vegetable oil instead of petroleum oil, and non-petroleum derived fibers [3]. However, just because some materials are from non-petroleum sources does not mean they are necessarily sustainable and renewable materials. Although silica is the most abundant compound in the Earth's crust and more abundant than petroleum, it is still a non-renewable and resource often sourced through open pit or dredge mining [4]. In addition, the remaining 3% of the formulation comprises of the numerous compounding additives which have potential to be derived from renewable and sustainable sources.

Companies have recently announced initiatives to produce 100% sustainable tires. Michelin did this in 2021 stating that by 2050, all their tires "will be made entirely from renewable, recycled, biosourced or otherwise sustainable materials" [5]. Shifting away from a petroleum-based economy and redirecting towards a sustainable and renewable biobased economy creates a channel of much scientific work to develop technologies for a sustainable planet. Therefore, a vital material to society, like a tire, could be re-envisioned as a completely biobased material.

The long-standing issue of bio-derived products is the food versus fuel debate, whether diverting farmland and crops for non-food uses is an effective use of resources [6]. One approach for working around this dilemma is by using otherwise low-value waste biomass as feedstock for bio-refinement. About 140 Gt of waste biomass is produced globally each year [7]. Generally, biowaste feedstocks can be split into lignocellulosic or non-lignocellulosic materials. Lignocellulosic materials are those which are composed of cellulose, hemicellulose, and lignin, or in other words dry plant matter. Non-lignocellulosic materials are those from non-plant sources such as from animal sources, algae, and anthropogenic biosolids [8]. By using these waste streams to produce various valuable chemicals, consumption of excess land, water, and food resources is avoided. These waste sources can provide affordable, abundant, and sustainable supplies of raw material.

Previous reviews have focused on optimizing fillers in rubber tires, with a few recent reviews focusing on potential bio-derived rubber additives [9-12]. Some reviews have also focused on the potential for specific biowaste-derived rubber additives [13, 14]. No review has focused on the feasibility of a completely biowaste-derived rubber additive formulation. This review herein describes the anatomy of rubber tire composite formulations (reinforcing fillers, processing oils, protectants, and cross-linking systems), their mechanisms in composite formulations, current commercially used additives, provides critical discussion of current research on biowaste-derived alternatives, and determines other hypothetical candidates which match the profile of current additives. Where applicable, potential synergistic effects of biowaste products in rubber formulations are also discussed. For the purposes of this review, formulations and compatibility will be focused on natural rubber composites.

2.2 Reinforcing fillers

Reinforcing fillers are loosely defined as additives which serve a primary function to physically reinforce the rubber to improve longevity and toughness. Rubber is almost never used industrially without reinforcing fillers, as unfilled rubber has poor strength and a significantly shorter usable life [15]. Reinforcing fillers dramatically change the properties of rubber, making the resulting composite useful for a wider-ranging array of applications. Reinforcing fillers in elastomers simultaneously increase modulus and deformation at break, unlike in plastics where

reinforcement increases modulus but decreases deformation at break [16]. This unique phenomenon in elastomeric reinforcement is what makes reinforcing fillers critical for producing high quality rubber composites. The main reinforcing fillers used in rubber tire production are carbon black and silica, in varying proportions and loadings. The use and proportion of each depends on the specifications and applications of the resulting tire, and many newer tires use some combination of the two [17]. Silica began to be used alongside carbon black due to silica's ability to reduce rolling resistance, in turn lengthening the usable lifetime and fuel efficiency of the tire due to reduced friction [18]. These two prominent fillers behave in somewhat similar fashion in the polymer-filler network, with some important distinctions outlined in the following section.

2.2.1 Mechanism

Reinforcing fillers do not only fill void space or cut cost as other non-reinforcing fillers such as calcium carbonate or talc do [19]. They impart material properties that are integral to the function and lifetime of a rubber tire. The mechanisms behind elastomer reinforcement and rubber-filler interactions are not clearly understood [20, 21]. Fillers with particles larger than 1 µm do not reinforce, and possibly negatively affect the reinforcement properties of the elastomer. Reinforcement is mostly apparent at <100 nm size, and the structure in this range becomes more important than purely particle size [22]. Both carbon black and silica demonstrate a somewhat fractal multilevel structure from particle to aggregate to agglomerate, and the interactions of these aggregates and agglomerates is what is believed to be most contributive to physical reinforcement. There are interactions between the filler surfaces, chemical surface bonding, or a combination of the two. Chemical surface bonding may not necessarily involve direct reactions between the filler surface and the polymer but could be a result of generated free radical reactions and sulfur-bonding during vulcanization.

There have been numerous attempts to understand the carbon black-rubber network and how this contributes to its impressive reinforcement. Robertson & Hardman (2021) extensively reviewed the various theories of carbon black reinforcement and the knowledge to date on these mechanisms, concluding that a combination of extensive physical adsorption and less pervasive

but stronger chemical bonding creates the reinforcement network, with capacity for polymer chains sliding and re-linking [20]. In addition, the complex chemistries present during vulcanization can further contribute to the reinforcement network. The dynamic interactions of filler and elastomer contribute to the well-observed phenomena of the Mullins and Payne effect in reinforced rubbers [23]. Carbon blacks tend to have very few polar functional groups at their surface, leading to compatible polarity between carbon black and natural rubber [24]. It is known that carbon black is composed of layered graphene sheets. However, carbon black is distinct in its turbostratic structure, meaning that the carbon sheets are not perfectly aligned when stacked atop each other. This is due to some interspersed 5- and 7-carbon rings and a mixture of sp² and sp³ hybridized carbon [25]. It is theorized that the fast quenching of carbon black during production leads to the generation of these slightly unordered turbostratic sheets [20]. It has been demonstrated that the increased graphitization of carbon black, occurring after heat treatment at temperatures from 500-3000 °C, decreases the reinforcement index (defined as the ratio of the stress at 300% strain to the stress at 100% strain) of the resulting rubber and the concentration of surface functional groups of the carbon black without significantly impacting the surface area [20]. This generally demonstrates that a more graphitic structure hinders the reinforcement capabilities of carbon black. The edges of these turbostratic sheets are where van der Waals bonds form the highest energy filler-polymer interactions [24]. In summary, the slightly imperfect graphitic structure of carbon black, its surface area, its polarity, and its aggregate structure all significantly influence its reinforcement potential.

Silica has some similarity in mechanism to carbon black in the filler-polymer network, especially due to the similarities in aggregate formation and small initial particle size. However, silica is significantly more polar than carbon black. Precipitated silica alone presents relatively poor reinforcement properties due to the large polarity difference between the hydrophilic silica and the nonpolar natural rubber [26]. The surface of the silica is made up of siloxane (Si-O-Si) and silanol (Si-O-H) groups, and the concentration of silanol groups determines the characteristics of the silica [24]. The three types of silanol surface groups are:

- Isolated: one hydroxyl group on the surface,
- Geminal: two hydroxyls on the same silicon atom.
- Vicinal: one hydroxyl each on two adjacent silicon atoms.

It is difficult to pinpoint the location and distribution of these different surface groups as amorphous silica has a highly irregular hydroxyl group arrangement [27]. A silica with a surface completely saturated in silanol groups is deemed hydroxylated and is related to its apparent polarity. A high geminal content increases silica water absorbing capacity and lessens dispersibility, related to increased polarity. High dispersibility is critical for silica to perform as an effective reinforcement filler [24]. Silane coupling agents (SCAs) are used to improve the filler-polymer network interactions by creating a chemical bridge between the polar silica surface and the less polar polymer, allowing for increased compatibility. A common coupling agent is TESPT, which also acts as a sulfur donor in the curing process [28, 29]. A general SCA molecular formula is R-Si(OR')₃. The silvloxy (Si(OR')₃) group hydrolyzes the siloxane groups and covalently bonds with the surface hydroxyl groups. The -R group will infiltrate and bind to the organic polymer [30]. This mechanism allows for proper dispersibility of silica in the fillerpolymer network and therefore, much improved reinforcement. It is evident that a varied combination of physical characteristics such as surface area, surface structure, particle size, and chemical characteristics related to the surface functional groups are important key traits to identify useful reinforcement fillers.

2.2.2 Commercially available reinforcement fillers

Commercial tire products always contain reinforcement fillers of some kind. Unless the tire is specifically marketed as petroleum-free, the tire will almost always contain carbon black for reinforcement. Carbon black has been used in rubber production for over 100 years and continues to be the most widely used reinforcement filler [1]. Usage of silica for reinforcement has increased in the past 30 years as reduced rolling resistance has become increasingly favorable for fuel efficiency and tire longevity. Most modern tires contain a combination of the two fillers, to maximize performance within the "magic triangle" of tires: wet traction, wear resistance, and reduced rolling resistance [31]. The following sections will detail these two ubiquitous fillers.

2.2.2.1 Carbon Black

Carbon black is a fine, carbonaceous powder produced through thermal decomposition of heavy petroleum products, usually in the absence of oxygen [32-34]. Carbon black significantly

improves a rubber's physical properties [35]. This includes improved tensile strength, hardness, tear resistance, hysteresis, abrasion resistance, and dynamic modulus. The structure of carbon black can vary, impacting its applications. Table 2-1 outlines the multilevel structure of carbon black and the scale for particles, aggregates, and agglomerates. The particle size, surface area, particle size distribution, aggregate structure, and surface functional groups all play a major role in carbon black's properties [35]. It is important to note that the manufacturing process and feedstock used in producing carbon black will influence the properties of the carbon black, but the details of the manufacturing processes and feedstocks are beyond the scope of this review [33].

Table 2-1: Multilevel carbon black structures

Name	Size (width)
Particle	20-100 nm
Aggregate	50-300 nm
Agglomerate	10 ³ -10 ⁶ nm

The three-dimensional arrangements of aggregates are what determines the structure of the carbon black. The various properties of different carbon blacks led to the creation of the ASTM classification of carbon black using a four-character code, N_{xyz} [36]. The *N* refers to "normal curing", indicating that the carbon black does not affect the vulcanization of the rubber. The three-digit code, *xyz*, refers to the properties of the carbon black. *x* inversely correlates to the average specific surface area as per ASTM D1765-96 (i.e., N800 would have a lower specific surface area than N200) [36]. *yz* is not standardized, but generally a higher number is a more intricate structure and therefore better reinforcement (i.e., N489 would have higher reinforcement than N422). Different grades are used in various parts of rubber tires depending on whether it's the tread compound, the sidewall, inner liner, etc. [1].

Various analyses are used to characterize the properties of carbon black, and therefore the reinforcement potential. Committee D24 of the ASTM exclusively develops standards for carbon black testing, which includes tests to characterize the void volume, the surface area, the structure,

etc. [37]. The oil absorption tests can be used to characterize the structure while the iodine number can characterize the surface area, and these values correlate with a carbon black's grade [1].

2.2.2.2 Amorphous Silica and SCAs

Following the initiation of the Green Tire Technology shifts in tire formulation, precipitated silica gained significant attention as a petroleum-free carbon black alternative. Silicas improve reinforcement, decrease rolling resistance, and improve wet traction – properties highly sought after in the tire industry. Oftentimes, rubber formulations use a combination of carbon black and silica. Amorphous silicas are generally produced through precipitation or are 'fumed', which is the pyrogenic production of silica. Some formulations, like the ENASAVE97 mentioned previously, use silica in complete replacement of carbon black to meet the standards on petroleum-free tire formulations. Like carbon black, there is a multi-scale structure to silicas ranging from particles to aggregates to agglomerates as shown in Table 2-2 [22, 24].

Table 2-2: Multilevel silica structure

Name	Size (width)
Particle	2-20 nm
String of pearls (aggregates)	100-150 nm
Clusters (agglomerates)	10 ³ -10 ⁵ nm

As mentioned in the previous section, SCAs are often required to increase compatibility between the hydrophilic silica surface to the hydrophobic natural rubber polymer chains. There are numerous silanes used for this purpose, all with variations in reactive functional groups that affect its performance in aiding reinforcement [38]. The most common SCAs used in rubber composites are TESPT, TESPD, and MEPTS, with TESPT being especially common due to its free sulfur-donating property and its synergistic effect in cross-linking during vulcanization [38-40]. Silicas are generally characterized through similar analytical techniques to carbon black: surface area through BET analysis and CTAB absorption, mean particle size, particle-size distribution, pH, and oil absorption numbers [24]. The varied surface chemistry, as detailed in the section above, is also characterized through various chemical and spectroscopic techniques.

2.2.3 Biowaste candidate replacements

Quality candidates for replacement of current commercial reinforcing fillers would either have similar physical characteristics to carbon black and silica – such as high surface area, void volume, absorption capacity, and hydrophobicity – or have demonstrated reinforcing capabilities through previous research.

2.2.3.1 Biochar

Biochar is a carbon-rich material than contains structures and properties comparable to carbon black. It is produced through the pyrolysis of biomass and has been made for thousands of years in forms such as charcoal. There are multiple pyrolysis methods, all involving an oxygendeprived environment [41]. Like carbon black, the properties of biochar strongly depends on the process conditions and the composition of the feedstock [42]. Unlike carbon black, feedstock quality and composition of biomass can be less consistent and reproduceable when compared to petroleum feedstocks. Also, pyrolysis of biomass produces two co-products alongside biochar: a liquid bio-oil and a gaseous syngas. Different process conditions can be used to produce ideal yield proportions of the three components. During pyrolysis, volatilization and char formation mainly occurs at temperatures from 200-400 °C, and as the temperature is further increased, more transformations occur and the carbon continues to aromatize, and the surface functional group concentration decreases [43]. The carbonization process, the feedstocks used, and the potential post-treatments of the biochar have been researched quite extensively for various applications of biochar, including as a potential replacement for carbon black as a reinforcing filler.

The pyrolysis process of biochar determines much of its relative properties. This includes temperature, residence time, gas blanketing, and the type of pyrolysis (conventional, microwave-assisted, hydrothermal, etc.). Some reviews on biochar have described the effects of pyrolysis

temperatures on several biochar properties [44, 45]. The char yield, polarity, hydrogen, and oxygen content decrease with increasing temperature, while carbon content, ash content, aromaticity, and pH increase. Although the polarity decreases with increasing temperature, hydrophobicity increases with temperature until aromatization reactions occur more frequently above 400 °C and the biochar begins to decrease in hydrophobicity. Surface functional group concentration also tends to decrease with increasing pyrolysis temperature, changing the potential for chemical interactions on the biochar surface [8].

Ippolito et al. (2020) conducted an extensive meta-analysis of feedstocks, pyrolysis temperatures, and pyrolysis processes of different biochars. They presented the properties of the resulting biochars from 5400 peer-reviewed studies, elucidating much valuable information on feedstock and process condition choices [45]. They organized feedstock sources as either wood-based, crop wastes, grasses, or manures and biosolids. Table 2-3 is adapted from their meta-analysis. From this meta-analysis, it is evident that lignocellulosic feedstocks produce biochars with significantly more desirable properties across the board, and this should direct future choices on feedstock.

Feedstock source	Carbon content	Specific Surface Area	Total Pore Volume	Ash (%)
	(%, dry basis)	(m^{2}/g)	(m^{3}/t)	
Wood-based	70.5 ± 0.39	184 ± 11.4	7.01 ± 3.07	10.2 ± 0.43
Crop wastes	61.4 ± 0.41	98.2 ± 5.45	2.05 ± 0.91	21.1 ± 0.54
Grasses	63.6 ± 0.72	63.4 ± 8.84	3.36 ± 3.30	18.0 ± 1.01
Manures & Biosolids	41.6 ± 0.68	52.2 ± 4.23	0.82 ± 0.30	44.6 ± 0.97

Table 2-3: Adapted from [45]

This meta-analysis does not include algal biochar. Algal residues are produced as a waste product after the extraction of oils from algae used for biodiesel production, and are a potentially viable candidate for biochar production as algal biodiesel developments increase [46]. Algae differ from lignocellulosic plant matter as they contain significant amounts of proteins and lipids in addition to carbohydrates [47]. In their review on algal biochar for potential use as soil

amendment and wastewater adsorbent, Yu et al. (2017) collected data from numerous papers that derived biochar from different micro and macro-algae species, and found that these biochars tend to have a lower carbon content and higher nitrogen and ash contents when compared to lignocellulosic biochars [48].

