Novel Renewable Materials from Natural Rubber and Agro-Industrial Residues

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

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2016

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Abstract

Natural rubber is currently one of the most important crop-produced industrial bio-based materials in the world. Further improvements in rubber inherent properties are obtained by the addition of fillers, enabling polymeric products suited to highly demanding applications. However, most existing fillers are neither renewable nor sustainable. Agro-industrial residues are highly abundant solid wastes that represent a promising source of alternative fillers. Moreover, the renewable character of these residues could improve the sustainability of natural rubber products while adding value to these waste materials.

Fillers obtained from agro-industrial residues, namely, eggshells, carbon fly ash, processing tomato peels and guayule bagasse, were used for the manufacture of composites with both hevea and guayule natural rubber. The effect of amount, type and particle size of waste-derived fillers on power consumption during mixing of the rubber compounds, and on mechanical properties of compression molded test pieces were investigated. Waste-derived fillers were used as partial and complete replacement of petroleum-derived carbon black (industrial reference reinforcing filler). Unfilled compounded rubber and composites containing carbon black with no other filler were used as reference materials.
Reinforcement of unfilled hevea and guayule rubber compounds was obtained with most waste-derived fillers used, particularly composites containing micro and nano sized eggshells and tomato peel particles. This can be attributed to different factors related to filler characteristics including particle structure, size, bulk density, alkalinity and surface activity. The introduction of co-filler systems, in this case carbon black with various waste-derived materials at low loadings, generated materials with superior or similar mechanical properties than those of composites made solely with carbon black.

This reinforcement may reflect a combined synergistic reinforcing effect of carbon black particles, which possess a strong polymer-filler interaction, with the formation of a unique network between the rubber and the waste-derived materials. This effect was more pronounced in guayule than hevea rubber as a result of differences in rubber structure and composition (non-rubber components) between these two natural rubber matrixes. These differences affect the overall reinforcement achieved with the waste-derived fillers. These results could strengthen ongoing commercialization efforts of guayule products. Unusual combinations of mechanical properties were achieved with both types of rubber. Also, this work showed that micro sized fillers are effective reinforcing fillers. Micro-fillers can be produced at a far lower cost than their nano-sized versions.
Dedicated to my family, especially to my mother, Denys Martinez.
Acknowledgments

I would like to thank my advisor Dr. Katrina Cornish for her continuous guidance and support during my graduate career. Also, I would like to thank all the members of my committee, Dr. Kurt Koelling, Dr. Ajay Shah and Dr. Alfred B.O. Soboyejo for their guidance and commitment. Thanks to my family, friends and Luis Faisca for their support and encouragement. Lastly, I would like to thank Fulbright Colombia for their financial support during my graduate program.
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Chapter 1: Introduction

The amount of research on renewable materials has increased in recent years, due to environmental concerns regarding ecological footprint and the need to reduce reliance on petroleum (Afiq and Azura, 2013; Faruk et al., 2012; Jacob et al., 2004; Jong, 2014). Historically natural rubber has been one of the most important crop-produced industrial bio-based materials in the world. An average consumption of 9.67 million metric tons per year was reported between 2000 and 2015 (Malaysian Rubber Board, 2016). Natural rubber possesses unique properties, such as malleability under cold temperatures, heat dispersion and strain induced crystallization, that cannot be matched by its synthetic counterpart (Cornish, 2001; Steinbüchel, 2003). These characteristics make this elastomer essential for the production of over 50,000 products including more than 400 medical applications (Mooibroek and Cornish, 2000; Priyadarshan, 2011).

Currently, 90% of the total natural rubber production comes from South-east Asia, due to the climatic requirements of the only commercial source, the para rubber tree (*Hevea brasiliensis*) (Kohjiya, 2014). Most of the rest is produced in western Africa. Much research has been driven by the need to obtain alternative natural rubber sources to satisfy the increasing global demand and to increase biodiversity. These researches have led to the selection of guayule (*Parthenium argentatum*), which can produce not only large amounts of rubber, but rubber with high molecular weight, an important
characteristic required in rubber for commercial applications (Ray et al., 2005; van Beilen and Poirier, 2007).

The guayule shrub grows under very different agro-climatic conditions from hevea, so it does not compete for production (Foster et al., 2011). Furthermore, guayule rubber lacks the proteins associated with Type I IgE-mediated latex allergies found in hevea rubber (Hamilton and Cornish, 2010; Siler et al., 1996), which makes it attractive for different rubber applications. Despite historical attempts (Nakayama, 2005), commercial production of natural rubber from guayule is still under development, not fully commercialized. Product development to create specific markets for guayule products applications is required.

A complementary solution to minimize natural rubber shortages is to reduce the amount required for the manufacturing of rubber products, and fillers can be used for this purpose. Fillers are polymer additives commonly used as diluents, to reduce cost of rubber products by reducing the amount of the more expensive polymeric matrix, but some also can be used to reinforce the mechanical and dynamic properties of the polymer (Donnet and Custodero, 2013; Fröhlich et al., 2005; Leblanc, 2002). Fillers also are used to improve processing parameters and to achieve desirable qualitative characteristics such as texture and color.

Currently, the main source of fillers for natural rubber is carbon black. Global consumption of this material reached 11.8 million metric tons in 2013 (Notch Consulting Inc., 2015). Approximately 90% of carbon black production is used in rubber products (International Carbon Black Association, 2004). Despite its excellent reinforcing
characteristics, carbon black is derived from petroleum, making this a non-renewable source. Existing non-black fillers include inorganics derived from the grinding or precipitation of minerals such as silica, calcium carbonate and clay. Composites filled with these non-black fillers have shown lower mechanical properties compared to carbon black-filled composites, although silica can be comparable in performance (Byers, 2001; Donnet and Custodero, 2013).

The development of new filler sources, that can offer similar reinforcing and processing properties to carbon black, but being derived from renewable materials, is desired. Therefore, increasingly research is focusing on the utilization of waste-derived materials as fillers for natural rubber (Bras et al., 2010; Pasquini et al., 2010; Visakh et al., 2012). This field of research is driven by eco-innovation initiatives that seek zero waste manufacturing processes (Mirabella et al., 2014). The successful development of bio-based materials in natural rubber composites could have multiple benefits to industry. Economic benefits should be achieved by adding value to wastes, reducing cost associated to disposal and reducing polymer product cost, and also by positive environmental gains by minimizing the amount of materials deposited in landfills. An additional advantage to the use of bio-based fillers in rubber products is the acceleration of material decomposition after disposal (Afiq and Azura, 2013). The main concerns when using bio-based materials for the manufacture of natural rubber composites are the final cost of manufacture, and the performance, durability and availability of the filler materials (Andresen et al., 2012).
Chapter 2: Statement of the Problem

Current human lifestyle requires the use of large amount of materials, particularly elastomers like natural rubber. A large fraction of the world’s rubber demand is covered by synthetic elastomers obtained from crude oil. However, synthetic rubber cannot replace natural rubber in the most demanding applications (Cornish, 2014). Furthermore, consumption of natural rubber is expected to increase due to growing demands from emerging economies, leading to potential shortages of 1.5 - 3 million metric tons by 2020 (Cornish, 2014). Despite of being produced by over 2500 plant species, commercial natural rubber is obtained almost exclusively from a single plant species, *Hevea brasiliensis* (van Beilen and Poirier, 2007). To address increasing demands for natural rubber, extensive research has focused on the breeding and domestication of alternative rubber-producing species, especially guayule (Foster et al., 2011; Jorge et al., 2006; Ray et al., 2005; Sfeir et al., 2014).

Unfortunately, sustainability of the rubber industry is compromised by dependency on non-renewable petroleum derivatives, not only for the manufacture of synthetic elastomers but also of fillers. Hence, the development of renewable fillers and the understanding of reinforcing mechanisms also has been a significant area of research in the rubber industry (Abraham et al., 2013b; Pasquini et al., 2010; Visakh et al., 2012). Our work focuses specifically on evaluating potential applications of waste-derived agro-
industrial residues for the manufacture of sustainable natural rubber composites, both for guayule and hevea rubber.

Valorization of waste material is not only an environmental trend nowadays but also an important economic goal. The large amounts of waste generated in the production chain, in addition of representing significant losses on raw material, increase costs associated with disposal. Agricultural and industrial food processing waste can be considered for polymer fillers applications. These materials not only are generated in very high volumes, which ensures their continuous availability, but also can help to improve the sustainability of rubber products by replacing or reducing the amount of petroleum-derived carbon black. The composition of waste-derived materials is varied and complex, which offers the possibility to generate new composites and tailor composite properties to meet specific application requirements.

Characterization of mechanical properties as result of the variation of filler type, particle size and loading will be the starting point for the identification of possible applications for different composites. Analysis and optimization of findings through statistical methods is required to ensure the reliability and significance of the results.

The overall goal of this research is to advance the sustainable development of natural rubber through the expansion of the number of feasible fillers for natural rubber composites, while strengthening commercialization efforts of alternative natural rubber sources. To accomplish this goal the following specific objectives are proposed:

- **Objective 1:** Engineer new natural rubber composites utilizing low-cost, waste-derived material.
- **Objective 2**: Identify individual contributions of filler characteristics influencing the reinforcement of natural rubber.

- **Objective 3**: Optimize natural rubber composite mechanical properties using mathematical modelling.
Chapter 3: Literature Review

3.1. Natural Rubber

Natural rubber (NR) is a strategically important material for industry and the economy, and is included in over 50,000 products with applications that encompass the transportation, industrial, consumer, medical and defense sectors (Cornish, 2014; Priyadarshan, 2011). NR is the only large scale, naturally occurring, bio-based elastomer. As an agricultural product, NR is a renewable material with a more environmentally-friendly production system than synthetic rubbers (Rasutis et al., 2015; Venkatachalam et al., 2013).

Currently, most of the global demand for NR is satisfied by a single plant species, the para rubber tree (Hevea brasiliensis) (van Beilen and Poirier, 2007). H. brasiliensis only grows in tropical areas, more exactly in a band 10° on each side of the equator (Barlow, 2001). Although this plant is native to the Amazon region of South America, less than 4% of NR is produced there due to susceptibility of H. brasiliensis to the South American fungal leaf blight caused by Microcyclus ulei (Cornish, 2014). Hence, NR production has concentrated in South-east Asia, particularly in Thailand, Indonesia, India, Malaysia and Vietnam, where expansion of rubber plantations competes with food production and threatens forest biodiversity (Rasutis et al., 2015; Venkatachalam et al., 2013; Warren-Thomas et al., 2015).
The development of alternate domestic sources of NR is considered critical in industrialized countries. Much research has been done in the development and commercialization of alternative NR sources (Mooibroek and Cornish, 2000; Ponciano et al., 2012; Rasutis et al., 2015; Ray et al., 2005; Schloman et al., 1996; Sfeir et al., 2014). Among plants known to produce rubber, two plant species have been identified as the most promising alternatives for NR production, Parthenium argentatum (guayule) and Taraxacum kok-saghyz (rubber dandelion) (Venkatachalam et al., 2013).

Guayule is a perennial shrub native to the Chihuahua desert of Texas and North Central Mexico (Ponciano et al., 2012). Guayule has very different climatic requirements than hevea, hence it is considered a feasible source to complement hevea rubber production. Furthermore, guayule commercialization efforts have particularly focused on hypoallergenic latex products (Cornish, 1996), due to its lack of the proteins associated with Type I IgE-mediated latex allergies which are found in hevea rubber (Hamilton and Cornish, 2010; Siler et al., 1996).