The properties of biochar are not only influenced by pyrolysis conditions and feedstock types, but they can also be altered through different pre- and post-treatments. These modifications can allow for more specifically engineered biochars. Pre-treatments include any physical, chemical, or biological transformations of the feedstock prior to pyrolysis. The most common pre-treatment is physical through drying and milling. Chemical and biological pre-treatments utilize various chemicals or microbes to enhance the resulting char properties such as enlarging the surface area, pore structure, and adsorption capacity, or to modify the types of functional groups on the biochar's surface [49]. Post-treatment includes chemical and physical modifications which are used to increase surface area and pore volume, and favorably modify functional groups on the surface. Many of these post-treatments are often named "activations", which generally means that the treatments enhance the surface area and adsorption potential of the material. Table 2-4 summarizes the various types of treatments for biochar. Reviews by Sajjadi et al. on chemical and physical activation of biochar are highly recommended as references for extensive data on the effects of various activations [50, 51].

Step	Туре	Example
	Dhysical	Drying
	Physical	Milling
Pre-treatment		Impregnation
[49]	Chemical	Acidification
		Basification
	Biological	Anaerobic digestion
Post-treatment	Physical	Milling
	[50]	Gaseous activation

Table 2-4: Summary of types of pre- and post-treatments of biochar

Ultrasonic activation Electro/electrochemical activation Acidification Basification [51] Amination Impregnation		Thermal activation
Electro/electrochemical activation Acidification Chemical [51] Amination Impregnation		Ultrasonic activation
activationAcidificationChemicalBasification[51]SulfonationAminationImpregnation		Electro/electrochemical
Acidification Basification Chemical [51] Amination Impregnation		activation
Chemical [51] Basification Sulfonation Amination Impregnation		Acidification
Sulfonation [51] Amination Impregnation	Chemical [51]	Basification
Amination Impregnation		Sulfonation
Impregnation		Amination
		Impregnation

There has been some research on using biochar as a partial or complete replacement of carbon black and silica for reinforcement in rubber tires. Steven C. Peterson from the USDA research labs has made significant strides in the specific applications of biochar in rubber tire composites for reinforcement made from woody waste, corn stover and starch, and coconut shells [52-61]. His findings demonstrate that partial replacement of carbon black in tire formulations performs as well as, or better than 100% carbon black in regards to reinforcement, tensile strength, and elongation at break. Biochars produced from dead leaf [62], waste lignin [63], and citrus tree trim [64] have also been used as successful reinforcement fillers in rubber composites. However, results demonstrated that biochar only had the capacity to replace up to 50% of carbon black before there were significant losses in material properties. Future investigations will need to consider the development of a biochar with potential to completely replace carbon black. The massive amount of different biomass that has been made into biochar as compared to the minimal number of types of biochar used in rubber is a huge avenue for future investigation, exploiting feedstocks with optimal properties for biochar.

One property of biochar that has been highly valuable in its applications as a soil amendment or a wastewater treatment material is its high microporosity. As shown in Table 2-5, microporous is defined as pores less than 2 nm in diameter [65]. However, this property can be a hindrance in biochar's application in rubber compounds as additives in the rubber matrix are larger than the heavy metals and excess nutrients that biochar adsorbs in its other applications. Treatments that increase mesoporosity of biochar may improve the efficacy of its reinforcement.

Porosity type	Pore diameter	
Microporous	<2 nm	
Mesoporous	2-50 nm	
Macroporous	>50 nm	

Table 2-5: Delineation of porosity type based on pore diameter

Biochar tends to be more hydrophilic than carbon black due to the presence of more surface functional groups. Issues related to the hydrophilic nature of silica may apply to biochar as well. Some studies have investigated this possibility to improve hydrophobicity and therefore compatibility with polymer. Several recent studies from the Environmental Pollution Control Theory and Technology lab out of Guilin University of Technology have investigated the use of a common industrial SCA (KH-570) on biochar to increase hydrophobicity and therefore methane absorbance in soil cover [66-68]. They determined by microscopy that the coupling agent effectively formed an organic layer on the biochar's surface and validated the compatibility of the coupling agent with the biochar. Other studies have investigated the use of non-SCAs with natural lignocellulosic fibers, and their performance as reinforcing fillers in various polymers [69, 70]. Thus far, coupled-biochar reinforcement of rubber has yet to be investigated and may be a valuable route for future research.

2.2.3.2 Bio-derived silica

There are some plants which are known to have significant accumulation of silica through uptake of soluble $Si(OH)_4$ or $Si(OH)_3O^-$ from soil [71]. Accumulation of silicon species has been found mostly in grasses and grass-like plants, known as monocotyledons of the families Poaceae, Cyperaceae, and Equistaceae [71, 72]. Poaceae includes a wide variety of vastly important grasses such as cereals, bamboos, as well as natural and cultivated grassland grasses. Cyperaceae and Equistaceae encompass less anthropogenically important species of sedges and cattails, respectively. Therefore, wastes from species of the Poaceae family should be targeted for silica capture, as it encompasses six of the seven most widely planted crops in the world [73].

The most extensively researched bio-derived silica is from rice husk ash (RHA) [74-79]. This is due to the significant proportion of silica in rice husk as compared to other agri-wastes. The raw rice husk is 20 wt% ash, with 94 wt% of the ash being silica [79]. This is significantly more than other cereal grasses as the rice plant absorbs more silicon from the soil [80]. For example, corn cob ash contains about 60% silica, bamboo leaf ash about 80%, and elephant grass ash about 50% [81-83]. Silica has also been derived from several grass wastes such as sugarcane bagasse [84, 85], oat wastes [86], wheat wastes [87], and some non-grass sources such as palm waste ash [88]. Although rice husk has been widely accepted as the most promising source of biowaste-derived silica, regional access would need to be considered for feedstock sourcing as well.

RHA as a reinforcing filler in rubber has been researched for many decades [89-92]. These studies have shown that RHA does not perform as well as industrial silica or carbon black for reinforcement of rubber, especially in high performance applications. Recently, Chen et al. (2021) ball milled their RHA in ethanol, hydroxylating the ash surface and therefore encouraging silane coupling reactions [93]. The hydroxylated and coupled RHA performed significantly better than the uncoupled and un-hydroxylated RHA and performed comparatively with the N774 carbon black filled natural rubber/butadiene rubber composites, having the highest tensile strength, elongation at break, and tear strength of all samples. This indicates a possible treatment route to make bio-derived silica a promising reinforcing filler and warrants further research.

2.2.3.3 Other reinforcement fillers

There are several other biowaste-derived reinforcement fillers which do not necessarily mimic the mechanisms of carbon black or silica but provide reinforcement in other capacities. Plant fibers have been researched for reinforcing capabilities with promising results [19, 69]. Waste fibers are part of the massive amount of agricultural waste produced, and therefore have the capacity to provide a steady supply of feedstock. These additives have issues related to their hydrophilicity interfering with filler-polymer interaction as well as their potential for microbial degradation [94, 95]. Surface modification of the fibers to improve hydrophobicity is a large focus of research into these alternative reinforcement fillers, and involve either chemical modification of the surface or grafting of hydrophobic-compatible compounds [95]. These fibers have been investigated as reinforcement fillers in rubber compounds quite extensively, but have

not been investigated for use in tires as a carbon black replacement as of yet [95]. This may be a promising avenue of future investigation.

Waste lignin from paper pulping has also been investigated as a promising reinforcement filler in rubber [96-98]. A recent study compared butadiene rubber compounds filled with kraft lignin to silica and carbon black-filled compounds [99]. They investigated uncoupled filler as well as use of the coupling agent TESPT. Use of TESPT increased the efficacy of lignin reinforcement to comparable levels of carbon black or silica but it experienced a much more pronounced hysteresis loop.

Chitin and starch are other biopolymers that have reinforcement potential. Dominic et al. (2020) created chitin nanowhiskers from shrimp shell waste to reinforce acrylonitrile-butadiene rubber [100]. They demonstrated that the nanowhiskers are effective reinforcing fillers but did not compare them to carbon black or silica filled samples. Future investigations warrant conducting experiments to compare the reinforcement between the nanowhiskers and traditional fillers. Chitin whiskers from crab shell waste have also been investigated [12, 101]. Starch has generally been utilized as an important food material, and although it has been investigated for use in rubber composites, it may not meet the criteria for waste-sourced feedstocks [102-105]. A recent review has outlined new research into starch extraction from fruit processing wastes such as pulps, seeds, skins, etc. which may make starch a viable candidate for a biowaste-derived reinforcement filler [106].

Eggshell waste has also been investigated as a potential reinforcement filler due to its high content of calcium carbonate [107, 108]. However, calcium carbonate is identified as a less effective reinforcement filler as compared to carbon black and silica, but has been effectively used as a partial replacement to cut costs without a drop in material properties, making eggshell waste a potential candidate for a combination reinforcement filler [109].

2.2.3.4 Coupling agents

To generate a completely biowaste-derived tire that uses SCAs, sources of biological SCAs or similar replacements must be identified. There has not been extensive research into sourcing

biobased SCAs. One recent study synthesized SCAs by modifying eugenol from clove oil [110]. Future investigations could identify other potential biological feedstocks, such as eugenol analogs, that could undergo the hydrosilylation reaction to produce biobased SCAs. In addition, identifying biowaste sources of these feedstocks would be necessary. Citrus peels could be a very viable candidate, with significant concentrations of limonene, which has a similar structure to eugenol, although lacking a hydroxyl group [111, 112]. There is much potential for further investigation into biobased SCAs.

2.3 Processing Additives

Processing additives are a broad category of additives which primarily improve handling and workability of the rubber during processing and vulcanization [113]. Compatibility of processing additives with the elastomer matrix is very important to ensure proper dispersion. There are a wide variety of additives which fall under the categorization of 'processing additives', and categorization of different processing additives varies between sources due to lack of standard definitions. In addition, the breadth of knowledge, application, and variability in processing additives for various rubbers is extensive. Herein will be discussed plasticizers and dispersion aids, process oils, and resins as use for rubber tire manufacture.

2.3.1 Mechanism

Generally, addition of processing additives improves the workability of the compound material. However, the mechanisms by which each of these additives function varies. Plasticizers are added to lower the glass transition temperature and soften the compound, making it much more flexible and easier to process and improves dispersion [114]. There are several theories on the mechanism of plasticizers, but all incorporate conceptualization of plasticizers as inserting themselves between polymer chains and reducing the rigidity of the polymer matrix. Peptizers are types of dispersion aids which reduce the polymer viscosity through reduction of the average molecular weight. They prevent the recombination of polymer chains as shear stress breaks chains during the initial phase of rubber mixing prior to vulcanization [1]. This lowers the average molecular weight of the rubber which in turn lowers the viscosity, which makes the material more workable. The lower viscosity facilitates the dispersion and incorporation of fillers and compounding agents into the rubber matrix during formulation as well. Process oils are chosen based on compatibility with the elastomer by polarity and miscibility. They are also

referred to as extenders, as they function to dilute the mixture and do not react with the components of the compound [115]. Resins include a large group of chemicals which have a couple different uses in the rubber compound. They can be used similarly to plasticizers and process oils to aid in handling and dispersibility of the pre-vulcanization mixture, while some have attributes which also improve tack and mechanical properties of the cured rubber [114].

2.3.2 Commercially available process additives

Processing aids are essential to the rubber compounding process to allow for better processibility. Process oils sourced from petroleum derivatives are the predominant processing aids used in tire compounding, as they are much cheaper than other more specialty processing additives [116]. Aromatic oils are being phased out due to their highly carcinogenic properties in favor of treated distillate aromatic extracts (TDAE) [117]. Plasticizers, peptizers, and resins have more specific applications and higher cost, so they find more use in specialty and performance rubber formulations [114]. Table 2-6 outlines common examples of additives used in rubber compounding.

Category	Examples		
	Phthalates		
Plasticizers and	Pine tars		
dispersion aids	Low molecular weight PP & PE		
	Organothio compounds		
	Paraffinic oils		
Process oils	Napthanic oils		
	Treated distillate aromatic extracts (TDAE)		
Resins	Hydrocarbon resins		
	Phenolic resins		

Table 2-6: Overview of	of processing	additives in	rubber compound
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Compatibility of the additives and the polymer is essential to prevent surface migration, in which the additive will migrate to the surface of the tire and no longer be properly dispersed, resulting in losses in physical properties. Compatibility is related to the viscosity, molecular weight, and molecular composition.

2.3.3 Biowaste candidate replacements

Biological systems generate significant amounts of chemicals and compounds with similar properties to commercial petroleum-derived processing additives. General tendencies for hydrophobic fats and oils in tire formulations indicate potential replacement with biological fats.

2.3.3.1 Cashew nut shell liquid

Cashew nut shell liquid (CNSL) is a byproduct of cashew farming [118]. Its main component is cardanol, a phenol group with numerous potential applications within the bio-valorization field including as a processing additive for rubber [119]. Alexander et al. conducted various studies on cardanol as a rubber additive including using cardanol versus aromatic oil as a processing additive in natural rubber filled with carbon-black [119] and filled with silica [120], using cardanol versus various commercial plasticizers in silica-filled nitrile rubber [121], and as a replacement for commercial plasticizers, activators, and antioxidants in natural rubber [122]. They found that the mechanical properties of the rubber filled with cardanol performs comparably with rubber filled with commercial additives, and cardanol demonstrated superior thermal stability during aging.

Cardanol has recently been investigated as a processing additive by way of grafting it onto natural rubber due to its highly viscous nature, making direct addition a difficult process [123-126]. Mohapatra et al. (2015) compared grafted natural rubber filled with carbon black to ungrafted natural rubber filled with carbon black and aromatic oil. They found comparable mechanical properties between the samples, and the grafted rubber had higher cross-link density and better dispersion than the ungrafted rubber [127]. Cardanol is obviously a very promising route for processing additive research.

2.3.3.2 Other processing aids

Vegetable oils have been investigated for use as processing additive in rubber due to similar properties to petroleum oils. Sovtić et al. (2020) and Roy et al. (2021) reviewed the usage of

various vegetable oils as processing additives for rubber compounding [115, 128]. Of the oils reviewed, only one was from a waste source: fried-palm oil [129]. Linseed oil, palm oil, and soybean oil seem to be the most used oils for this research. Recent studies have synthesized plasticizers for PVC from waste cooking oil. Investigation into potential use in rubber is worthwhile.

Identifying promising sources of biowaste oil can direct future investigation into sustainable biowaste plasticizers. Jayasinghe and Hawboldt (2012) reviewed various sources of bio-oils from waste biomass with a focus on fish industry waste specifically for potential use for biofuel production [130]. Recovered crude fish oil may be a promising plasticizer source. Sulaiman et al. (2013) extracted oil from solid coconut waste [131]. Coconut oil has been studied as natural rubber plasticizer previously, meaning waste-extracted oil may be an effective plasticizer [132]. Recent studies have also investigated the extraction of high-quality oil from waste date seeds, another potential plasticizer feedstock [133, 134].

Božeková et al. (2021) used wood flour waste as both a reinforcement filler and processing additive [135]. They found that the wood flour does not perform well as a reinforcement filler and can only replace a small fraction of carbon black, but it shows promise as a processing additive and demonstrates decent dispersion.

As mentioned in the biochar section above, two side products are produced during pyrolysis: biooil and syngas. This bio-oil fraction may be a promising feedstock for purification and extraction of oils to be used as effective processing additives. It also opens an avenue for a biorefinery system to process biowaste, produce biochar and bio-oil for use in tires, and recycle syngas for energy.

2.4 Protectants

Since many rubbers are composed of unsaturated backbones (natural rubber, SBR, BR, NBR, etc.) the stability of the vulcanized rubber requires protection from degradation by oxidation and ozonation. As such, antioxidants and antiozonants are added to protect the rubber and bolster longevity of the material. In the construction of rubber tires, generally internal components only
require the addition of antioxidants, while external components require both antioxidants and antiozonants due to exposure to UV radiation, heat, and shear stress [136].

2.4.1 Mechanism

Polymers are degraded through a free radical process of autoxidation through initiation, propagation, and termination [136]. The energy from UV, heat, or shearing breaks chemical bonds in the polymer, releasing free radicals. The chain propagates in reaction to atmospheric oxygen to produce more free radical products and oxidizes to form hydroperoxides. The propagation terminates when two free radicals react to form stable non radical products when oxygen is limited.

Oxidation of the rubber backbone leads to a decrease in the desired material properties and shortens the lifespan of the tire. Ozonation of surface rubber can induce crack initiation and propagation, a significant failure of rubber materials [1]. Antioxidants function to stabilize polymers and prevent the autoxidation process from propagating. There are two general categories of antioxidants: primary and secondary antioxidants. Primary antioxidants are chain terminators through removal of free radical species, while secondary antioxidants decompose hydroperoxides to nonradical species. The chemistries involved in rubber antioxidation are complex and varied, and there has been extensive research on the subject [136].

Chemical antiozonants function to prevent ozonation of vulcanized-rubber by reacting with ozone and producing inconsequential ozonation products. As for the antioxidants, more detailed descriptions of antiozonant chemistries can be found in literature [136]. Ozonation is generally only a concern for surface-exposed parts of the tire, and as such antiozonants are used only in these parts.

Petroleum waxes are also used as antiozonants. They have poor solubility and readily bloom to the surface in rubber materials [137]. Although this property is usually unfavorable for other additives, this is what gives waxes their effective antiozonant properties, by creating a protective film on the exterior of the rubber compound to prevent ozone penetration [138]. Waxes

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deteriorate under dynamic conditions which decreases their antiozonant capacity, meaning they alone cannot provide full antioxidant protection in a dynamic material such as rubber [139].

2.4.2 Commercially available protectants

The criteria for choosing which protectants to use in a rubber tire formulation are: staining and discoloration, volatility, solubility, chemical stability, concentration, and environmental health, and safety (EHS) considerations [1]. Staining and discoloration are generally insignificant in carbon black-filled tires. There are numerous types of synthetic antioxidants available to use for rubber composites, the details of which can be found extensively in literature [139]. This review will focus on the most common protectants used in tire compounding. In modern tire formulations, the most prominent are the antioxidant TMQ and the antiozonant 6PPD [1].

In rubber composites, hindered phenolics and secondary aromatic amines are generally the most used primary antioxidants. Hindered phenolics such as BHT are used in applications requiring food contact and those requiring non-staining. However, for applications in rubber tires, these properties are irrelevant and aromatic amines are much more common since they are more effective antioxidants [136]. Secondary antioxidants, less common in rubber tire formulations, include phosphite esters and sulfur-containing compounds such as thioesters [136]. The types of commercial antioxidants used in rubber processing are summarized in Table 2-7 below. The main classes are phenolics, secondary aromatic amines, and hydroperoxide-decomposers.

Class	Category	Examples	Mechanism	
Primary	Phenolic	BHT		
	Secondary aromatic amine	TMQ N,N'-Dialkylated p-phenylenediamines (DAPD)	Chain termination	
Secondary	Hydroperoxide- decomposing	Organic phosphite esters Sulfides	Reduce rate of chain initiation	

Table 2-7: Summary of rubber antioxidants

There are several test methods to determine the antioxidant activity, and the effective determination of the antioxidant activity generally requires performing multiple different tests [140]. The three most commonly used methods are Trolox equivalent assay (ABTS), 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay, and the ferric reducing antioxidant power (FRAP) assay, each with a different mechanism of determining antioxidant activity [140]. Oxygen radical antioxidant capacity (ORAC) and Folin–Ciocâlteu assays are also common [141]. Using two or more assays for antioxidant comparison is essential.

Commercial chemical antiozonants in rubber tires are almost exclusively *p*-phenylenediamines (PPDs) [136, 139]. The structure of PPD is shown in Figure 2-1. These analogs of PPD each have slightly differing mechanisms of antiozonation, but are essentially related to ozone attacks of their nitrogen-bonded hydrogen [136].



Figure 2-1: Structure of PPD

The waxes used are either paraffinic or microcrystalline, and blends can be engineered for specific protection in different formulations.

2.4.3 Biowaste candidate replacements

Biological organisms are full of various antioxidants used to scavenge oxidizing free radicals that contribute to oxidative stress and ultimately cause cellular damage, a well-documented biological defense mechanism [142-145]. These antioxidants encompass a large spectrum of compounds, generally grouped into either enzymatic or non-enzymatic. For the purposes of rubber compounding, non-enzymatic antioxidants will be discussed.

Plant-derived antioxidants, or phyto-antioxidants, have seen much growth in research and use for industries such as pharmaceuticals, food ingredients, cosmetics, and polymers [145-147]. These

phyto-antioxidants can be used either as isolate extracts, mixtures, or plant extracts. They are generally grouped either by molecular structure or by miscibility. The vast majority of biological antioxidants are phenolics such as flavonoids or terpenoids such as carotenoids, which are responsible for phyto-pigmentation, with some vitamins and other categories documented as well [145]. Natural rubber is in fact one of the most industrially important natural terpenes.

Sourcing biowaste antioxidants has been attempted from many different sources and through both traditional and newly developed extraction techniques, a summary of which can be found in Table 2-8. As with all biomass-sourced chemicals, proper feedstock selection is critical to achieve consistent and desirable results. There are many considerations beyond just the plant species to acknowledge when sourcing waste streams. Many of these wastes will even have multiple streams, for instance olive mills produce wastewater and pomace from pressing, as well as waste branches and leaves from harvest [148]. One study determined that leaves exposed to the sun contain 4.2 times more flavonoids than leaves exposed to the shade in a species of deciduous tree, an important consideration when sourcing feedstocks [149]. Sreeramulu et al. (2013) reviewed the antioxidant activities of various foods in the Indian diet and assessed their antioxidant activity using both DPPH and FRAP assays, as well as assessing the total phenolics content (TPC) [140]. Nuts and oil seeds had by far the highest antioxidant activity, followed by dry fruits and green leafy vegetables. This knowledge will aid in future sourcing of target agricultural waste feedstocks.

Waste Source	Antioxidants	Extraction Type	Source
Spent coffee	Carotenoids and	Microwave-assisted, organic	[150-153]
grounds	polyphenols	extraction	
Coffee silverskin	Melanoidins, caffeine,	Subcritical water, hydroalcoholic,	[154-157]
	chlorogenic acids	ultrasound-assisted extraction	

Table 2-8: Various phyto-waste sources used for antioxidant extraction

Olive waste leaf	Phenolics, mainly oleuropein and derivatives (only 2% of olive tree phenolics in the oil)	Methanolic extraction	[158]
Olive pomace	Various phenolics	Ethanol organosolv pretreatment	[159]
Spent sulfite liquor	Various phenolics	Ethyl acetate extraction	[160]
Grape pomace	Anthocyanins, syringic acid, (+)-catechin major compounds	Methanolic, hydroalcoholic extraction	[161, 162]
Wine wastewater	Phenolic acids	Hydrophobic eutectic solvents, pulsed electric fields, biobased solvent extraction	[163-165]
Rambutan peel	Geraniin, corilagin, ellagic acid, gallic acid	Methanolic extraction	[166]
Pyrolysis bio-oil	Various phenolics	Alkali extraction	[167]
Tomato waste	Phenolics, flavonoids	Microwave-assisted extraction	[168]
Palm oil mill effluent	Polyphenols, phenolic acids, water-soluble vitamins	Patented decanting and membrane separation	[169]
Oil palm waste leaves	Various phenolics	Methanolic extraction	[170]
Olive mill wastewater	Various phenolics	Surfactant separation, membrane separation	[171-174]
Okara	Polysaccharides	Alkaline extraction	[175]
Juice pomace	Anthocyanins, phenolic acids	Hydroalcoholic, microwave- assisted extraction	[176, 177]

As stated previously, the targeted antioxidants can be used as general plant extracts which contain a multitude of other phytochemicals or as isolate extracts of purified antioxidant compounds. This will largely depend on the composition of the material, ease of isolation, and the relative efficacy of isolates versus general extracts. Some general plant extracts may provide additional benefit than just antioxidant performance. For instance, Anandhan et al. (2011) used a methanolic extract of oil palm waste leaves as an antioxidant in natural rubber composites and compared the aging properties with three commercial antioxidants: TMQ, BKF, and IPPD and one control formulation [170]. They found that the cure characteristics and aging properties were very comparable between all the antioxidants. The oil palm extract had a secondary effect of increasing tack strength by 40%, and this multifunctional capability can be profitable by limiting the loading of other additives.

Apart from direct derivation of phyto-antioxidants, some researchers have investigated the production of antioxidants through metabolism of waste. For instance, Safafar et al. (2015) derived a process to extract antioxidants from microalgae that were grown on industrial wastewater [178]. They were able to effectively treat wastewater and extract high quality antioxidants through a methanolic extraction of the microalgae. These microalgae have significant concentrations of antioxidants, and extraction has been investigated for potential use in pharmaceuticals and food [179, 180]. As far as is known, the use of microalgae-derived antioxidants in polymer formulations has no previous investigation. Future investigations into microalgae-produced antioxidants in polymers may be of interest.

Natural antioxidants have been investigated for use in various polymers, both traditional and newer biopolymers. Brito et al. (2021) reviewed the use of polyphenolic antioxidants in polymers, but mainly limited to food and biomedical applications with no mention of elastomeric applications [181]. Öncel et al. (2019) studied the use of Henna as biological antioxidant for use in vulcanized natural rubber compared with TMQ [182]. The cure profiles and aging properties were very similar to TMQ formulations, proving that Henna is a strong candidate for antioxidant activity in rubber. However, Henna is not a biowaste and it has many current uses. The main antioxidant compounds at work in Henna are lawsone – a quinone – and gallic acid. Biowaste identification should focus on wastes with high amounts of quinone-related and gallic acid-related compounds. Lu et al. (2020) used quantum mechanics and molecular dynamics simulations of 18 natural antioxidants to determine promising candidates for use in natural rubber composites [183]. From their simulations, they determined that thymol, α -tocopherol, and

lipid-soluble epigallocatechin gallate (IsEGCG) are promising candidates. Biowastes with high concentrations of these compounds should be investigated. Komethi et al. (2012) used antioxidants derived from oil palm leaves in natural rubber vulcanizates and compared the mechanical properties and aging to compounds filled with TMQ or BHT, finding less desirable initial mechanical properties, but comparable aging properties [184]. Sukatta et al. (2022) used rambutan peel extract and compared it with TMQ and 6PPD at equal loadings in natural rubber compounds and found similar mechanical and aging properties [166]. Guo et al. (2022) developed a novel antioxidant by bonding precipitated silica to green tea polyphenols and used it in styrene-butadiene rubber composites, then compared the resulting properties to composites filled with commercial antioxidants [185]. Not only did the silica-polyphenol additive perform as well in antioxidant and compound testing, but it had the best dispersibility of all tested additives. Trying this antioxidant with a bio-silica is a good route for future investigation.

2.5 Cross-linking systems

The category of cross-linking systems encompasses various chemicals with different properties and purposes which are used in conjunction during the cross-linking of rubber composites. Rubber products require cross-linking to impart stability to the composite. Vulcanization – cross-linking with sulfur – is by far the most common cross-linking reaction used in the rubber industry [186]. Vulcanization systems generally contain five components: activators, vulcanizing agents, accelerators, retarders, and reversion resistors [1].

2.5.1 Mechanism

In *The Science and Technology of Rubber*, vulcanization is defined as, "a process that increases the retractile force and reduces the amount of permanent deformation remaining after removal of the deforming force" [187]. The rubber becomes increasingly elastic as vulcanization forms a network of sulfur cross-links.

The vulcanization process begins with activators which initiate and enhance the effects of the accelerators in the matrix [186]. The accelerators react with the vulcanizing agents which then form sulfur cross-links between two carbon-carbon double bonds in the polymer chains. Retarders become important in managing the scorch of the rubber. Scorch is the initiation of

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vulcanization due to the heating of the compound, when cross-links start to form. This results in an increase in elasticity as expected, but prevents further initial molding or shaping of the compound as it loses its fluidity [188]. In industrial practices, retarding the scorch allows for a longer time in which the compound can be heated and shaped before it becomes too elastic from vulcanization initiation. Reversion resistors are necessary to prevent sulfur cross-links from breaking at high temperatures at the end of the curing period.

Rheometric studies of vulcanization provide a lot of key information on the kinetics and mechanism of a cure. The information from a cure profile includes: the minimum torque, the max torque, ts2 (time required for cure state to increase two torque units above minimum), t25 (time required to reach 25% full cure), t90 (90% full cure).

2.5.2 Commercially available cross-linking systems

As previously stated, sulfur vulcanization is by far the most common method of cross-linking, with peroxide systems being used in some limited applications. Table 2-9 provides an overview of the components of a sulfur vulcanization system.

Category	Purpose	Current commercial types
Vulcanizing	Forms chemical crosslinks	Elemental sulfur
agent	between polymer chains	
Accelerator	Reduces vulcanization time	Guanidines (DPG), sulfenamides (CBS, TBBS,
		TBSI), thiurans (TMTD, TMTM), thiazoles
		(MBT, MBTS)
Activator	Initiates accelerator	Zinc oxide + fatty acid (stearic most often)
Retarder	Delays scorch	CTP

Table 2-9: Overview of sulfur vulcanization system components

2.5.2.1 Vulcanizing agents

Almost all commercial cure systems of rubber utilize sulfur for crosslinking, using generally elemental sulfur and an organic accelerator. However, there is a trend of lower proportions of

sulfur and higher proportions of accelerator in conjunction with sulfur donors in new vulcanization systems which has improved rubber properties [188].

2.5.2.2 Accelerators

Accelerators have varying degrees of cure speed and scorch delay, allowing a rubber formulator to fine tune the speed of a cure profile. Guanidines, which lack sulfur, are generally slower than sulfenamides, thiazoles, and thiurans which can be extremely fast [188].

2.5.2.3 Activators

The zinc oxide and fatty acid activation system is ubiquitous in sulfur vulcanization systems. The presence of zinc in a vulcanization system greatly improves the state of cure that is achievable [188]. One of the main issues regarding zinc oxide is that it is recently known to be highly toxic to aquatic environments [189]. Therefore, many rubber formulators are researching less ecotoxic alternatives.

2.5.2.4 Retarders

CTP is considered the ideal retarder, or pre-vulcanization inhibitor, as it predictably delays vulcanization proportional to loading in the formulation [188]. Formulators can dial in the dosage of accelerators and retarder to fine tune the cure profile for various formulations.

2.5.3 Biowaste candidate replacements

Research into biowaste-derived vulcanization system or components is sparse. It can be divided into two avenues of investigation: biowaste sources of sulfur vulcanization components or biowaste-derived alternative cross-linking systems.

Guo et al. (2017) separated saturated fatty acids and unsaturated fatty acids from waste cooking oil using a urea inclusion method [190]. Stearic acid, the most common fatty acid used for the activation complex, is a long chain saturated fatty acid. Investigation into refined saturated fatty acids derived from waste cooking oil as a replacement for stearic acid has potential as a sustainable source. Saturated fatty acids could also be derived from algae bioreactors using food waste as feedstock [191].

DeButts et al. (2019) investigated the replacement of zinc oxide with two types of plant protein from corn and wheat in isoprene rubber sulfur-based vulcanization [192]. They determined optimal loadings of each and demonstrated that zinc oxide could potentially be replaced by plant proteins. However, the controls had either zinc oxide or carbon black, not in tandem. Experiments with zinc oxide and carbon black versus plant protein and carbon black may provide further insight. In addition, attempting the vulcanization with proteins derived from biowaste may also be a viable route of investigation.

Kamoun et al. (2020) developed a two-part biobased accelerator system using garlic powder and cystine, both sulfur-containing biocompounds [193]. Their experiments showed improved crosslinking with the addition of this two-phase system compared to systems without accelerator. However, there was no control group that contained commercial accelerator, so making deductions as to the commercial viability of these accelerators requires further research. Garlic peel waste could be a biowaste to source these sulfur-containing biocompounds for future investigation.

Zhang et al. (2020) developed a novel elastomer cross-linking system using epoxidized soybean oil as a cross-linking agent both alone and in combination with zinc oxide in carboxylated nitrile rubber [194]. The system used epoxy-acid reactions to form cross-link bonds between the polymer chains and provided similar cure profiles and material properties to the sulfur-cured control, albeit slightly inferior. However, the use of zinc oxide appears essential for this system as the soybean oil rubber without zinc oxide demonstrates an incomplete cure profile and much worse mechanical properties. Utilizing waste oils for epoxidation and investigation into possible uses as cross-linking systems may be valuable.

2.6 Conclusion

The production of the highly-engineered complex rubber compound for tires is a major industrial process with large stakes in global supply chains. As industries shift focus to more sustainable processes and products, the traditional petroleum-based additives that have been used extensively in tire production are being reconsidered. Identifying, investigating, and implementing new

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sustainable additives is a must for a viable future for tire production. The complex set of compounds abundant in the biological world can be found in the extensive supply of biowaste available for the opportunistic engineer.

Reinforcement fillers made from various biochars to mimic carbon black or biowaste-derived silica show great promises as potential additives. Reinforcement fillers deserve a significant amount of attention as they compose such a significant fraction of the rubber compound formulation. Process oils can be derived from the vast array of waste oil sources available to use, especially in food production byproducts. Techniques are being explored to harness the powerful antioxidant capacity of nutrient-rich food waste. Curing systems that complement or completely re-envision the traditional sulfur vulcanization cross-linking system are being explored in light of environmental risk concerns for traditional additives. Even considering the vast current research on biowaste-derived compounds, further research is necessary to confirm their efficacy in rubber formulations and further, to produce effective, commercially competitive car tires. In addition, there are unexplored avenues for future research into biowaste additives such as alternative coupling agents and comprehensive biorefinery approaches to additive development. While different additive candidates are in varying stages of development from conceptual to commercial application, the feasibility of an effective biowaste tire is well within reach.