Rubber dandelion is native to Kazakhstan and Uzbekistan and can produce high molecular weight rubber within laticifers located in the roots (Van Beilen and Poirier, 2007; Venkatachalam et al., 2013). It grows in temperate regions which make it attractive for the production of NR in the Northern USA (Puskas et al., 2014). Currently both guayule and rubber dandelion are at different stages of commercial development. However guayule production is more commercially advanced.
3.2. Chemistry of Natural Rubber

NR consists of high molecular weight (> 1,000,000 g/mole) cis-1,4-polyisoprene (Fig.3.1) (Tanaka, 2001). Elasticity and green strength of NR primarily result from high molecular weight and monomer microstructure and the ability of NR to crystallize under strain (Valodkar and Thakore, 2012). Weak intermolecular forces between polyisoprene chains allow a reversible response when the material is subject to deformation (Shanks, 2014). Moreover, high stereoregularity of NR contributes to strain induced crystallization, an unique and important characteristic that allows self-reinforcement of NR when is stretched (Chenal et al., 2007a). Also high molecular weight and non-rubber components have been identified as important parameters in strain induced crystallization (Chenal et al., 2007a; Thuong et al., 2016).

**Fig. 3. 1:** Chemical structure of cis-1,4-polyisoprene.

Uniqueness of NR goes beyond characteristics of the rubber component. Differences in non-rubber components set this biopolymer apart from its synthetic
counterpart and distinguish NRs from different plant species. 94% of hevea NR is polyisoprene and 6% has been identified as non-rubber components, including proteins (~2.2%), phospholipids and neutral lipids (~3.4%, e.g., triacylglycerols), carbohydrates (~0.1%), and metal ions (~0.2%) (Amnuaypornsrri et al., 2008; McMahan and Lhamo, 2015; Tanaka, 2001). These non-rubber components greatly affect NR physical and chemical properties. Non-rubber constituents contribute to NR vulcanization behavior, thermal stability, bulk viscosity, and strain induced crystallization (Choi and Roland, 1997; McMahan and Lhamo, 2015). These non-rubber components differ among plant species (Cornish et al., 2008).

Non-rubber components also may determine macromolecular structure of NR. In hevea NR, rubber chains consist of a ω-terminal followed by two units of isoprene in the *trans*-1,4 configuration, over 5000 cis-1,4-isoprene units and a α-terminal (Amnuaypornsrri et al., 2008; Puskas et al., 2014; Tanaka, 2001) (Fig. 3.2). The α and ω terminals allow linkage of polyisoprene chains with non-rubber components generating chain branching. The α-terminal contains mono and diphosphate groups that allow hydrogen or ionic bonding with phospholipids, while the ω-terminal contains a functional group that links the rubber chain with proteins (Amnuaypornsrri et al., 2008; Mekkriengkrai et al., 2006).
Despite the advancement in polymer chemistry, replication of NR properties has not yet been possible. Synthetic polyisoprene contains 98% of cis-1,4-polyisoprene, yet mechanical properties are much lower than NR due to lack of non-rubber components. Furthermore, the addition of non-rubber components such as amino acids and proteins has proven not to be sufficient to replicate NR properties due to complex interactions.
between rubber and non-rubber components (Amnuaypornsri et al., 2008; McMahan et al., 2015).

The influence of non-rubber components also has been observed among different NRs. Guayule rubber has only 1% of the proteins in hevea (Cornish et al., 2008). Proteins in hevea greatly affect strain induced crystallization and curing rate, and hence performance properties (Choi and Roland, 1997; Ramos-De Valle, 1981). Proteins in hevea also contribute to better oxidative stability (Schloman, 2005). Depending on the extraction method (water or solvent based) guayule rubber may contain up to 40% of terpene resin and degraded rubber that can act as plasticizer and affect the resistance to deformation of the material (Schloman, 2005). However, guayule rubber extracted as latex contains much less resin and no degraded rubber (polydispersity less than 1.5) (Cornish et al., 2005).

In contrast, as result of its low protein content, guayule has been particularly attractive for the production of hypoallergenic latex products. Guayule not only has lower protein than hevea, but 90% of the trace protein in guayule latex is a non-allergenic cytochrome P450 oxidase, allene oxide synthase (Cornish, 2001). Furthermore, guayule has a linear chain structure (Rensch et al., 1986), which enables a different stress-strain behavior. For instance, softer and more elastic films have been obtained with guayule than hevea when the same compounding formulation has been used. As consequence of differences in non-rubber components guayule rubber also possess a very unique property, malleability at extreme cold temperature, not observed in hevea rubber (Cornish
Rubber dandelion is very similar to hevea rubber in composition (Cornish, 2014).

3.3. Crosslinking of Natural Rubber

Crosslinking of NR refers to the chemical process used to bond individual rubber chains and form a continuous polymer network (Donnet and Custodero, 2013; Rader, 2001). This process is essential for the attainment of performance properties required in elastomers’ industrial applications. Crosslink reactions require the heating of NR compounds with the selected crosslinking system (Coran, 2013). In these systems, the rubber and the crosslinking agent are the most important components. However, crosslinking of NR using only the crosslinking agent is not commercially practical, due to the long time needed for the reaction. Instead, current crosslinking systems include three main group of chemicals; crosslinking agents, activators and accelerators, which together induce a faster and more effective crosslinking process (Coran, 2013; Rodgers and Waddell, 2013).

The most common commercially used crosslinking agent is sulfur. The long chains of rubber molecules are linked together by one or more sulfur atoms (Rader, 2001). The crosslinking reaction of NR with sulfur is simply depicted in Fig.3.3:
Sulfur binding occurs at the allylic hydrogen atom adjacent to the C-C double bond. The eight-membered ring of elemental sulfur can undergo either homolytic or heterolytic cleavage. Therefore, both free-radical and the ionic mechanism, or even a combination of both mechanisms, have been associated with the crosslink reaction (Akiba and Hashim, 1997).

The other two groups of compounding ingredients involved in the crosslinking reaction of NR are the activators and accelerators, which function is to speed the crosslinking reactions considerably reducing the reaction time (Coran, 2013). Most common activator systems consist of zinc oxide and stearic acid, while sulfenamide accelerators represent the largest class of accelerators used in the rubber industry (Rodgers and Waddell, 2013). The main function of the accelerators, as their name indicates, is to increase both the rate of sulfur crosslinking and crosslink density. This is achieved by the formation of a complex between sulfur, accelerator and zinc oxide. The stearic acid aids the solubilization of the zinc oxide to form this complex (Rader, 2001).
Depending on the ratio of sulfur to accelerators used in compounding of NR, a distribution of crosslinks with various amounts of mono and polysulfide crosslinks is generated (Coran, 2013; Rader, 2001). High sulfur to accelerator ratio leads to generation of vulcanizates with a high concentration of polysulfide crosslinks. This type of sulfur link has lower thermal stability than mono-sulfide crosslinks, hence reversion or network loss can occur, which negatively impacts the mechanical properties (Akiba and Hashim, 1997; Rader, 2001).