Connecting statement

The review in Chapter 2 demonstrates the multitude of biowaste materials available to produce important rubber composite additives. The review discussed the current commercial additives in tire production and the current or potential biowaste-derived replacements. It is demonstrated that the depth of research into biowaste derivatives available differs widely depending on the additive classification. As of the current state of research, reinforcing fillers demonstrate considerable interest as they compose the greatest proportion of the composite mixture. Biochar, as described in Chapter 2, has many variables able to be exploited for improved reinforcement properties in rubber composites such as feedstock type, processing conditions, and treatments. In Chapter 3, biochar derived from corn stover was used as a reinforcing filler in styrene-butadiene rubber composites. The biochar was activated with steam in three different ways and then characterized for an array of properties potentially related to reinforcement performance such as the composition, structural characteristics, and surface functional groups. The different corn stover biochars were then used to create rubber composites and analyzed for their mechanical performance against a carbon black control. The effects of steam activation on biochar characteristics and its performance as a reinforcement filler was assessed.

Chapter 3: Physicochemical characterization of different steam activations of corn stover biochar and their reinforcement of styrene-butadiene rubber composites

Abstract

Reinforcing fillers account for most of the mass of additives in a rubber composite mixture. The most common reinforcing filler is carbon black, a petroleum-sourced powder with high carbon content, high surface area, and low ash content. Recent research has demonstrated the possibility for replacement of carbon black with biochar for reinforcement in rubber. To develop a biochar that performs as well or better than carbon black, it is necessary to identify and analyze effective feedstocks and pyrolysis processing conditions. This study used biochar from corn stover, an abundant crop waste, in styrene-butadiene rubber composites and compared the mechanical properties to those filled with traditional carbon black N772 filler. Biochar samples also underwent three different types of physical steam activation. This study firstly presents the physicochemical characterization of the biochars produced, then evaluates the mechanical properties of the resulting vulcanized rubber composites. The results demonstrate that unactivated corn stover biochar and gaseous steam-activated corn stover biochars have poor performance as reinforcement fillers in comparison to N772. However, slurry-based activation of the corn stover biochar proved to be an effective treatment method to improve the mechanical properties of a biochar-filled rubber composite with comparable performance to the N772-filled composites.

3.1 Introduction

The need to transition away from fossil fuels to more sustainable sources of energy and products is now well-established as our climate rapidly changes and petroleum reserves deplete. Not only is the need for alternative energy sources necessary, but alternative sources of petroleum-derived products as well. Rubber tires are an essential product of modern society for transportation at all levels, and the demand continues to grow exponentially [1]. Carbon black is a fossil fuel-derived product used in concentrations of up to 60 parts per hundred units of rubber (phr) of a tire's

weight as a reinforcement filler, making vulcanized rubber significantly stronger and durable [20]. As tires are produced in more significant quantities, the demand for carbon black is following suit. Transitioning from a petroleum-based economy to a more sustainable bio-based economy requires optimization of novel materials derived from biological sources, ideally waste sources with no other major uses [195].

Biochar, a carbon-rich product produced from biomass pyrolysis, has been the focus of much research in recent years, being derived from a multitude of different waste feedstocks at different processing conditions for various applications such as for soil amendment, wastewater treatment, and carbon sequestration [8, 45, 49, 196]. Some biochar types do hold comparable characteristics to carbon black, marking a promising material for use as reinforcement filler in rubber composites [14, 52, 59]. However, none of these studies have determined that biochar can completely replace carbon black while retaining the same desirable properties; instead, they have concentrated on replacing only a portion of carbon black with biochar [54, 55, 60, 64].

Corn stover is an abundant biowaste, with about 1 kg of stover produced for every kg of grain resulting in about 80-100 million dry tons/year available in the United States alone [197, 198]. Biochar has been produced from corn stover and tested as a potential reinforcement filler in styrene-butadiene rubber (SBR) in combination with corn starch [53, 199]. However, for corn stover biochar to completely replace carbon black, improvements to its physicochemical properties are necessary. This can be achieved through either chemical activation by using strong acids, bases, and salts on the feedstock to improve carbonation during pyrolysis, or by physical activation using steam, CO₂, or other gases on the biochar itself in order to increase the surface area and porosity [200]. For the purposes of sustainable and 'green' treatments, this study will focus on using steam for activation to prevent further use of caustic chemicals and excess release of CO₂. In this study, corn stover biochars were physically activated with three different steam treatments to identify if steam activation could improve reinforcement by biochar and to determine which kind of steam activation method produced the most effective reinforcement filler. All steam activations significantly changed the structural properties of the biochar and produced varied improvements to composite performance. A combination slurry and steam activation, deemed type II in this study, was found to significantly improve the biochar's

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reinforcement capacity at comparable levels to carbon black, warranting further research into this low-impact activation method.

3.2 Materials and Methods

3.2.1 Biochar preparation

Corn stover (CS) was collected from a cornfield at the Macdonald Campus farm of McGill University, Ste-Anne-de-Bellevue, QC. The collected CS was dried at 105 °C until constant mass and then pulverized using a soil grinder. The pulverized material was kept in air-tight polyethylene containers until use.

Pyrolysis was conducted using stainless steel cylinders in a heating apparatus. The PID controller was an Omega Platinum CN32PT-220 (Omega Engineering, USA), and the temperature was recorded with a K-type thermocouple inserted to the center of the sample cylinder. N_2 purge gas was supplied at a rate of 0.5 L/min co-currently along the length of the cylinder to create an inert environment. Bio-oil was condensed and collected for later disposal and syngas was vented to the exterior.

Pyrolysis was conducted at 700 °C with a ramping of 20 °C/min. 700 °C was chosen for this study due to trends in research for higher pyrolysis temperatures to result in biochars with higher surface area [201]. In addition, higher pyrolysis temperatures generally produce biochars with higher carbon content and lower oxygen and hydrogen content. However, yields tend to decrease and ash content tends to increase with higher temperatures [201]. Identifying low-ash feedstocks maximizes the benefits of higher temperature pyrolysis without significant amounts of ash content. The temperature was held constant at 700 °C for one hour, and then left to cool. The resulting biochar yield was calculated as the dry mass of the produced biochar over the dry mass of the feedstock loaded into the sample cylinder. Depending on the yield per run, pyrolysis was repeated to obtain at least 100 g of dry biochar which was stored in air-tight containers for later formulation and analyses.

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The corn stover biochar (CSBC) was activated with three different steam activation methods, denoted as Type I, II, and III. All three activation methods include a base method of an additional 1 hour of pyrolysis at 700 °C with co-current 0.5 L/min N₂ and 31 g/min steam flow, followed by a 15-minute cool down with steam. The initial CSBC was produced identically for all samples, according to the pyrolysis methods described in the previous section. Biochar was not crushed or milled prior to activations. Table 3-1 defines the different activation methods.

Activation	Description
Method	
Type I	Following initial pyrolysis, the biochar is cooled to room temperature.
	Activation is conducted following the base method.
Type II	Following initial pyrolysis, the biochar is cooled to room temperature.
	Water is added to the unactivated biochar to form a slurry. The resulting
	slurry is activated following the base method.
Type III	Following initial pyrolysis, the biochar is immediately activated
	following the base method with no in-between cool down period.

Table 3-1: Description of different physical activation methods

Biochar was manually crushed and sifted through a 40-mesh sieve. Milling was conducted to ensure comparable particle size to carbon black N772 for formulation and analysis. Biochar samples were milled with a commercial blender to < 220 mesh, followed by planetary ball milling (MSK-SFM-1 from MTI inc.) with four stainless steel 500 cc jars with 1 mm yttria stabilized zirconia (YSZ) grinding media. The jars contained 750 g media, 15 g biochar, and 60 g of ethanol solvent. This was done at 450 rpm for six hours. The sample was then placed in a vacuum oven at 70 °C overnight then sieved to remove media.

3.2.2 Biochar analyses

Various analyses were conducted on the biochar and carbon black N772, including their surface area, porosity, proximate composition, functional groups, and pH. These analyses were conducted on biochar that was sieved through 40 mesh, but not ball-milled.

3.2.2.1 Surface area and porosity

Surface area and porosity was analyzed using a TriStar 3000 Surface Area and Pore Size Analyzer (Micromeritics, USA). All samples were degassed under vacuum at 120 °C overnight. Surface area was calculated per gram of biochar (m²/g), based on the Brunauer, Emmett and Teller theory. The t-plot method determined micropore surface area, and the average pore size was calculated using the Gurvitsch 4V/A BET method and the Barrett–Joyner–Halenda (BJH) method.

3.2.2.2 Proximate composition

Moisture content, volatile matter, ash content, and fixed carbon values of materials were obtained following the experimental methods described by Enders and Lehmann [202]. These analyses were conducted in triplicate for all samples. Moisture content was not obtained for biochar samples, as they were oven-dried immediately following pyrolysis, prior to storage.

3.2.2.3 Spectroscopic analysis

Fourier-transformed infrared spectroscopy (FTIR) was conducted on all biochars for identification of surface functional groups over a range of 4000 to 550 cm⁻¹ with a 4 cm⁻¹ resolution, using a Nicolet iS5 FTIR Spectrophotometer (ThermoFisher Scientific, USA) with an iD5 ATR accessory. Resulting absorbance spectra were baseline-corrected and smoothed using OriginPlus. Absorption peaks were assigned to functional groups based on literature values.

3.2.2.4 pH

pH was determined following an adapted version of previous methods [203]. To obtain pH values of the biochars, 1 g of biochar was mixed with 10 mL of deionized water. The mix was agitated for one hour then left to stand for 30 minutes. The triplicate pH measurements were taken using a glass calomel pH electrode. The logarithmic mean was taken of the triplicate values.

3.2.3 Composite preparation

The compound was formulated with styrene-butadiene rubber (SBR), N-(1,3-dimethylbutyl)-N'phenyl-1,4-benzenediamine (6PPD) antioxidant, diphenyl guanidine (DPG) accelerator, zinc oxide activator and stearic acid. Table 3-2 details the relative amounts of each component. N772 was loaded at 50 phr, as opposed to 55 phr for the biochars, to account for the difference in structural complexity between biochar and carbon black. Carbon blacks are graded with a threenumber system. The first number denotes the surface area with a higher number indicating lower surface area, and the last two numbers are approximately related to its relative complexity in structure, with higher numbers denoting lower complexity [1]. Although N772 is a less structurally complex carbon black, increase in biochar loading was necessary to allow for similar levels of moduli between biochar-filled samples and N772 filled samples.

Ingredient	Per hundred parts rubber (phr))
	NRC	CRC	CRC I	CRC II	CRC III
SBR	100	100	100	100	100
N772	50				
CSBC		55			
CSBC I			55		
CSBC II				55	
CSBC III					55
6PPD	2.0	2.0	2.0	2.0	2.0
DPG	2.0	2.0	2.0	2.0	2.0
Zinc oxide	2.0	2.0	2.0	2.0	2.0
Stearic acid	3.2	3.2	3.2	3.2	3.2
Sulfur	1.5	1.5	1.5	1.5	1.5
CBS	3.0	3.0	3.0	3.0	3.0

Table 3-2: Formulation of the rubber composites

Mixing was conducted in a HAAKE PolyLab OS RheoDrive 16 rheometer (ThermoFisher Scientific, USA), following the mixing schedule in Table 3-3. Following mixing of non-

vulcanizing components, the compound was milled at 55 °C and 9 rpm using a two-roll mill (C.W. Brabender, USA) to mix in sulfur and n-cyclohexyl-2-benzothiazole sulfenamide (CBS).

Time	
(min)	Directions
0	Add elastomer at 90 rpm
1	Decrease to 30 rpm, add half of biochar or carbon black
2	Add other half of biochar or carbon black
3	Add 6PPD, DPG, zinc oxide, and stearic acid. Increase to 70 rpm
4	Clean piston
5	Drop

Table 3-3: Composite mixing schedule

3.2.4 Composite analyses

A 2000 rubber process analyzer (RPA) (Alpha Technologies, USA) was used to calculate scorch and cure times and to visualize mechanical behavior of the composite during vulcanization. Analyses were conducted on unvulcanized, mixed samples for one hour at 150 °C. Afterwards, the samples were placed in a mold and cured in a Carver Press (Carver, Inc., USA) at 150 °C for 25 minutes under two platens at 12,000 lbf. The curing rate index (CRI) was calculated using the scorch time and the cure time. Scorch time (ts2) was determined as the amount of time from start for the torque to increase two units. Cure time (tc90) was determined as the amount of time to reach 90% of max torque. The equation for CRI is shown below.

$$CRI = \frac{100}{tc90 - ts2}$$

Tensile properties were determined on dumbbell coupons using a 5966 Extensometer (Instron, USA) according to ISO 37 to generate stress-strain data at a rate of 500 mm/min until failure.

Four samples per formulation were tested. The true secant modulus was then calculated and graphed. The reinforcement index (RI) is a way to provide a quantitative value for reinforcement using the slope of the curve. RI was calculated using the equation below, which divides the MSV at 300% strain by the MSV at 100% strain.

$$RI = \frac{M300}{M100}$$

Dynamic mechanical analysis (DMA) was conducted using a DMA 450 Newton (Metavib, USA). Strain sweeps were conducted at 23°C and 100°C and temperature sweeps at 0.7 MPa stress at 10Hz. This data was used to determine glass transition temperature, Payne effect intensity, and other dynamic performance values.

3.3 Results and Discussion

3.3.1 Biochar characterization

3.3.1.1 Proximate composition

Proximate composition of the corn stover feedstock, as shown in Table 3-4, had somewhat comparable values to previous research. However, the corn stover used in this study had higher volatile matter and lower or comparable fixed carbon than two other studies [204, 205]. The ash content of the corn stover in this study was considerably lower (3.46% vs 5% & 10%) which may be beneficial to the development of effective biochars, as previous research indicates better reinforcement with low ash biochars [52, 204, 205]. Ash content was decreased by all three types of steam activation, with type I activation demonstrating the most significant reduction in ash content. The decrease in ash percentage could be described by various phenomena. Carbon within the ash content of CSBC could be further aromatized by the activations, contributing to the increase in fixed carbon and decrease in ash [206]. However, this does not explain the sharp difference in ash content between the activation types. This is most likely due to the variability in the feedstock used to create the biochars, as stover is a combination of many different parts of the corn plant, with wide variability in composition which is a result of different harvest years, harvest locations, and corn varieties [207]. This variability must be considered when deciding on effective feedstocks for consistent biochar production.

Sample	Activation	Moisture	Volatile	Ash (%)	Fixed	pН
	yield (% of	content (%)	matter		Carbon	
	initial		(%)		(%)	
	feedstock					
	mass)					
CS	Not	10.41 ± 1.48	$84.32 \pm$	$3.46 \pm$	$12.22 \pm$	Not
	applicable		0.24	0.08	0.23	applicable
CSBC	Not	Not	$16.32 \pm$	$20.67 \pm$	$63.01 \pm$	10.06 ± 0.18
	applicable	applicable	0.71	1.01	1.93	
CSBC I	17	Not	$16.49 \pm$	$10.15 \pm$	$73.35 \pm$	10.32 ± 0.04
		applicable	0.89	0.20	0.34	
CSBC II	17	Not	$16.30 \pm$	$16.48 \pm$	$67.22 \pm$	10.21 ± 0.02
		applicable	0.77	0.43	0.65	
CSBC III	21	Not	$17.11 \pm$	13.21 ±	$69.68 \pm$	10.67 ± 0.07
		applicable	1.16	0.44	1.54	

Table 3-4: Proximate composition of CS feedstock and biochars on a dry basis

3.3.1.2 pH

The pH of the biochar samples are all quite high (pH > 10), which is typical for biochars [208]. Although it may be statistically insignificant, the activation raised the pH in all cases by about 0.15-0.61. This increase can possibly be attributed to an increase in basic functional groups, or a decrease in acidic functional groups like carboxylic acids. Of note however, is that CSBC II and CSBC overlap in margin of error and therefore no conclusion can be made on any significant change in pH for type II activation.

3.3.1.3 Structural characterization

The physical structure of the biochar is greatly influenced by processing conditions. One of the main goals of activation is to increase the pore size and surface area of the biochar [200]. The results of the surface area and porosity analysis as shown in Table 3-5 indicate a very significant increase in BET surface area due to activation for all samples from 18-25-fold, with a decrease in

average pore diameter. This demonstrates that all three activation methods were effective in increasing surface area, as intended. CSBC II has 72-75% of the BET surface area and 55-78% of the t-plot micropore area of CSBC I and III while having between 3-4 times the BJH average pore diameter. This indicates that type II activation results in a more mesoporous char product than the non-slurry activations.