Peroxides also are used as crosslinking agents for NR (Coran, 2013; Rader, 2001). Peroxide crosslinking of NR involves free radical reactions, which are initiated by the hemolytic cleavage of O-O bonds (Akiba and Hashim, 1997; Rader, 2001). The resulting polymer network contains links analogous to mono-sulfide bonds. This type of network is more rigid than those containing di- or polysulfide bonds, thus properties of the crosslinked material are different than those achieved with sulfur crosslinking (Rader, 2001). Also, the used of peroxide crosslinking is limited due to relative instability of O-O bond in peroxide compounds.

Independent of the crosslinking system used, this chemical process dramatically impacts the properties of NR, transforming the soft raw material into a strong elastic material (Akiba and Hashim, 1997). Crosslinked NR properties are highly dependent on the crosslink density, which is a measurement of the number of crosslinks per unit of volume and is inversely proportional to the average molecular weight of polymer chain between crosslinks (Coran, 2013; Rader, 2001). As the crosslink density increases, strong bonds connecting the polymer chains serve as retractile forces that pull polymer chains
together and allow the recovery of original geometric arrangement after the removal of deformation force. This means an increase in elasticity and resistance to deformation (modulus) as the crosslink density increases (Coran, 2013; Rader, 2001).

Changes in crosslink density also affect mechanical properties of NR rubber including elongation and tensile strength. Increased crosslink density decreases the elongation of the material because of restriction of chain movement by the chemical bonds. When strain is applied the limited chain motion prevents chain rearrangement (Coran, 2013). On the other hand, tensile strength achieves a maximum value when the rubber is close to saturation of crosslinks. With additional crosslinking the rubber behaves more like a brittle solid, so tensile strength decreases to a minimum (Samsuri, 2013). Properties such as tear strength, fatigue resistance, and toughness depend on the energy to break the material. Hence, it is expected that an increase in crosslink density will cause increases in these properties. Nevertheless, these properties maximize at intermediate crosslink densities, and decrease with additional increases in crosslinking (Coran, 2013; Rader, 2001).

Increased crosslinking decreases hysteresis, reduces tackiness of the material, improves NR resistance to heat, light and aging and increases glass transition temperature (Rader, 2001; Rodgers and Waddell, 2013; Visakh et al., 2012). Also, NR becomes essentially insoluble in solvents because of network formation. When in contact with a compatible solvent, a crosslinked NR sample will not dissolve, but swell until the osmotic pressure of the solvent is equal to the elastic retractive forces of the stretched
polymer chains. This characteristic has been used as indirect measurement of rubber crosslink density (ASTM International, 2013a).

3.4. Fillers

Fillers are the second most important component in NR composites by volume. These important polymer additives are used as diluents, or for the improvement of processing characteristics such as extrudability, and for reinforcement (Donnet and Custodero, 2013; Rattanasom et al., 2007; Samsuri, 2013). Reinforcement of NR by fillers has been studied for decades, yet complete understanding of this phenomena has not yet been achieved (Bradley, 1956; Payne, 1962; Samsuri, 2013; Watson, 1956). In general, reinforcement of NR by fillers is the enhancement of properties such as modulus, tensile and tear strength, abrasion resistance, increase hardness and stiffness (Fröhlich et al., 2005; Hamed, 2000; Leblanc, 2002). Most industrial applications of NR would not be possible without fillers. Properties like fatigue resistance, tensile and tear strength, and toughness reach a maximum value with an optimum crosslink density. Additional crosslinking generates a brittle material and decrease of these properties (Coran, 2013; Rader, 2001). Fillers enhance these properties beyond the values achieved with optimum crosslink density.

3.4.1. Filler Characteristics

Reinforcement of NR by fillers depends on filler characteristics, namely surface area, loading, surface activity, and shape and structure (Byers, 2001; Donnet and Custodero, 2013; Fröhlich et al., 2005; Kohls and Beaucage, 2002). These factors
determine the type and strength of interactions between the polymer and the filler, hence the final composite properties.

3.4.1.1. Surface Area and Loading

Surface area is the most important morphological characteristic affecting filler reinforcing potential (Donnet and Custodero, 2013; Khan and Bhat, 2014; Leblanc, 2002). This is because of the direct impact of this filler characteristic on the interfacial contact area with the polymer. Large surface area and high filler loading (amount of filler in the composites), facilitate more interfacial contact between the filler and the polymer, thus increasing reinforcing potential (Byers, 2001; Fröhlich et al., 2005; Szeluga et al., 2015). Particle size is directly related to the reciprocal of particle surface area; hence this parameter is commonly used as a simple criterion to describe the filler (Fig.3.4).
Based on this classification, reinforcing fillers are only those with particles with at least one dimension in the nano scale (<100 nm), known as nano particles. Superior reinforcement achieved with these small particles compared to larger size particles, relies on having greater numbers of particles per volume of rubber, hence greater interfacial contact area (Hamed, 2000; Szeluga et al., 2015). In addition to the lower surface area offered by big particles, these particles can have detrimental effects on mechanical properties of the composite. Big particles act as localized stress-raising inclusions, generating flaws within the composite that can initiate failure and low tear resistance (Byers, 2001; Hamed, 2000).
Nevertheless, important drawbacks have been associated with the use of nano particles, particularly for non-carbon black composites. These limitations include complexity and high production cost of nano particles compared to macro and micro size particles, and challenging dispersion within the polymer (Abraham et al., 2011; Byers, 2001; Fang et al., 2014; Galimberti et al., 2014; Peddini et al., 2014). The higher surface area of these particles increases the attraction between the particles, leading to agglomeration that can reduce composite performance (Chao and Riggleman, 2013; Donnet and Custodero, 2013; Kueseng and Jacob, 2006). To achieve homogeneous dispersion of nano particles in the rubber, complex mixes that often involve high power consumption are required, increasing processing costs (Galimberti et al., 2014; Szeluga et al., 2015).