Sample	BET	t-plot external	t-plot	BJH adsorption	BJH desorption
	surface	surface area,	micropore	average pore	average pore
	area, m²/g	m^2/g	area, m²/g	diameter (4V/A),	diameter (4V/A),
				Å	Å
CSBC	11.91	9.576	2.333	195.1	691.9
CSBC I	272.7	56.29	216.4	43.55	40.78
CSBC II	204.5	34.12	170.4	155.2	155.2
CSBC III	281.5	64.30	309.9	47.35	44.14

Table 3-5: Structural characterization of biochars

3.3.1.4 FTIR

The FTIR results for the four biochars, as shown in Figure 3-1, indicate familiar functional groups for biochars [50]. There is an evident aromatic C-H bending and stretching at 870 cm⁻¹ and approximately 3000 cm⁻¹, respectively. The broad O-H stretching at 3300 cm⁻¹ and the O-H bending at 1400 cm⁻¹ denotes alcoholic/phenolic functional groups on the surface of the biochars. The peak at 1050 cm⁻¹ (1010 cm⁻¹ for CSBC III) is assigned to C-O vibration. Of note is the almost identical FTIR pattern between all four biochars. This indicates that steam activation of any kind does not significantly affect the surface functional groups. However, minor increase in the intensity of both O-H peaks of the activated biochars may indicate an increase in hydroxyl groups on the biochar surface due to steam activation. This increase in surface hydroxyl groups would in turn potentially increase the surface polarity and affect the compatibility with a non-polar polymer such as SBR.



Figure 3-1: FTIR spectra of the biochars

3.3.2 Composite characterization

3.3.2.1 Vulcanization curves

The vulcanization curves of the four CSBC-filled rubber composites (CRC) and the N772-filled rubber composite (NRC) are shown in Figure 3-2. All five samples had comparable scorch times. However, NRC had the lowest initial modulus, indicating better mixing of additives due to less initial resistance in the rubber gum. CRC, CRC I, and CRC III all had very similar initial moduli and scorch times, demonstrating a lack of improvement in vulcanization characteristics through type I and type III activation. CRC II has a lower initial modulus approaching that of NRC, indicating an improvement in initial processibility through type II activation. Low initial moduli are favorable as they allow for improved processibility and indicate a lack of pre-emptive interactions in the polymer-filler matrix [188]. The cure rate of the NRC is much higher than the other samples. Again, CRC II demonstrates an improvement towards NRC in terms of vulcanization properties while the rest remain similar. Also, CRC II shows the most minimal marching modulus of the four CRCs, an indication of better dispersion and less filler-filler

interactions [209]. Marching modulus is a phenomenon typically apparent in silica-filled rubber composites and can be indicative of interactions between curative agents and polar surface functional groups of silica, hindering curative activity in the mixture. These results may indicate that CSBC II has the highest removal of surface functional groups following activation of the biochars, resulting in minimal curative adsorption and minimal marching moduli.

CRC II has a lower final modulus around 1400 kPa versus NRC at around 1750 kPa, while the other composites demonstrate noticeable marching moduli that increase between the modulus values of CRC II and NRC. This indicates the production of a less stiff rubber by CRC II while still achieving a more complete and well-dispersed cure as opposed to the other CRCs.



Figure 3-2: Vulcanization curves from RPA for composites

As shown in Table 3-6, all the samples have relatively similar scorch times, which indicates no significant variation in pre-emptive crosslinking. The CRI describes the speed of vulcanization

of the rubber composites. NRC has the highest CRI, approximately 5-6 times higher than CRC, CRC I, and CRC III, indicating a relatively much faster rate of cross-linking. Again, CRC II demonstrates a noticeable change in CRI compared to the other CRCs, at 60% of the CRI of NRC. The curing behaviors of these composites demonstrate that type II activation of corn stover biochar results in a filler with curing behaviors more like N772.

Sample	ts2	tc90	CRI
	(min)	(min)	(min ⁻¹)
NRC	3.75	8.5	21.1
CRC	3.75	30	3.81
CRC I	3.5	20.7	5.81
CRC II	3.5	11.4	12.7
CRC III	3.75	26	4.49

Table 3-6: Cure characteristics of reinforced rubber

3.3.2.2 Tensile properties

MSV (true secant modulus) tensile curves of the five composites demonstrate the reinforcement properties and relative strength of the rubber composites. Reinforcement behavior is indicated by the slope of the upturned tensile curve, with more highly reinforced materials demonstrating more stress in response to the same strain as less reinforced materials. From the tensile curves in Figure 3-3, it can be deduced that activation of any kind improves the reinforcement properties of the resulting rubber composite, as the unactivated corn stover biochar has a much lower slope. CRC I and III have comparable slope and ultimate tensile strength while NRC and CRC II have comparable slope and ultimate tensile strength. These curves also provide insight into the polymer-filler matrix dynamics at small strains. CRC, CRC I and CRC III all have the same high initial MSV with a sharp decline within 50% initial strain. This is sharply contrasted by NRC which has nearly half the initial modulus and minimal downward movement before beginning to demonstrate reinforcement behavior. CRC II shows a change in properties compared to the other CRCs as it has a lower initial modulus approaching that of NRC. A large differential in initial MSV indicates prominent rigidity of the filler in response to initial stress. However, the lack of

reinforcement for CRC, CRC I, and CRC III at higher strains in comparison to NRC or CRC II denotes poor filler dispersion. Initial rigidity at lower strains may be a result of the less-dispersed fillers exhibiting the hydrodynamic effect more prominently as the filler is clumped and is still able to redistribute the stress of minimally stretched polymer chains. As the strain increases and polymer chains are stretched, the poor dispersion of the filler may result in more filler-filler interactions and breakdown of filler agglomerates. This prevents the filler from exhibiting the stress amplification as observed for NRC and CRC II. So, this high initial MSV is most likely due to poor dispersion and clumping of the filler, resulting in poor reinforcement at high strains as it lacks a well-distributed polymer matrix to distribute the stress properly.



Figure 3-3: Stress-strain curve of the biochar-filled composites

As shown in Figure 3-4, CRC I, II, and III improved the RI over CRC by 19.3%, 49.9%, and 28.6%, respectively. CRC II has a RI that is 95.5% of the RI of NRC, indicating very effective reinforcement behavior for CSBC II and promise for its use as a potential replacement for N772.



Figure 3-4: Reinforcement indices of filled rubber composites

3.3.2.3 Dynamic behaviors

The results of DMA indicate no significant change in the glass transition temperature (T_g) as interpreted from Figure 3-5a between all the CRCs, with NRC having a slightly higher T_g . The T_g of rubbers is not significantly affected by different carbon black structural properties and loadings, indicating that the difference in NRC from the biochar composites may be a result of compositional differences more than physical differences [210-212]. The curves for CRC I and III are nearly identical and overlap throughout the temperature range. A similar trend is notable for CRC and CRC II, with higher maximum tan δ values at about 1.2. The max tan δ values correspond to the ratio of the loss modulus to the storage modulus, or in other words of the viscous to the elastic behavior. NRC has both the highest tan δ value as well as a significantly broader peak. The area under the tan δ curve relates to a material's damping properties and the capacity to dissipate energy [213]. From these results, NRC has the highest damping capacity of the composites, followed by CRC and CRC II, with CRC I and III having the lowest damping capacity. This indicates that type I and III activations decrease the viscous behavior of the resulting composite while type II has no significant effect when compared to CRC. An interesting behavior occurs at around 25 °C and above, where the loss modulus of NRC begins to drop significantly while the CRCs all begin to plateau. The high tan δ of NRC and its lower G'_{rubbery} indicate that NRC is less elastic than the CRCs. However, at temperatures above 25 °C, the NRC starts to become exceedingly elastic in behavior while the CRCs become slightly more viscous. In terms of filler dynamics, as the polymer matrix softens at these higher temperatures, the biochar fillers appear to retain rigidity in entanglements with polymer [212]. This may be due to the poor filler dispersion of the biochars as clumping would become more prominent as the matrix softens. In practical use, the CRCs appear to have better capability for energy dissipation at temperatures above 25 °C, which would be valuable for filled-rubber applications in which dissipation is important such as tires. Whether this is due to poor filler dispersion or high-density cross-linking is unclear.

Figures 3-5b and 3-5c show the storage modulus and loss modulus of the composites against temperature, respectively. Distinct glassy and rubbery plateaus of the storage modulus can be seen below and above the T_g , respectively. Generally, the rubbery plateau is an indication of the degree of crosslinking and filler interactions within the compound matrix, with a higher rubbery storage modulus (G'_{rubbery}) associated with a higher degree of crosslinking [214]. This can also be described as having a lower monomer count or chain length between crosslinks. The value of G'_{rubbery} was determined as the storage modulus at 30 °C above T_g as done by Berki & Karger-Kocsis [214]. Table 3-7 summarizes values obtained from Figures 3-5a & 3-5b.

Sample	Tg	G'rubbery @ Tg+30 °C
	(°C)	(MPa)
NRC	-28.80 ± 0.14	2.088 ± 0.224
CRC	$\textbf{-31.80}\pm0.14$	3.805 ± 0.327
CRC I	-31.63 ± 0.51	4.393 ± 0.333
CRC II	$\textbf{-32.07} \pm 0.81$	3.281 ± 0.271
CRC III	-31.83 ± 0.64	4.278 ± 0.349

Table 3-7: Crosslinking density of cured rubber composites

The Tg of the CRCs demonstrate insignificant variation indicating no influence on Tg by activation. NRC demonstrates comparable Tg to other studies which demonstrate a lack of variation between carbon black grades as well as loading percentage [211, 212]. In ascending order of G'rubbery, the composites are ranked NRC<CRC II<CRC<CRC III<CRC I. As stated previously, the modulus of the rubbery plateau can be indicative of the degree of crosslinking, with higher moduli denoting higher crosslinking. However in this study, NRC has the lowest rubbery modulus which is more likely due to the increased filler volume fraction of the biochars relative to N772. This may indicate that the structural differences between biochar and carbon black were overcompensated for. In addition, if rubbery modulus was used to determine relative crosslinking, higher moduli would be correlated to higher Young's modulus as demonstrated previously [215]. It would appear to be nearly opposite in the case of these experiments. Even if the variability between carbon black and biochar is accounted for and the CRCs are compared only to each other, this unexpected trend stands. In comparisons of DMA properties of different carbon black-filled SBR composites, lower storage moduli and higher tan δ are associated with larger particle sizes and lower surface areas [211]. This may provide an explanation as to why N772 is the superior reinforcement filler but exhibits rheological properties that indicate the opposite as the activated CRC fillers have significantly larger surface areas. These results are likely unrelated to crosslinking density.



Figure 3-5: tan δ (a), G' (b), and G'' (c) versus temperature at constant stress 0.7 MPa

Figure 3-6 illustrates the Payne effect, in which materials exhibit nonlinear decay of G' and G'' under increasing strain [216]. Much information can be deduced from the Payne effect regarding filler properties and interactions in the polymer matrix. These phenomena are attributed to the hydrodynamic effect of the composite fillers in which nondeformable fillers transfer their stress to the sliding polymer chains occurring between crosslinks, resulting in increased strain and allowing for increased reinforcement [217].

The pronounced Payne effect of CRC I and III in Figure 3-6 alongside the high apparent crosslink density would suggest that these two composites would perform exceptionally well in

terms of reinforcement. However as noted above, this is not the case. Table 3-8 quantifies the Payne effect as the ratio between the storage modulus at 0.1% strain to the storage modulus at 100% strain. NRC exhibits the Payne effect the least. This variation in the Payne effect can most likely be attributed to differences in filler dispersion, as higher Payne effect is associated with poorer filler dispersion [218]. In addition, higher initial moduli at low strains are indicative of more filler-filler interactions and poor dispersion [219]. Carbon black demonstrating better filler dispersion may be due to its better compatibility with the nonpolar SBR polymer chains than the slightly polar biochar surfaces. Alternatively, higher Payne effect can also be attributed to increased surface area of the filler. N772 has a BET surface area of 32 m²/g, significantly lower than the surface areas of CSBC I, II, and III. Furthermore, CSBC I and III have comparable BET surface area with CSBC II being slightly lower, correlating to their respective Payne effect ratios. However, CSBC has the lowest BET surface area of all fillers, yet the second smallest Payne effect. This may be contributed to a combination of poor dispersion increasing the Payne effect and its minimal surface area decreasing the Payne effect. Further analysis would be necessary to confirm these relationships.



Figure 3-6: Graph of storage modulus versus deformation for sweep at 23 °C

Sample	G'@ 0.1 %	G' @ 100 %	Payne Effect
	deformation	deformation	[G'(0.1)/G'(100)]
	(MPa)	(MPa)	(MPa)
NRC	2.20	1.45	1.52
CRC	3.50	1.95	1.79
CRC I	4.00	2.05	1.95
CRC II	3.00	1.65	1.82
CRC III	3.95	2.00	1.98

Table 3-8: Payne effect

3.3.3 Biochar to composite property correlation

Finding methods to predict and assess the efficacy of a filler in a rubber vulcanizate by its inherent properties prior to formulation would provide a cost-effective and time-saving method to screen future potential biochars for reinforcement applications. As carbonaceous reinforcement fillers have a significant correlation between physical structure and their reinforcement capabilities, the structural properties of the biochar may have a distinct correlation with resulting reinforcement or curing characteristics [20]. Common methods for determining the physical characteristics of biochar are surface area and porosity analyses as conducted in this study. Surface area analysis methods that account for more mesoporosity, such as the cetyl trimethyl ammonium bromide (CTAB) surface area analysis, may better correlate with filled rubber physical properties than BET surface area. In the case of the CTAB analysis, the main difference is that the size of the CTAB molecule prevents it from entering micropores, and therefore may better estimate the surface area of the filler that is accessible to larger components of the compound mixture, avoiding inclusion of microporous surface area in the calculation. Biochar is renowned for its adsorption capacity [49, 220-222]. If a microporous biochar adsorbs accelerators, curing agents, activators, etc. during mixing and isolates them from the larger monomer components, then these additives may be essentially inactivated in the polymer matrix and this would significantly affect the vulcanization of the composite. Table 3-9 lists the longest lengths of each of the additives used in the cured composite. These measurements were obtained

by constructing the molecule in Chem3D (PerkinElmer, United States) and using the measurement tool to measure the longest length of the compound. The mean pore diameters for CSBC I and III are of the same scale as the additives in Table 3-9, while CSBC II has a mean diameter three times the size. This may provide an explanation as to the efficacy of CSBC II as a reinforcing filler as compared to CSBC I and III, preventing isolation of necessary additives from the polymer matrix. The only major variation between the three activated biochars is the surface area and porosity, as FTIR and proximate composition are only slightly varied. CSBC I and III have similarly high BET surface area and high t-plot micropore area, but their average pore diameter is significantly smaller relative to Type II. Following this trend, an ideal filler may potentially have both a high surface area and a high percentage of mesoporosity. It is important to note however that these structural analyses were conducted prior to final grinding and milling that occurred before vulcanization. This may affect porosity measurements and should be investigated further to determine if there is significant variation in structural characteristics before and after this processing.

Ingredient	Length (Å)		
6PPD	14.9		
DPG	11.2		
Zinc oxide	1.63		
Stearic acid	23.1		
Sulfur	4.78		
CBS	13.9		
Zinc Stearate	51.1		

Table 3-9: Longest lengths of rubber composite components (measured in Chem3D)

To evaluate this, various physical measurements of biochar (BET, t-plot micropore, and BJH average pore diameter) were plotted against different characteristics of the resulting composites (RI & CRI). The correlative p-values of these plots are listed in Table 3-10. From these results, the micropore surface area calculation multiplied by the average pore diameter has a very significant correlation with the resulting RI with p-value <0.01. If either of the biochar values are compared independently there is no significant correlation whatsoever. This informs the potential

strong influence of mesoporosity on the performance of reinforcing fillers. However, the data points in this study are limited, preventing the formation of conclusive assertions. Further studies on characterizing biochar and its reinforcement as a carbon black replacement can elucidate this further.