Although filler reinforcing potential has been shown to be highly dependent on particle size, this is not the only characteristic affecting NR reinforcement by fillers. The strength and nature of the polymer-filler interaction is dependent on surface activity of the filler (Kohls and Beaucage, 2002). Moreover, particle surface area is not only a consequence of size, but also structural features such as porosity of the material. Hence, differences in extent of reinforcement can be achieved by different fillers with similar particle size.

Different methods have been developed to measure surface area. These methods include adsorption methods, namely: nitrogen, cetyl triethyl ammonium bromide (CTAB) and iodine adsorption (Byers, 2001; Donnet and Custodero, 2013). Currently, nitrogen
adsorption is the most widely used method and the calculation of the filler surface area is based on the Brunner, Emmet and Teller (BET) method (Donnet and Custodero, 2013).

3.4.1.2. Surface Activity

Filler surface activity is a critical characteristic influencing the dispersibility and compatibility of the filler, and hence reinforcement of NR. This filler characteristic determines the ability of the filler to interact with the polymer, as well as type and strength of interaction within the composite (Papirer et al., 1988; Stöckelhuber et al., 2011). Differences in surface activity have been related to chemical groups on the surface of the particles (Byers, 2001; Fröhlich et al., 2005), but may also reflect structural heterogeneities within the particle (Leblanc, 2002). These differences can result in variations of surface free energy, a parameter that describes the interaction potential of a given surface (Cordeiro et al., 2011a; Nardin et al., 1990).

Surface free energy ($\gamma_S$) of a solid surface is the result of dispersive ($\gamma_S^D$) and specific components ($\gamma_S^{SP}$) (Stöckelhuber et al., 2010; Voelkel et al., 2009):

$$\gamma_S = \gamma_S^D + \gamma_S^{SP}$$

The dispersive component represents the solid’s ability to interact through London type interactions (Papirer et al., 1988; Strzemecka et al., 2014). These weak intermolecular forces play the main role in the interaction with non-polar molecules such as NR. In contrast, the specific component represents the interactions due to all other types of interactions, such as acid–base, magnetic, metallic, and hydrogen bonding (Mohommadi-Jam and Waters, 2014). Therefore, fillers that have a high specific
component and a low dispersive component have been associated with weak polymer-filler interactions and strong filler-filler interactions (Leblanc, 2002).

Contrary to surface area measurement, there are no standardized methods for the quantification of surface energy. Currently the most commonly used methods for the quantification of this filler characteristic include contact angle and inverse gas chromatography (Papirer et al., 1988; Strzemiecka et al., 2014). Contact angle methods have been designed for macroscopic flat surfaces, thus the accuracy of surface energy measurements using this method is limited by the size of the particles, surface roughness and chemical heterogeneity (Hole et al., 2011; Riedl and Matuana, 2006). Inverse gas chromatography is a more accurate technique for the characterization of small particles’ surface energy (Cordeiro et al., 2011b; Mohammadi-Jam and Waters, 2014; Strzemiecka et al., 2014).

3.4.1.3. Shape and Structure

Fillers exist in a variety of shapes including spheres like carbon black and silica, plate-like fillers such as mica, talc and kaolin, and rod-like fillers obtained from cellulosic materials and carbon nanotubes or other irregular particles (Byers, 2001; Szeluga et al., 2015). Filler shape depends on the source and method used to prepare the particles (Bandyopadhyay-Ghosh et al., 2015). Also, primary filler particles can aggregate into complex tri-dimensional objects due to bonding forces between the particles (Leblanc, 2002). Random spatial arrangement of the primary particles generates different degrees of irregularity that define the structure of the filler (Fröhlich et al., 2005). Moreover, complex filler structure also can result from naturally occurring pores.
and surface roughness. This morphological filler characteristic can contribute to reinforcement of the composite by mechanical interlocking of the polymer chain which restricts their mobility when subject to deformation (Fröhlich et al., 2005; Kohls and Beaucage, 2002).

Despite being easy to define qualitatively, filler structure is difficult to measure quantitatively. For conventional fillers like carbon black, structure is characterized in terms of the volume of dibutylphthalate (DBP) absorbed (Donnet and Custodero, 2013; Fröhlich et al., 2005). However, this measurement only represents the empty volume between the agglomerates, not an actual description of the shape of the primary particle nor of the structure. Furthermore, DBP measurement is sensitive to surface chemistry of the filler, so it is not a reliable measurement for most non-black fillers (Donnet and Custodero, 2013). Electron microscopy also has been employed as a tool to characterize filler shape and structure. However, this technique is very time consuming, only a few particles/aggregates can be observed at the time, and the observations are done in two-dimensional space (Donnet and Custodero, 2013; Kohls and Beaucage, 2002).

3.5. Reinforcing Mechanisms

The reinforcement of NR by fillers is the result of a combination of physical and chemical interactions (Chenal et al., 2007b). These complex interactions allow to maintain flexibility of the material, while enhancing strength and resistance to deformation (Donnet and Custodero, 2013). A simplified way to understand reinforcement of polymer by fillers is to think of it as the restriction of polymer chain motion caused by filler inclusion (Ahmadi and Shojaei, 2013; Byers, 2001). When the
composite is subject to deformation, limited mobility of chains near a filler particle hinders molecular separation, which increases resistance to formation of cracks that can lead to failure of the material (Hamed, 2000). Restriction of chain motion has been ascribed to polymer-filler interaction and filler-filler interaction (Byers, 2001; Donnet and Custodero, 2013; Samsuri, 2013). The addition of fillers can also affect the properties of the rubber as result of hydrodynamic effects (Donnet and Custodero, 2013; Heinrich et al., 2002; Sarkawi et al., 2014).