	RI	CRI	RI x CRI
BET	3.77 x 10 ⁻¹	7.88 x 10 ⁻¹	7.62 x 10 ⁻¹
Micropore	4.23 x 10 ⁻¹	9.14 x 10 ⁻¹	8.72 x 10 ⁻¹
BJH average pore diameter	8.63 x 10 ⁻¹	7.63 x 10 ⁻¹	7.83 x 10 ⁻¹
BET x BJH	3.00 x 10 ⁻²	4.69 x 10 ⁻²	3.21 x 10 ⁻²
Micropore x BJH	3.06 x 10 ⁻³	1.25 x 10 ⁻¹	9.80 x 10 ⁻²

Table 3-10: p-values of various filler-composite correlations

3.4 Conclusions

In this study, biochar was made from corn stover waste and processed by three different types of steam activation. The biochars were characterized and then used as reinforcement fillers in SBR composites as a sustainable alternative to the ubiquitous petroleum-derived carbon black used in industry today. The properties of the resulting biochar-filled composites were compared to a traditional carbon-black filled SBR composite. It was shown in this study that corn stover biochar and purely steam-activated corn stover biochars have little potential in fully replacing carbon black as a reinforcement filler. However, corn stover biochar activated through slurry and steam flow demonstrated considerable reinforcement properties and showed promising potential as a reinforcement filler. These results indicate that type II activation is a highly effective activation method for the purposes of reinforcement by biochar, and further studies in type II activation of biochars from different feedstocks is warranted. In addition, a possible correlation between mesoporosity in biochar and resulting composite reinforcement is presented.

Connecting statement

In Chapter 3, corn stover biochar was produced and activated with three different steam activation methods. These biochars were characterized for their physicochemical properties. Styrene-butadiene rubber composites were then prepared using the produced biochars and tested for various mechanical properties and compared alongside a carbon black-filled composite. The results demonstrated that unactivated corn stover biochar does not perform well as a reinforcing filler in comparison to N772 carbon black. In addition, corn stover biochar activated with two different gaseous steam activations produced little to no improvements in the biochar reinforcement properties. However, slurry-based activation produced considerable improvements to the reinforcing properties of the corn stover biochar and could produce comparable mechanical properties in rubber composites to N772. In Chapter 4, two grain husks (oat and rice) and two nut shells (hazelnut and walnut) are used as biowaste feedstocks for biochar production. Husks were chosen for high silica content while nut shells were chosen for low ash content, both theorized to be favorable characteristics for reinforcement performance. These biochars were produced both unactivated and with slurry-based activation. The biochars were analyzed for their physicochemical properties and then used to produce styrene-butadiene rubber composites. The impact of feedstock composition and slurry-based activation on composite mechanical properties was investigated.

Chapter 4: Nut shell and grain husk waste biochar as carbon black replacements in styrene-butadiene rubber composites and improvements through steam activation

Abstract

Carbon black is the premier reinforcement filler for rubber composites, having been in use for over a century. However, petroleum-independence has become increasingly desirable in recent years and has pushed researchers to develop ways to replace essential petroleum-derived products. In recent decades, silica has become an increasingly common reinforcing filler in tandem with carbon black. Biowaste has attracted significant attention as a feedstock for bioeconomy development as it is readily available, cheap, and has little to no competing markets. Due to some compositional similarities, biochar has been used in research as a full or partial replacement of carbon black in rubber composites to varying degrees of success. The limitations of biochar in this application include its higher ash content, higher polarity, and lower structure. Choosing the right feedstocks and developing effective treatment methods of biochar can improve upon its properties and lead to a more effective reinforcement filler. This study creates and characterizes biochar from two different low-ash nut shell feedstocks (hazelnut and walnut) and two high-silica grain husk feedstocks (oat and rice). These biochars are subjected to slurrybased steam activation and used to create and characterize vulcanized rubber composite formulations and compared to a traditional carbon black filled rubber composite. The results demonstrate that the nut shell biochars provide high reinforcement properties that meet or exceed those of carbon black and that slurry-based activation of biochar improves mechanical properties in the filled composite. The study presents correlations of low ash content and high lignin content in potential feedstocks with improved reinforcement performance.

4.1 Introduction

Rubber composites have been one of the most important industrial materials of the past century, recognized for their physical properties such as their high tensile and tear strength [37]. Incorporation of reinforcing fillers into rubber composites increases these desirable properties considerably and can be added in amounts up to 60 parts per hundred of rubber [20]. Carbon

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black has been the prominent reinforcement filler used in rubber composites since the late 19th century, with 11.6 million metric tons used annually worldwide as of 2016 [223]. Carbon black is sourced from petroleum, in which hydrocarbon feedstock is heated in an oxygen-deprived environment. As the pressures of climate change and societal priorities of sustainability have reshaped the industry, researchers are seeking petroleum-independent alternatives to carbon black. In recent years, much research has been conducted to find alternatives for carbon black such as silica, which is now used in major rubber industries like tire production [19]. Identifying and investigating viable bio-sources for reinforcement alternatives to petroleum derived carbon black or mined silica fillers can open avenues for further sustainable production.

There have been some investigations into reinforcement fillers for rubber composites derived from materials such as plant fibers [94, 224], starch [103, 225], chitin [12, 101], lignin [98, 226], eggshells [107, 108] and biochar [9, 11, 14, 53, 54, 63, 64]. Biochar is the most similar in material properties to carbon black, being a porous, high surface area, turbostratic carbon powder with demonstrated reinforcement capacity [14]. Biochars have been produced from a multitude of biomass feedstocks for applications such as contaminant removal, soil amendment, carbon storage, catalysis, and fuels [45, 227]. These materials have gained traction as potential rubber composite fillers with biochars made from sources such as wood [54, 56, 59], lignin [63], rice bran [228-231], rice husk [232-235], corn starch and stover [53], corn cob [235], citrus tree trim [64], waste proteins [236], bamboo [235], and coconut shell [59] being used in various rubber composites as reinforcement filler.

To maximize the sustainability of bioproducts like biochar, crop wastes should be exploited as feedstock as opposed to virgin biomass. Cereal wastes such as grain husks are the most abundant crop waste globally and have minimal high value usage [237]. Rice husks (RHs) are notable for high concentrations of silica, and RH ash has already been commercialized as a silica filler in rubber formulations by Goodyear and Michelin [238-240]. One research group has done much investigation into RH biochar as a filler in natural rubber composites with focus on milling methods [93, 232, 234]. Their studies demonstrated that RH biochar does provide reinforcement, and that ethanol-assisted ball milling as well as the addition of a silane coupling agent improve its reinforcement capabilities. The mechanical properties these biochars provided to natural

rubber composites show very promising potential, but there is still space to generate biochar fillers that can eventually completely replace carbon black or silica in rubber compound. To the best of our knowledge, oat husk (OH) biochar has not been investigated as a potential reinforcing filler in rubber composites. OH has a lower ash content than RH, but like RH, this ash content is almost exclusively silica [241]. The impacts of different proportions of silica composition in the grain husk biochars needs to be assessed. Nut shells have extremely low ash content, compared to other typical agricultural waste biomass [242]. Walnut shells (WS) and hazelnut shells (HS) are both available crop wastes with limited current uses. To the best of our knowledge, neither have been used thus far as biochar fillers in composites.

Biochars can be subjected to different treatment methods to improve certain desirable qualities such as surface area, porosity, surface functional groups, and structure. Most commonly, this involves some type of activation, either physical or chemical in nature [227]. To develop a truly sustainable product, avoidance of chemical treatments is necessary and physical activation is preferred for further treatment. Physical activation is generally divided into steam or gaseous activation, with both resulting in larger pores and higher specific surface area. Higher grade carbon blacks are noted for their smaller particle size as well as high average surface area. Therefore, increasing biochar surface area through physical activation may improve reinforcement capabilities.

This study describes the methods used to prepare and activate biochars from two grain husks and two nut shells, and to formulate the rubber composites. Physicochemical properties of the biochars and mechanical properties of the composites are presented and discussed. The correlations between the biochar or feedstock properties and the resulting filled composite behavior are presented. Results demonstrate that nut shell-derived biochars provide mechanical properties in rubber composites that meet or exceed those of carbon black. Additionally, slurry-based activation of biochar is shown to improve mechanical performance of filled composites. The findings of this study indicate that biochar can fully replace carbon black as a reinforcing filler. The findings also indicate that high lignin content and low ash content are favorable properties for biochar feedstocks for reinforcement performance. Future investigations should focus on identifying feedstocks that meet these criteria.

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4.2 Materials and Methods

4.2.1 Biochar preparation

Biochar was prepared from four different feedstocks: two grain husks and two nut shells. OH was sourced from Quaker Oats (United States). RH was sourced from a homebrewing supply store in Quebec, Canada. HS was sourced from the Ontario Hazelnut Association (St. George, ON, Canada). A 14-grit blasting media from McMaster-Carr (United States) was used as feedstock for WS biochars. HS was ground with a soil grinder while WS did not require additional grinding. OH and RH were not ground prior to pyrolysis due to the husk size being comparable to the coarse shell grindings.

Biomass was pyrolyzed in a cylindrical stainless steel heating apparatus under N_2 at 0.5 L/min. The PID controller was an Omega Platinum CN32PT-220 (Omega Engineering, USA), connected to a K-type thermocouple inserted to the center of the sample cylinder. Control settings were set to ramp at 20 °C/min to 700 °C. The final temperature of 700 °C was then held for an hour, followed by cooling. This study used 700 °C as pyrolysis temperatures since higher pyrolysis temperatures are related to higher specific surface area (SSA) [201]. Additionally, higher pyrolysis temperatures are associated with higher proportions of carbon and lower proportions of oxygen and hydrogen, which relates to increased aromaticity. This, however, is at the expense of decreased yields and increased ash content [201]. Pyrolysis was repeated with new raw feedstock until 100 g of dry biochar was produced and the yield was calculated on a dry-weight basis.

The biochars were activated using a slurry-based steam activation. Biochar produced from the initial pyrolysis is allowed to cool prior to mixing with water to form a slurry. The ratio of water to biochar, necessary for slurry formation, was calculated for each feedstock. The slurry was then reloaded into the pyrolysis unit and underwent an additional 1 hour of pyrolysis at 700 °C under N_2 . 31 g/min steam was also injected into the pyrolysis chamber concurrently. After an hour, the biochar was allowed to cool.

Biochars were ground using a countertop blender and then passed through a 40-mesh sieve. Biochar analyses were conducted on the sieved samples. Prior to composite preparation and analyses, the biochar was further processed in a commercial blender and passed through a 220mesh sieve, prior to planetary ball milling (MSK-SFM-1, MTI inc.). Ball milling was conducted with four 500 cc stainless steel jars at 450 rpm for six hours. Each jar contained 750 g of 1 mm yttria-stabilized zirconia griding media, 15 g biochar, and 60 g ethanol. Following milling, samples were placed in a 70 °C vacuum oven overnight and then sieved to remove residual grinding media. The biochars are named in this manuscript, following Table 4-1.

Table 4-1: Biochar naming convention

Composite	Abbreviation
Oat husk biochar	OHB
Activated oat husk biochar	OHBA
Rice husk biochar	RHB
Activated rice husk biochar	RHBA
Hazelnut shell biochar	HSB
Activated hazelnut shell biochar	HSBA
Walnut shell biochar	WSB
Activated walnut shell biochar	WSBA

4.2.2 Biochar analyses

Biochar samples were analyzed for physicochemical properties such as structural characteristics, chemical composition, and the presence of functional groups.

4.2.2.1 Yield

Yield of initial pyrolysis and after steam activation were calculated on a dry-weight basis. Pyrolysis was conducted, in triplicate or higher, depending on the amount of pyrolysis runs required to obtain 100 g of dry biochar. Activation was conducted once for each biochar. Pyrolysis yield was calculated as final mass over initial mass, while activation yield was calculated as percent burn-off, as follows [243].

Activation burn of
$$f(\%) = 100 - \frac{final mass(g)}{initial mass(g)} * 100$$

4.2.2.2 Specific surface area and porosity

Samples were analyzed with a TriStar 3000 Surface Area and Pore Size Analyzer (Micromeritics, USA). After degassing under vacuum at 120 °C overnight, samples were analyzed for various structural properties. Specific surface area was calculated following Brunauer-Emmett-Teller (BET) theory. Micropore and external surface area and micropore volume were calculated using the t-plot method. Pore width was analyzed using the Gurvitsch 4V/A BET and the Barrett-Joyner-Halenda (BJH) methods.

4.2.2.3 Proximate composition

Samples were analyzed for their composition in moisture content, volatile matter, ash content, and fixed carbon, following methods described by Enders & Lehmann [202]. Triplicate samples were analyzed. As biochar samples were oven-dried overnight immediately after pyrolysis, moisture content was not determined.

4.2.2.4 Ultimate composition analysis

Biochar samples were sent to the Laboratoire de Chimie Analytique, Laboratoire des Technologies de la Biomasse at the Université de Sherbrooke (Sherbrooke, Québec, Canada). Following an adaptation of ASTM D-5373-16, samples were analyzed for mass percentage of carbon, hydrogen, nitrogen, oxygen, and sulfur (CHNOS), in triplicate, on a 2000 Organic Elemental Analyzer (Thermo Scientific, USA). The limits of detection for N, S, O were 0.01%, 0.2%, and 0.01%, respectively. Atomic ratios of oxygen to carbon (O/C) and hydrogen to carbon (H/C) were calculated for each biochar based on the ultimate composition analysis results.

4.2.2.5 Spectroscopic analysis

Spectroscopic analyses were conducted using attenuated total reflectance Fourier-transformed infrared spectroscopy (ATR-FTIR) with a Nicolet iS5 FTIR Spectrophotometer (ThermoFisher Scientific, USA) and the iD5 ATR accessory. The spectra were analyzed from 4000 to 550 cm⁻¹ with a 4 cm⁻¹ resolution. Absorbance spectra were baseline-corrected, smoothed, and had peaks assigned functional groups in OriginPlus.

4.2.3 Composite preparation

Styrene-butadiene rubber (SBR), N-(1,3-dimethylbutyl)-N'-phenyl-1,4-benzenediamine (6PPD), diphenyl guanidine (DPG), zinc oxide, stearic acid, sulfur, and n-cyclohexyl-2-benzothiazole sulfenamide (CBS) were used as base components of the polymer formulation. Table 4-2 contains the formulation composition of the composites. As there is considerable difference in the structure complexity between biochar and carbon black, N772 is added at 50 parts per hundred rubber (phr) while biochar is added at 55 phr. This loading difference was determined experimentally to provide comparable levels of final modulus of the vulcanized composite to compensate for structural differences. This allows for better comparison of reinforcement behavior.

Ingredient	Parts per hundred						
	rubber (phr)						
	NRC	Biochar					
SBR	100.0	100.0					
N772	50.0						
Biochar		55.0					
6PPD	2.0	2.0					
DPG	2.0	2.0					
Zinc oxide	2.0	2.0					
Stearic acid	3.2	3.2					
Sulfur	1.5	1.5					
CBS	3.0	3.0					

Table 4-2: Formulation of the rubber composites

The composite was mixed with a HAAKE PolyLab OS RheoDrive 16 rheometer (ThermoFisher Scientific, USA), according to the mixing schedule in Table 4-3. Once mixed, the composite was milled at 55 °C and 9 rpm using a two-roll mill (C.W. Brabender, USA), mixing in sulfur and CBS.

Table 4-3: Composite mixing schedule

Time	
(min)	Directions
0	Add elastomer at 90 rpm
1	Decrease to 30 rpm, add half of biochar or carbon black
2	Add other half of biochar or carbon black
3	Add 6PPD, DPG, zinc oxide, and stearic acid. Increase to 70 rpm
4	Cleanse piston
5	Drop

The composites were named following Table 4-4.

Composite	Abbreviation
N772-filled rubber composite	NRC
Oat husk biochar-filled rubber composite	ORC
Activated oat husk biochar-filled rubber composite	OARC
Rice husk biochar-filled rubber composite	RRC
Activated rice husk biochar-filled rubber composite	RARC
Hazelnut shell biochar-filled rubber composite	HRC
Activated hazelnut shell biochar-filled rubber composite	HARC
Walnut shell biochar-filled rubber composite	WRC
Activated walnut shell biochar-filled rubber composite	WARC

Table 4-4: Composite naming conventions

4.2.4 Composite analyses

Scorch and cure times were calculated using the results from a 2000 rubber process analyzer (RPA) (Alpha Technologies, USA). Samples were placed in a mold and cured in a Carver Press (Carver, Inc., USA) at 150 °C for 40 minutes under two platens at 12,000 lbf. Scorch time (ts2) was determined as the amount of time from start for the torque to increase two units, and the cure time (tc90) was determined as the amount of time to reach 90% of max torque. The cure rate index (CRI) was then calculated as follows [244].

$$CRI = \frac{100}{tc90 - ts2}$$

The relative intensities of marching moduli between the cured samples was determined by calculating the marching modulus index (MMI) using an equation adapted from that used by Jin et al. (2021) [245]. MSV_{40} and MSV_{15} are the true secant modulus values at 40 min and 15 min, respectively.

$$MMI = \frac{MSV_{40} - MSV_{15}}{40\,\mathrm{min} - 15min}$$

Four dumbbell-shaped coupons per formulation were analyzed for tensile properties at 500 mm/min until failure on a 5966 Extensometer (Instron, USA) following ISO 37. True secant modulus (MSV) was determined from the test results and plotted. Reinforcement performance of the fillers was determined using the reinforcement index (RI), calculated using the equation below, where M300 and M100 are the MSV values at 300% and 100% strain, respectively.

$$RI = \frac{M300}{M100}$$

Dynamic mechanical analysis (DMA) was conducted with a DMA 450 Newton (Metavib, USA). Strain sweeps were conducted at 100 °C at 10Hz. This data was used to analyze and compare the amplitude of the Payne effect for each of the experimental composites, quantified as the difference in storage modulus at 0.2% strain and 100% strain, as shown [246].