3.5.1. Polymer-Filler Interaction

Interaction between NR and the filler can result from weak interfacial adhesion forces like van der Waals and/or strong chemical bonds. The extent of these interactions depends on the compatibility of the filler with the rubber, as a consequence of surface energy, and the available contact area (Donnet and Custodero, 2013; Fröhlich et al., 2005; Samsuri, 2013).

In composites with strong polymer-filler interactions, the polymer chains are adsorbed on the surface of the filler, resulting in a immobilized glassy-like rubber layer described as bound rubber (Khan and Bhat, 2014; Stöckelhuber et al., 2011). The adsorption can be from (a) attachment of a single chain segment on the surface of the particle, (b) multiple attachments of segments of a rubber chain and (c) attachment of a single chain to multiple particles (Fig. 3.5). In all these possible configurations, the adsorbed chains can also entangle with each other, further restricting their motion (Hamed, 2000; Sarkawi et al., 2014).
Different degree of chain restriction is also consequence of the structure and spacing between particles and/or aggregate. Rubber chains adsorbed onto the external aggregate surface, are called shell rubber, while rubber that is trapped within filler structure is called occluded rubber (Kohls and Beaucage, 2002). At low strain bound rubber increases the filler volume, but under high deformation these filler-polymer structures can break releasing the rubber and allowing load transfer (Hamed, 2000; Kohls and Beaucage, 2002).

3.5.2. Filler-Filler Interaction

Interaction between the particles allows the formation of a filler network within the composite that can considerably contribute to the enhancement of mechanical properties (Bandyopadhyay-Ghosh et al., 2015; Bras et al., 2011; Samsuri, 2013) (Fig.3.6). Contribution of filler network to the reinforcement of NR is mainly due to
interlocking of the chains in the network, which allows load transfer and energy
dissipation when the material is subject to deformation (Hamed, 2000).

Fig. 3. 6: Representation of the filler network in polymer composites. Modified from
(Kohjiya et al., 2006).

A specific volume of particles, known as the percolation threshold, is required to
form the filler network. This threshold depends on the filler aspect ratio (length to
diameter ratio) and the degree of dispersion (Bandyopadhyay-Ghosh et al., 2015; Peddini
et al., 2014; Roland, 2016), hence it varies among different fillers. Beyond the
percolation threshold, attraction between particles can lead to agglomeration, which
increases the viscosity and has an adverse effect on the reinforcement of the polymer due
to decreased filler surface area (Peddini et al., 2014). Furthermore, interaction between
the filler particles and interaction of the particles with the rubber are competitive forces
within the composite (Sarkawi et al., 2014). Reinforcement achieved through filler-filler
interactions is lower compared to the reinforcement obtained from polymer-filler interactions (Jong, 2014).

3.5.3. Hydrodynamic Effect

The introduction of fillers (a non-deformable phase) to the elastomer amplifies the strain on the polymer chains near individual particles and leads to local heterogeneities. This is known as a hydrodynamic effect and mainly affects the viscosity and elastic modulus of the material (Chenal et al., 2007b; Fröhlich et al., 2005; Roland, 2016). This hydrodynamic effect has been described as a function of the volume fraction of the filler in a vulcanizate by the Guth and Gold equation (Roland, 2016; Samsuri, 2013):

\[ G = G_0 (1 + 2.5\phi + 14.1\phi^2) \]

where \( \phi \) is the volume fraction of the filler and \( G \) and \( G_0 \) are the elastic modulus of filled and unfilled rubber, respectively. Nevertheless, this equation is based on the assumptions that the particles are spherical, freely dispersed and entirely non-elastic (Roland, 2016; Samsuri, 2013). These assumptions are rarely met, particularly the ideal, perfectly spherical, particle shape. Although modifications of this equation have been performed to account for different shapes, this equation cannot accurately predict the resulting property due to complexity of the system.

3.6. Filler Sources

3.6.1. Conventional Fillers

Currently the main commercially used filler in NR composites is carbon black. This filler is the oldest and most widely studied filler due to its excellent reinforcing characteristics (Dizon, 1976; Janzen, 1982; Janzen and Kraus, 1971; Leblanc, 2002;
Medalia, 1978; Papirer et al., 1999; Strzemiecka et al., 2014; Studebaker, 1957). Carbon black reinforcement results from high surface area, relatively non-polar surface and highly branched structure from aggregates of primary particles (Gerspacher and Wampler, 2001; Leblanc, 2002). However, carbon black is a non-renewable filler source obtained from the partial combustion or thermal decomposition of hydrocarbons (Gerspacher and Wampler, 2001; Studebaker, 1957). Moreover, carbon black production generates large quantities of greenhouse pollutants, such as sulfur dioxide, nitrogen oxide and particulate matter. Strict environmental regulations placed for carbon black production in North America and Europe, combined with increasing demand from the tire industry are expected to lead to shortfalls and rising prices in the near future (Moore, 2015; Pourriahi, 2016).

Although initially not considered as a reinforcing filler due to its highly polar surface, which is incompatible with NR, silica is currently an important filler for NR (Tohsan and Ikeda, 2014). To overcome unacceptably strong filler-filler interactions, and improve compatibility with NR, silica requires the use of expensive coupling agents (Choi et al., 2003; Kato et al., 2014; Murakami et al., 2003). Silica has gained increasing attention as a reinforcing filler since the early 1990s, particularly in the tire industry due to improvements in rolling resistance at equal wear resistance and improved wet grip compared to carbon black composites (Rattanasom et al., 2007; Stöckelhuber et al., 2010). Decreased rolling resistance largely impacts the fuel efficiency of the car, hence decreasing CO₂ emissions. Nevertheless, the production of silica requires the use of harsh chemical and high temperatures (Byers, 2001).
Other fillers commonly used for NR are minerals, including clays, talc, and alumina trihydrate among others. However, these fillers are used as diluents or as pigments and flame retardants rather than to provide reinforcement (Byers, 2001; Rodgers and Waddell, 2013).

3.6.2. Waste-derived and Bio-based Fillers

Waste materials generated in agriculture and food processing are generated in large quantities (Barrera and Cornish, 2015; Mangut et al., 2006; Ujor et al., 2014), yet most of them lack of a valuable application and are treated as wastes that require disposal. Increasingly, research is focusing on the utilization of these residues as alternative, more sustainable fillers for NR and other polymers (Angellier et al., 2005a; Bras et al., 2011; Intharapat et al., 2013; Poompradub et al., 2008; Visakh et al., 2012). Some of the waste-derived fillers studied include cellulose, starch, cuttlebone, and eggshells among others. Reinforcement of NR has been achieved particularly at low loadings of these materials.

One of the limitations of these materials is lower compatibility with NR, due to the polar character of some of the fillers (Abraham et al., 2011; Angellier et al., 2005a). However, these limitations can be overcome with the use of surface functionalization (Liu et al., 2008; Parambath Kanoth et al., 2015).
Chapter 4: Novel Mineral and Organic Materials from Agro-industrial Residues as Fillers for Natural Rubber

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Abstract

Bio-based materials are being developed increasingly because of the need for sustainable, environmentally-friendly, processes and products. We have made natural rubber composites containing low cost fillers derived from agro-industrial wastes, namely, eggshells, carbon fly ash, processing tomato peels and guayule bagasse. Composites manufactured with 35 phr (parts per hundred rubber) of carbon black (particle size 108 ± 31 nm) were used as a reference filled material. The amount of carbon black was gradually replaced by a specific waste-derived macro (<300 µm diameter) or micro (<38 µm diameter) filler. Despite differences in particle size
distribution and surface chemistry, the tensile properties of micro sized tomato peels composite were similar to those of the carbon black reference composite. Composites manufactured using micro sized particles at low loadings (5 phr and 10 phr) of carbon fly ash and eggshells, as co-fillers with carbon black, also demonstrated comparable tensile results to those of composites manufactured solely with carbon black. Hierarchical cluster analysis partitioned the data into five groups of composites having statistically similar mechanical properties. Composites with the highest tensile strength and 300% modulus were clustered in groups 1, 2 and 5 conformed mainly by composites containing the smallest particles at low loadings (5 phr and 10 phr). As the amount of non-carbon black filler increased above 10 phr and up to 35 phr (maximum filler loading used), the composites became weaker than the carbon black filled composites and modulus decreased.

**Key words:** Renewable materials, natural rubber, bio-based composites, reinforcing.

### 4.1. Introduction

Natural rubber is an elastomeric material that possesses unique properties such as self-reinforcement, abrasion, tear, and impact resistance, among others (Chenal et al., 2007b; Steinbüchel, 2003; Visakh et al., 2012). These properties are required in enumerable applications including tires, conveyor belts, gaskets and hoses (Rodgers and Waddell, 2013). Further improvements in rubber inherent properties are obtained by the addition of reinforcing agents like carbon black and silica, neither of which is currently derived from renewable sources (Visakh et al., 2012) apart from a tiny amount of carbon
black. Carbon black is the oldest, most widely used and studied filler for rubber compounds (Fröhlich et al., 2005).

There is increasing interest in developing bio-based materials in order to reduce dependency on fossil fuels, valorize agricultural and industrial residues, and generate more sustainable materials while concomitantly minimizing pollution. Nevertheless, studies on natural rubber and plastic composites in the last decade have mainly focused on cellulosic fillers (Andrio et al., 2000; Bai and Li, 2009; Bras et al., 2010; Ismail et al., 2002; Jacob et al., 2004) due to their renewable characteristics, degradability, abundance and diversity of sources, as well as for the high mechanical properties of these naturally structural materials (Bendahou et al., 2010; Majeed et al., 2013; Pasquini et al., 2010). Little evaluation has been done on other waste streams that could confer high performance characteristics to composites.

Four abundant agro-industrial residues, processing tomato peels, carbon fly ash, guayule defoliated stem bagasse (potentially abundant) and eggshells, were tested in this study as alternative fillers for natural rubber composites. Some waste-derived materials, such as eggshells (Intharapat et al., 2013), rice husks (Ishak and Bakar, 1995) and fibers from bamboo (Ismail et al., 2002) and sugar cane (Bras et al., 2010) have been evaluated singly but not in direct comparison with other materials. This paper explores the diversity of mechanical properties obtained for different rubber composites as result of their different composition and loading, using the waste fillers as partial and full replacements of petroleum-derived carbon black. Tomato peels and eggshells are significant solid wastes generated from the food processing sector. In 2012, 12 million tons of processing
tomatoes were harvested in the United States (Thornsbury et al., 2013) generating a processing waste of 437,574 metric tons of skins, while 95.176 billion eggs were produced in the United States 2013 (United States Department of Agriculture, 2014) generating 596,754 metrics tons of shells. On the other hand, guayule bark bagasse is obtained as a by-product of latex extraction from the guayule shrub, and is not currently produced in large amounts. However, guayule is an important source of natural rubber, demand for which is increasing due to the lack of allergic responses associated with the latex, compared to the traditionally used natural rubber latex (Hamilton and Cornish, 2010). Carbon fly ash is a readily available and cheap material from power plants fueling many manufacturing processes.

The utilization of low cost materials as fillers could reduce the final cost of rubber products; however, due to the demanding conditions under which many natural rubber products are used, the properties of the composite materials must be evaluated to ensure that the composites meet or exceed performance requirements. These requirements suggest that reinforcing fillers will be required and that diluent fillers may have limited utility. Primary factors to consider when selecting reinforcing fillers are particle size, loading, structure, and surface activity (Byers, 2001). These factors affect the dispersion of the filler in the rubber matrix, as well as filler-filler and polymer-filler interactions, and determine the final physical properties (Fröhlich et al., 2005). The aim of this study is to analyze natural rubber composite properties achieved with different polymer-filler interfaces, particle sizes and loadings of waste-derived fillers.
4.2. Experimental

4.2.1. Materials

Hevea natural rubber (grade SMR-20), purchased from Centrotrade (Chesapeake, VA), was used as the polymer matrix. Compounding chemicals, namely, zinc oxide, stearic acid, sulfur, the vulcanization accelerator Butyl benzothiazole sulfonamide (TBBS), and carbon black N330 (mean particle size: 108 nm, SD: 31.42 nm), were purchased from HB chemicals (Twinsburg, OH). The waste filler raw materials were generously donated as follows: eggshells (ES) by Troyer’s Home Pantry (Apple Creek, OH), carbon fly ash (CFA) by Cargill Salt (Akron, OH), processing tomato peels (TP) by Hirzel Canning Co & Farms (Toledo, OH), and guayule bagasse (GB) was generated as a co-product of latex extraction at our facility from guayule shrubs donated by PanAridus (Casa Grande, AZ).