Payne effect amplitude =
$$G'_{.002} - G'_{.1}$$

4.3 Results and Discussion

4.3.1 Biochar characterization

Various properties of the unactivated and activated biochars were determined prior to their use in composite preparation. Analyses include the yields, composition, structural characterization, and the determination of their functional groups.

4.3.1.1 Yields

Table 4-5 shows the different yields obtained through pyrolysis and activation of each feedstock. It is shown that all four feedstocks demonstrate relatively comparable yields from pyrolysis, with losses between 64-74% of the initial feedstock weight. RH shows the highest yield by dry basis, 20% higher than the next largest-yielding feedstock. This is likely due to the presence of high concentrations of silica in RH which remains in the resulting biochar, following pyrolysis. The

husk biochars required considerably more water to form a slurry than the shell biochars, ranging from 2-4 times as much. All four biochars experienced similar mass loss upon activation. Mass loss during activation is expected as the biochar is exposed to elevated temperatures for more time. This promotes further graphitization and loss of functional groups, as steam flow produces syngas products when reacting with the biochar surface [43].

Table 4-5: Overview of activation characteristics								
	First		Activation					
	pyrolysis yield	Water to	burn-off					
Feedstock	(%, dry basis)	biochar ratio	(%, dry basis)					
OH	26.32 ± 1.01	2.30	25.86					
RH	36.98 ± 0.45	2.67	27.02					
HS	32.22 ± 2.60	1.07	26.09					
WS	28.04 ± 1.13	0.68	25.10					

4.3.1.2 Biochar and feedstock composition

Table 4-6 details the proximate and ultimate composition of the feedstocks and biochars. Generally, pyrolysis significantly reduced volatile matter and increased ash and fixed carbon content in all biochars, as expected. In addition, there is little variation in proximate composition between the activated and unactivated biochars for each feedstock, with all properties within the margin of error. The only standout of this trend is for the OH biochars, with OHBA exhibiting a 50% increase in volatile matter and a 70% decrease in ash content, compared to OHB. This is most likely a result of variation between feedstocks used to generate the different biochar samples.

Ash content of the shell biochars is very low, especially the WS-based biochars. This can prove to be advantageous in its use as a potential carbon black replacement. N772 has a maximum ash content of 0.75% and a carbon content >93% [247]. Based solely on proximate and ultimate analyses of the biochars in comparison to N772, WS-based biochars have the most promise as carbon black replacements. On the other hand, RH has a very high ash content. This is expected as RH is known to be exceptional high in silica, having the highest concentration of silica of all

the cultivated species of the grasses family [71, 79]. In addition, the mineral composition of RH ash is almost purely silica, indicating RH ash to be a valuable source of bio-derived silica [248]. Silica is another very common reinforcing filler in modern rubber, commonly used in conjunction with carbon black in modern tire production [24]. RH ash has been used before in studies as a rubber reinforcing replacement for mined and precipitated silica [74, 90, 93]. Therefore, although the rice husk has exceptionally high ash content, the fact that this ash content is almost exclusively silica may demonstrate synergetic behaviors in vulcanized rubber in contrast to predictions that high ash content is detrimental to reinforcement properties [52]. Table 4-7 shows the atomic ratios calculated from the mass percent values of the ultimate composition analyses of the biochars. All the samples show decreased O/C and H/C after activation, which is correlated to higher aromaticity and lower polarity [45, 249].

Table 4-8 presents values from other studies for the relative proportion of the lignocellulosic composition of the feedstocks. It is important to note that these values can vary significantly based on factors such as growing location, environmental conditions, and crop variety. For instance, Schmitz et al. (2020) found that oats grown in warmer and drier conditions than the typical conditions show decreases in their lignocellulosic content from 83% to 63% [250].

Proximate Analysis				Ultimate Analysis					
	Moisture	Volatile							
	Content	matter	Ash	Fixed carbon					Remainder
Sample	(%)	(%)	(%)	(%)	N (%)	C (%)	H (%)	O (%)	(%)
OH	12.57 ± 0.31	81.38 ± 0.54	3.43 ± 0.11	15.19 ± 0.55	0.3	43.9	5.4	46.5	3.9
RH	9.14 ± 0.21	69.01 ± 0.38	17.39 ± 0.24	13.60 ± 0.45	0.5	38.4	3.0	36.4	21.7
HS	12.09 ± 0.11	79.85 ± 0.44	0.50 ± 0.08	19.65 ± 0.45	0.2	50.8	6.2	41.9	0.9
WS	10.95 ± 0.07	82.09 ± 1.01	0.35 ± 0.03	17.56 ± 1.01	0.5	48.4	5.9	44.1	1.1
OHB	N/A	12.52 ± 0.46	13.49 ± 0.43	73.99 ± 0.63	0.72 ± 0.04	73.3 ± 0.5	1.50 ± 0.02	6.25 ± 0.22	18.23 ± 0.55
RHB	N/A	12.25 ± 3.59	46.76 ± 0.24	40.99 ± 3.60	0.39 ± 0.01	46.6 ± 1.2	1.13 ± 0.06	4.79 ± 0.09	47.09 ± 1.20
HSB	N/A	10.93 ± 0.27	2.80 ± 0.32	86.27 ± 0.42	0.24 ± 0.02	82.6 ± 0.9	2.68 ± 0.07	11.50 ± 0.60	2.98 ± 1.08
WSB	N/A	15.98 ± 1.04	1.58 ± 0.22	82.44 ± 1.06	0.26 ± 0.06	84.5 ± 2.2	2.12 ± 0.10	7.80 ± 0.36	5.32 ± 2.23
OHBA	N/A	19.30 ± 1.31	3.99 ± 0.27	76.41 ± 1.34	1.35 ± 0.07	79.9 ± 1.2	1.45 ± 0.05	4.89 ± 0.44	12.41 ± 1.28
RHBA	N/A	8.86 ± 1.29	46.11 ± 0.72	45.03 ± 1.48	0.10 ± 0.01	48.5 ± 0.8	1.00 ± 0.02	3.71 ± 0.12	46.69 ± 0.81
HSBA	N/A	11.14 ± 0.39	2.73 ± 0.01	86.13 ± 0.39	0.27 ± 0.03	83.4 ± 2.3	1.65 ± 0.07	5.60 ± 0.12	9.08 ± 2.30
WSBA	N/A	13.21 ± 2.71	1.67 ± 0.63	85.12 ± 2.78	< LOD	90.6 ± 0.3	1.64 ± 0.03	4.56 ± 0.24	3.20 ± 0.39

Table 4-6: Proximate and ultimate composition of feedstocks and biochars, dry basis. Note: sulfur percentages are not included as all samples were below the limit of detection. Ultimate composition data for feedstocks obtained from literature [242, 251, 252].

Sample	O/C (10 ⁻²)	H/C (10 ⁻¹)
OHB	6.39 ± 0.23	2.46 ± 0.13
RHB	7.71 ± 0.24	2.91 ± 0.53
HSB	10.44 ± 0.34	3.89 ± 0.26
WSB	6.92 ± 0.36	3.01 ± 0.47
OHBA	4.59 ± 0.58	2.18 ± 0.35
RHBA	5.74 ± 0.24	2.47 ± 0.20
HSBA	5.04 ± 0.27	2.37 ± 0.42
WSBA	3.77 ± 0.33	2.17 ± 0.18

Table 4-7: Atomic ratios of biochar for oxygen to carbon (O/C) and hydrogen to carbon (H/C)

Table 4-8: Chemical composition of biomass feedstocks (%, dry basis)

Feedstock	Lignin	Cellulose	Hemicellulose	Ash
Oat Husks[250]	25	23	35	5
Rice Husks[253]	19.4	40.6	21.8	15.7
Hazelnut	35.1	30.5	25.9	1.8
Shells[254]				
Walnut Shells[255]	53.9	32.6	9.8	1.2

4.3.1.3 Structural characterization

As detailed in Table 4-9 below, the structural characterization results indicate significant increases in surface area due to activation, in ascending order from OHBA to RHBA to HSBA to WSBA. This ranges from a 24% increase between OHB and OHBA to a 225% increase between WSB and WSBA, as determined by BET surface area tests. Higher structure and SSA have been correlated to higher reinforcement indices for different carbon blacks, possibly applicable to biochar fillers as well [20]. In addition to increased overall SSA, all samples demonstrate increases in micropore SSA and volume. It appears that the shell biochars experience significantly more change in structure in response to the slurry activation when compared to the husk biochars. This may be due to the higher carbon, oxygen, and hydrogen concentrations in the

shell biochars, providing more sites for pore enlargement by CO and hydrogen gas formation. In addition, the husks have more mineral content which is recalcitrant to steam activation and imparts some structure to the char in addition to the carbon.

				Adsorption	BJH
				average	Adsorption
		t-plot	t-plot	pore	average
BET	t-plot	external	micropore	diameter	pore width
surface	micropore	surface	volume	(4V/A by	(4V/A)
area (m ² /g)	area (m ² /g)	area (m ² /g)	(cm^3/g)	BET) (Å)	(Å)
211.4	171.5	39.91	0.09079	21.69	32.51
135.6	105.4	30.12	0.05521	26.09	48.83
127.5	101.6	25.90	0.05470	21.30	126.1
100.6	80.58	19.98	0.04371	21.16	465.7
262.6	219.4	43.17	0.1143	22.87	39.48
201.4	126.0	75.41	0.06843	26.27	44.95
292.6	237.9	54.62	0.1238	23.22	39.07
327.3	258.4	68.88	0.1339	23.12	36.05
	BET surface area (m ² /g) 211.4 135.6 127.5 100.6 262.6 201.4 292.6 327.3	BETt-plotsurfacemicroporearea (m²/g)area (m²/g)211.4171.5135.6105.4127.5101.6100.680.58262.6219.4201.4126.0292.6237.9327.3258.4	t-plotBETt-plotexternalsurfacemicroporesurfacearea (m²/g)area (m²/g)area (m²/g)211.4171.539.91135.6105.430.12127.5101.625.90100.680.5819.98262.6219.443.17201.4126.075.41292.6237.954.62327.3258.468.88	BETt-plott-plott-plotsurfacemicroporesurfacevolumearea (m²/g)area (m²/g)area (m²/g)(cm³/g)211.4171.539.910.09079135.6105.430.120.05521127.5101.625.900.05470100.680.5819.980.04371262.6219.443.170.1143201.4126.075.410.06843292.6237.954.620.1238327.3258.468.880.1339	Adsorption averageBETt-plott-plotporeBETt-plotexternalmicroporediametersurfacemicroporesurfacevolume $(4V/A by)$ area (m²/g)area (m²/g)area (m²/g)(cm³/g)BET) (Å)211.4171.539.910.0907921.69135.6105.430.120.0552126.09127.5101.625.900.0547021.30100.680.5819.980.0437121.16262.6219.443.170.114322.87201.4126.075.410.0684326.27292.6237.954.620.123823.22327.3258.468.880.133923.12

Table 4-9: Structural characterization results of sample biochars

Figure 4-1 shows the plots of incremental pore volume against the pore width for each of the samples. Mesoporosity is generally defined as when a material has pores between 20 and 500 Å [65]. All four feedstock sources demonstrate increases in incremental pore volume for pores with widths that fall into the range of mesoporosity. These plots demonstrate that not only does slurry activation increase the SSA of the biochars, but it also transforms the biochar from a highly microporous material to a mixed micro and mesoporous material, as all the activated biochars have marked increases in concentrations of pores with widths from 60-80 Å except for the OHBA, which shows increased pore volume of pores with widths >100 Å. The shell biochars had noticeably larger increases in mesoporosity than the husks. Interestingly, average pore width is largely unaffected by activation, with slight increases for all four feedstocks. In addition, the average pore width is similar among all the feedstocks. This may be a result of similar fiber

structures and orientation within the feedstocks, which has been correlated to pore width distribution [256].



Figure 4-1: Incremental pore volume vs. pore width for (a) OHB and OHBA, (b) RHB and RHBA, (c) HSB and HSBA, (d) WSB and WSBA

4.3.1.4 FTIR

As seen in Figure 4-2, all eight experimental biochars were analyzed by FTIR for the presence of surface functional groups. There is relative similarity of the spectrums between all the biochars for aromatic functional groups, which is expected for biochars produced at pyrolysis temperatures above 600 °C [257]. However, it is starkly apparent that the RH biochars have a significantly strong peak at approximately 1100 cm⁻¹. The OH biochars also have similar peaks at that wavelength, albeit less intense. Peaks at this wavelength correlate to the presence of silica, which remains in the ash content of the resulting biochar. As RH and OH are grasses, their biochars are expected to contain silica, with RH having a higher initial ash content than OH, resulting in more pronounced silica peaks for RH biochars. In addition to the prominent silica group peak, there is the presence of methylsilanes in the husk biochars as shown by peaks at 790

cm⁻¹. Aside from these silicon-containing peak indications, other peaks show typical functional groups of aromatic biochars as well as surface hydroxyl groups of comparable prominence between all eight samples. Carbon-carbon double-bond peaks at 1570 cm⁻¹ are prominent for all the biochars demonstrating strong presence of aromatic rings. Of note is a minimal change in spectra following activation.



Figure 4-2: Separated FTIR results for all tested biochars

4.3.2 Composite characterization

Composites were analyzed for their cure performance, tensile performance, and dynamic behaviors.

4.3.2.1 Vulcanization curves

Figure 4-3 shows the curves of the storage modulus, G' in function time, representing the vulcanization of all the biochar composites and the NRC. At time zero, the value of the initial modulus can provide insight into the dispersion and level of adequate mixing in the rubber gum. As shown, NRC has the lowest initial modulus, less than half of the next lowest sample. This is expected due to the hydrophobicity of N772 and SBR. Biochar has more polar surface functional groups, mostly hydroxyl and potentially silanol groups in the husk biochars, which hinder mixing with the nonpolar SBR polymer chains when compared to carbon blacks. This results in more difficulty achieving thorough dispersion of biochar fillers. WRC and OARC had the lowest initial modulus, so it is difficult to conclusively say that the WSB and OSBA have better mixing compatibility, especially in comparison to N772. The scorch times are comparable among all the composites. Of note in the initial scorch phase is a sudden uptick in storage modulus for HRC. This may be an indication of polymer-filler interactions prior to vulcanization which can be undesirable for processibility.

The main section of crosslinking, between the scorch (ts2) and full cure (t90) provides information into the dispersion, polymer-filler interactions, and cure state of the composite. One property of the curve in this region to note is the slope of the vulcanization section. Activation has increased the slope for HARC and WARC considerably, with less-pronounced changes for the husk biochar composites. Higher slopes, and therefore faster vulcanization, will indicate better dispersion, less clumping and filler-filler interaction, and more complete cure. The slope of the vulcanization state is related to the cure rate index (CRI), which provides a numerical index to compare vulcanization.



Figure 4-3: Cure profiles of the vulcanized composites from feedstocks a) OH, b) RH, c) HS, and d) WS

As shown in Table 4-10, a general trend is observed in which ts2 and t90 decreased through activation. Exceptions to this observation include no change between ts2 between HRC and HARC, and a 17% increase in t90 for RARC compared to RRC. The cure characteristics are captured in the CRI. A high CRI value indicates a very fast cure time, while a low CRI indicates the reverse. All the activated composites demonstrated increased CRI aside from RARC, with a 38% decrease. However, activation greatly increased the CRI of HARC and WARC by 90% and

54%, respectively. OARC experienced minimal increase in CRI. All the analyzed experimental composites had lower CRIs than NRC. This indicates that biochar fillers tend to increase cure time as compared to N772. This may be related to dispersion, as poorly dispersed fillers will take longer to reach a full cure state due to hindered additive interaction.

Marching modulus index (MMI) is reported for all the tested samples. This metric describes the slope of the marching modulus and allows comparison between samples. All the biochar composites demonstrated improved (lowered) MMI following activation ranging from 8% for RARC to 46% for OARC. Lower marching modulus has been shown to be related to better dispersion of silica in the rubber matrix as well as less filler-filler interaction [209]. In addition, surface functional groups of silica such as silanol groups may influence the degree of MMI during vulcanization. Curative agents present in the compound mixture may adsorb to the silica filler and therefore have hindered crosslinking activity. As biochar is more polar than carbon black, like silica, this observation may potentially be applied to biochar-filled rubber. The decrease in MMI after activation indicates that activation increases filler compatibility with the rubber matrix, lessens filler-filler interaction, and decreases the presence of surface functional groups which may interfere with curative activity. Increased mesoporosity developed by the slurry activation allows for greater access to more complex structures in the biochars that may have been inaccessible to polymer chains and other additives in their highly microporous unactivated state. Of note are the MMIs of OARC and HARC, which are very comparable to the MMI of NRC.

The final storage modulus of the cure profile can communicate the relative stiffness and elasticity of the final composite material. G'₄₀ values from Table 4-10 were used to compare final marching modulus. RRC has the highest final modulus at approximately 1870 kPA, significantly higher than NRC and the other biochar composites, which ranged from 1380-1600 kPA. OARC, and RARC demonstrate a decrease of 200-300 kPA in the final storage modulus as compared to their respective unactivated composites. However, WARC demonstrates a mild increase of about 200 kPA. HARC had little to no variation. The final storage moduli of the activated composites are comparable to NRC. This indicates that the N772 filler produces a

rubber that is similarly elastic and stiff as compared to the activated biochar-filled rubbers and validates the 5 phr increase in biochar loading to achieve comparable final moduli (Table 4-2).

Sample	ORC	OARC	RRC	RARC	HRC	HARC	WRC	WARC	NRC
G'15 (kPa)	1501	1324	1754	1444	1311	1362	1256	1478	1542
G' ₄₀ (kPa)	1603	1379	1873	1553	1436	1432	1407	1592	1594
MMI	4.1	2.2	4.8	4.4	5.0	2.8	6.0	4.6	2.1
(kPa/min)									
ts2 (min)	6.2	3.6	5.7	4.3	3.8	3.8	4.9	4.4	3.9
ts90 (min)	11.8	9.1	11.1	13	15.4	9.9	19.7	13.9	8.1
CRI (min ⁻¹)	17.9	18.2	18.5	11.5	8.6	16.3	6.8	10.5	23.8

Table 4-10: Cure characteristics of the reinforced rubbers

4.3.2.2 Tensile properties

The tensile properties of the rubber composites provide insight into the efficacy of biochar fillers in reinforcing the cured rubber. Figure 4-4 below shows the true secant modulus (MSV) versus the strain for each of the unactivated biochar-filled rubber samples. Of note is the slope of the curves, which represents the relative reinforcement occurring in the material in response to increasing strain. HRC and WRC have almost identical slopes in the plot, indicating similar reinforcing properties. ORC has a lower slope, while RRC has the lowest slope. This descending order of slope magnitude correlates with an ascending percentage of ash content in the feedstocks, a phenomenon that has been recognized in previous attempts to utilize biochar as a rubber reinforcement filler [52]. It was postulated that due to RH ash being almost exclusively silica, the high ash content of RH would be negligibly detrimental to reinforcement and in fact, would benefit the reinforcement properties in tandem with the turbostratic carbon content in the biochar. RH ash has already been commercialized as a natural source of silica in rubber tires by companies like Goodyear and Michelin [239, 240]. However, many commercial formulations of tires use silane coupling agents in addition to silica to improve filler-polymer interactions with nonpolar rubbers like SBR [258]. This study does not include a silane coupling agent which may prevent silica present in the rice husk biochar from forming effective filler-polymer interactions,

resulting in poor reinforcement performance. The poor performance of RRC and RARC does not agree with the results of a study using RH biochar in natural rubber composites which was ballmilled in a similar fashion [232]. It is not reported in the study the pyrolysis conditions or if there were any treatments other than pyrolysis performed so it is inconclusive why there is an apparent discrepancy.

As seen in Figure 4-4, NRC performed within its typical range, demonstrating better reinforcement than all the unactivated husk biochar-filled composites. However, the nutshell biochar-filled composites performed comparably with NRC in both reinforcement and ultimate tensile strength. This is a promising indication that nutshell-derived biochars are effective total replacements of traditional carbon black reinforcement fillers in rubber composites, even prior to activation.



Figure 4-4: True secant modulus versus strain for rubbers filled with unactivated biochar and NRC

Figure 4-5 shows the MSV versus strain curves for the activated biochar-filled composites and NRC. Substantial increases in reinforcement due to activation are apparent in WARC and OARC, with OARC outperforming HARC. Table 4-11 details the reinforcement indices of all the tested samples. Because the elongation at break (EAB) of OARC is less than 300%, the MSV of OARC was projected with linear interpolation using the slope between 250% and 100% strain to calculate a RI for OARC. It is shown that OARC, RARC, and WARC had 25%, 5%, and 9% increases in reinforcement index from their unactivated counterparts. However, HARC showed a 4.4% decrease in RI. Overall, activation seemed to have a minimal change in reinforcement properties of HS and RH biochar fillers while significantly improving the reinforcement properties of WS and OH biochar fillers. As seen in Table 4-11, activation also had considerable effects on the EAB for the composite samples, as all the samples containing activated biochar demonstrated decreases in their elongation at break compared to their unactivated counterparts, which represents a loss of ductility. OARC had the largest reduction in EAB, with over 30% reduced. This is a common observation in materials as a trade-off for improved reinforcement as reinforcement fillers reduce ductility of rubbers, or as a result of differing cross-link density [259, 260].



Figure 4-5: True secant modulus versus strain for rubbers filled with activated biochar and NRC

Of significant note is the performance of WARC versus NRC. WARC has a 13.8% higher reinforcement index and 20.2% higher max MSV than NRC and comparable EAB. The other three nutshell biochar-filled rubbers also demonstrated excellent physical properties which match closely with those of NRC. From these results it can be concluded that hazelnut shells and walnut shells are excellent feedstocks to create biochar that can completely replace N772 in a rubber composite without significant difference in reinforcement performance. In addition, physical activation through the slurry method can improve the reinforcement properties of biochars from different feedstocks considerably, like OARC.

Sample	EAB	Change	Max MSV	Change	RI	Change	
	(%)	(%)	(MPa)	(%)		(%)	
ORC	375	20.4	7.28	1 1	1.75	25.1	
OARC	261	-30.4	7.20	-1.1	2.19	25.1	
RRC	416	0.4	6.45	4.2	1.40	5	
RARC	377	-9.4	6.18	-4.2	1.47	5	
HRC	310	-3.5	8.56	-9.6	2.28	-4.4	
HARC	299	-5.5	7.74	-9.0	2.18	-4.4	
WRC	320	11	8.76	24.4	2.34	0	
WARC	306	-4.4	10.88	24.4	2.55	2	
NRC	310	N/A	9.05	N/A	2.24	N/A	

Table 4-11: Tensile properties of rubber composites and the change with activation

4.3.2.3 Dynamic behaviors

DMA was conducted for the composite samples at 100 °C with a strain sweep. These results exemplify the Payne effect and the relative intensities of the Payne effect between each composite. The Payne effect was quantified as the difference in value between the storage modulus at the initial and final strain for each sample. This can be used to determine relative filler dispersion between the composites [218]. Figure 4-6 shows the DMA results, with significantly lower Payne effect amplitude for NRC as compared to all the biochar filled composites. Generally, a higher Payne effect demonstrates stronger filler-filler interactions as opposed to filler-polymer interactions [261]. The biochar filled composites demonstrate a higher Payne effect which agrees with predictions of lower dispersion as well as lower compatibility with the polymer matrix than N772. These behaviors are present in silica-filled rubber composites as well when not compounded with a silane coupling agent due to lack of hydrophobicity, which encourages filler-filler agglomeration [261]. Additionally, the higher loading of biochar as opposed to N772 (55 vs. 50 phr) can further increase the Payne effect [261].



Figure 4-6: Storage modulus of composites during strain sweep at 100 C

As demonstrated in Table 4-12, the biochar filled composites experience minimal decrease in Payne effect intensity following activation except for WARC, which increases its Payne effect intensity considerably. However, the range of the Payne effect intensity among the biochar composites is negligible (0.65-0.89) when comparing to that of NRC (0.34). From these results, it can be concluded that NRC demonstrates significantly better filler-polymer interaction when compared to the biochar composites. This is expected due to N772 polarity compatibility with SBR. Of note is lack of correlation between SSA of the biochar and Payne effect in the biochar composites. For carbon blacks, higher SSA is correlated with a more pronounced Payne effect for carbon blacks of structural similarity. This correlation is not apparent for the biochar fillers as the SSA of the activated composites is considerably higher than of their unactivated counterparts, with no clear change in Payne effect, except possibly for WARC. It is unclear why WARC had a considerable increase in Payne effect, however it is noteworthy that WARC had the most significant increase in BET SSA of all four feedstock types. In addition, structural analysis of the biochars was conducted prior to further grinding treatment, which may change the structural properties such as porosity and SSA. Therefore, it may not be valid to draw conclusive relationships between curing properties and structural properties.

Sample	ORC	OARC	RRC	RARC	HRC	HARC	WRC	WARC	NRC
G'.002	2.08	1.88	2.31	2.13	2.05	1.95	1.86	2.17	1.58
G' ₁	1.32	1.18	1.42	1.29	1.30	1.27	1.21	1.35	1.24
Payne Effect	0.76	0.70	0.89	0.84	0.75	0.68	0.65	0.82	0.34

Table 4-12: Payne effect expressed in experimental composites. All values in units of MPa.

4.3.3 Biochar to composite property correlation

Biochar has shown to be a promising alternative to carbon black for rubber composite reinforcement. However, there is much space for further exploration of effective biochar reinforcement. A significant variability between biochars is feedstock choice. As the variety of choices is immense, having a quick and less-intensive way to screen candidates prior to rubber formulation may be useful for further investigations. The main numerical properties of interest for the rubber composites are the RI and the CRI which denote mechanical performance and processability, respectively.

Figure 4-7 demonstrates various plots of biochar and feedstock properties versus RI and CRI. Figures 4-7a and 4-7b attempt to correlate a multiplicative factor of BET SSA and BET average pore width to the composite properties. These biochar structural properties were multiplied to attempt to formulate a numerical factor capable of describing both SSA and pore width simultaneously. It is shown that there is little correlation between these properties and CRI. However, for RI there seems to be a positive correlation aside from two outliers. Of note is that these two outliers are HRC and WRC. The activated counterparts of these two composites fit along this correlation which when excluding the two outliers, has a R² of 0.9628, indicating a strong correlation. Further investigation into the relation between biochar structural properties and RI are warranted. Figures 4-7c and 4-7d show relationships between biochar ash content and RI (4-7c) and CRI (4-7c). A significant negative correlation between ash content and RI is observed, with a very good exponential fit. This agrees with previous studies in which low-ash biochars were shown to have better reinforcement [52]. Expansion of this plot with more biochar samples may reveal a very effective tool for screening biochar filler candidates. No correlation is apparent between the ash content and CRI.

Figures 4-7e and 4-7f show the relationships between the lignin content of the feedstocks and the composite properties. To note, these plots include both the unactivated and activated biochars with identical feedstock lignin values. Lignin content appears to exhibit a positive correlation with RI and a negative correlation with CRI. The positive correlation with RI may be related to previous observations that increased lignin content in biochar feedstocks correlates to higher porosity, SSA, carbon content, and aromaticity [45]. Increases in these properties can all contribute to biochars which further approach similarity to carbon blacks. The negative correlation between lignin and CRI can be explained through better dispersion of biochars from high-lignin feedstocks also having lower ash content in these samples. Additionally, high aromaticity and carbon content can indicate low polarity, as high carbon content indicates less elemental substitution in the carbon backbone of the graphitic sheets. High lignin feedstocks may be ideal for composite reinforcement applications.



Figure 4-7: Plots of various biochar and feedstock properties versus RI and CRI. BET SSA multiplied by BET average pore width versus RI (a) and CRI (b). Ash content versus RI (C) and CRI (d). Feedstock lignin content versus RI (e) and CRI (f).

4.4 Conclusions

The aim of this study was to determine the viability of two grain husks and two nut shells as feedstocks for biochars intended to reinforce rubber composites. In addition, the potential for slurry-based activation to improve biochar-filled rubber composite's mechanical properties was investigated. All biochars demonstrated reinforcement performance, with nutshell-based biochars having comparable mechanical properties to N772 composites, even prior to activation. Activation was demonstrated to improve the performance of biochars in rubber composites in various metrics, including increased reinforcement, decreased marching modulus, and faster cure times, especially for the oat husk products. Biochar fillers demonstrate poorer dispersion than N772 due to their less hydrophobic nature. Low biochar ash content and high feedstock lignin content appear correlated to better performing rubber composites, and both hazelnut shell and walnut shell biochars have the potential to fully replace carbon black filler without any mechanical property losses. Future studies should focus on low-ash, high-lignin feedstocks and investigate increasing biochar compatibility in the polymer matrix to improve dispersion.

Chapter 5: Conclusions and recommendations

5.1 Conclusions

This research aimed to develop effective sustainable biochar activation methods with the ultimate intention to improve biochar performance as a reinforcement filler in styrene-butadiene composites. The physicochemical characteristics of the biochars and the mechanical properties of the resulting composites were analyzed and used to determine effective activation for corn stover biochar. After determining effective activation methods, feedstock composition and its relation to reinforcement success was considered. Two low-ash nut shells and two high-silica grain husks were used for biochar production. This provided additional data on activation efficacy for a variety of biochars and additional data on the impacts of feedstock composition.

From these investigations, several conclusions were drawn. It was demonstrated that corn stover biochar is not an effective reinforcement filler. In addition, gaseous steam activation changes the structural characteristics of the biochar but provides little to no improvement on the resulting composite properties. Slurry-based activation, however, produces considerable improvement to the composite properties and demonstrates reinforcement on par with that of N772 carbon black. The efficacy of the biochar samples for reinforcement appears related to the level of mesoporosity, which is increased considerably upon slurry-based activation.

Nut shell-based biochars proved to be highly effective reinforcement fillers, with and without activation. Their very low ash content resulted in compositional properties that were more like the N772 carbon black than other biochars produced. The hypothesis that high silica content in the grain husk feedstocks would result in improved reinforcement performance was not shown to be true as rice husk biochars, both activated and unactivated, had the poorest performance of all the samples. All the biochars showed increase in mesoporosity upon slurry activation, which translated to varying degrees of improvement in reinforcement properties. Oat husk biochar proved to be the most greatly improved by activation, as the activated oat husk biochar had comparable reinforcement and marching modulus stability to carbon black. Overall, the results demonstrate that the effects of slurry activation of biochar lead to increased dispersibility and

filler-polymer interactions. In addition, lower ash content and higher feedstock lignin content are correlated to higher reinforcement performance in rubber composites.

5.2 Recommendations

Overall, the results demonstrate that biochar has promise as a reinforcement filler. However, its properties have room for improvement. Feedstock composition proved to be highly correlated to biochar reinforcement performance. Therefore, exploration of other feedstocks that share similar composition to the nut shells should be explored. This may include investigation of more nut shells such as almond, macadamia, pistachio, etc. or identification of other low ash biowastes. It is also recommended to explore other sustainable treatment methods capable of reducing ash content. This may include different types of pre-treatments or post-treatments. Having more data on the use of biochars from different feedstocks and with differing compositional make-up will provide further understanding of the relationship between feedstock choice, biochar properties, and reinforcement performance. Bolstering the correlations developed in this research will result in simplified screening processes for reinforcing biochars.

The results of the rice husk biochar appear to differ from results of other studies presented. Their studies developed composites with natural rubber and included addition of silane coupling agents. In comparing studies, natural rubber and the styrene-butadiene rubber used in this study share similar nonpolarity. This presents issues with biochars as filler as biochar tends to be slightly polar due to present surface functional groups. The use of silane coupling agents may improve the filler-polymer interactions and therefore the dispersibility of biochar in the rubber composite. This may explain the discrepancy in results between this study and previous studies. Since rice husk biochar is nearly 50% carbonaceous material and 50% siliceous material, improving the filler-polymer compatibility through inclusion of silane coupling agents may demonstrate rice husk biochar to be highly effective at reinforcement as opposed to its poor performance demonstrated here. Furthermore, silane coupling agents may also improve non-siliceous biochar reinforcement performance in nonpolar rubber composites and warrants investigation.

Lastly, once effective and consistent biochar reinforcing fillers are developed, it is recommended to explore the capability of biochar in tandem with other biowaste-derived additives such as those described in Chapter 2. Research into the performance of biowaste processing aids or protectants with biochar will advance progress towards a completely biowaste-derived rubber composite.

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