4.2.2. Preparation of Fillers

Raw materials were dried at 55°C and then ground to macro (diameter (d) of 300μm-38μm) and micro (d of 38μm-100nm) particle sizes. The macro fillers were dry milled using a mini Wiley mill, Thomas Scientific (Swedesboro, NJ) and sieved using a sieve with a mesh size of 50 (sieve opening 300μm), Fisher Scientific (Pittsburgh, PA). The micro fillers were wet-milled in a five liter ball mill, U.S. Stoneware (East Palestine, OH), dried, then dry-milled using a Planetary Ball Mill 100, Glen Mills (Clifton, NJ) and sieved using a mesh size 400 (sieve opening 38μm). Particle size distributions were verified using a Particle size analyzer LA-950V2, Horiba Scientific (Irvine, CA) (Fig. 34).
4.1). Filler bulk densities were determined by weighing a known volume of each filler and calculating the bulk density as mass/volume occupied (Table 4.1).

Fig.4. 1: Macro — and micro ... sized filler’s particle size distribution. a) Carbon fly ash; macro (median: 76.20 µm, mean: 89.32 µm, SD: 61.94 µm), micro (median: 11.25 µm, mean: 12.12 µm, SD: 4.93 µm), b) eggshells; macro (median: 230.33 µm, mean: 241.46 µm, SD: 111.01 µm), micro (median: 16.07 µm, mean: 23.19 µm, SD: 20.79 µm), c) guayule bagasse; macro (median: 243.10 µm, mean: 279.33 µm, SD: 188.56 µm), micro (median: 49.09 µm, mean: 54.75 µm, SD: 30.63 µm), d) tomato peels; macro (median: 170.70 µm, mean: 179.02 µm, SD: 154.91 µm), micro (median: 23.08 µm, mean: 26.95 µm, SD: 17.00 µm).
Table 4.1: Filler bulk densities.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Size</th>
<th>Density (g/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td></td>
<td>0.42±0.01</td>
</tr>
<tr>
<td>Carbon fly ash</td>
<td>macro</td>
<td>0.74±0.02</td>
</tr>
<tr>
<td>Carbon fly ash</td>
<td>micro</td>
<td>0.57±0.01</td>
</tr>
<tr>
<td>Guayule bagasse</td>
<td>macro</td>
<td>0.53±0.02</td>
</tr>
<tr>
<td>Guayule bagasse</td>
<td>micro</td>
<td>0.36±0.07</td>
</tr>
<tr>
<td>Eggshells</td>
<td>macro</td>
<td>1.32±0.02</td>
</tr>
<tr>
<td>Eggshells</td>
<td>micro</td>
<td>0.79±0.05</td>
</tr>
<tr>
<td>Processing tomato</td>
<td>macro</td>
<td>0.69±0.02</td>
</tr>
<tr>
<td>Processing tomato</td>
<td>micro</td>
<td>0.60±0.02</td>
</tr>
<tr>
<td>peels</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.2.3. Composite Preparation

The effect of different types of waste-derived fillers, particle size and filler loading, were determined using a standard compound formulation initially containing 35 phr of carbon black N330 and no other filler. Carbon black was gradually replaced by each specific waste-derived filler until no carbon black remained (Table 4.2). Fillers and compounding ingredients were incorporated into 790 g of rubber through mastication using a Farrel BR lab mixer, Rubber City Machinery Corporation (Akron, OH). The mixer chamber was charged with rubber blocks (approximately 5 cm cubes), followed by lowering the ram to allow the rubber to knead for 40s at 6.3 rad/s. Filler and stearic acid were then added and mixed until the mix temperature reached 82°C. Finally, the remaining compounding ingredients were added, the rotor speed was increased to 9.4 rad/s and the batch was allowed to mix until it reached 99°C. The ram was raised during the mixing to sweep materials deposited from orifices. The hot mix was discharged from
the mixer, and then milled while still hot using a two-roll EEMCO lab mill, roll diameter 15.24 cm and 33.02 cm face width, Rubber City Machinery Corporation (Akron, OH).

The samples were milled until a bank of rubber formed in between the rollers, and then three 24.8 cm width cuts (approximately ¼ of the distance across the rolls) were made along the face of the rubber from both the left and right sides of the mill. The rubber was cut from the mill, folded back on itself and passed through the rollers two more times. The composites were cured in an ASTM D3182 150 by 150 by 2 mm mold (ASTM International, 2016) at 160°C and 16 tons of force, for 12 min, using a Wabash 4-post, 30 ton heated press, Rubber City Machinery Corporation (Akron, OH). After curing, the material was conditioned at room temperature for 24 hours prior to assessment of tensile properties.

Table 4. 2: Compounding formulation used to prepare NR composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black</td>
<td>35 30 25 15 0</td>
</tr>
<tr>
<td>Filler</td>
<td>0 5 10 20 35</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.5</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
</tr>
<tr>
<td>Butyl benzothiazole sulfonamide (TBBS)</td>
<td>0.75</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
</tr>
</tbody>
</table>
4.2.4. Materials Characterization

4.2.4.1. Composite Testing

Five dumbbell specimens of each composite were cut using ASTM Die C. Tensile properties were measured along the grain direction, according to ASTM D412 (ASTM International, 2013b), using a tensiometer, Model 3366, Instron, (Norwood, MA), with a crosshead speed of 500 mm/min. The resulting properties of these composites (300% modulus, tensile strength and elongation at break) were compared.

4.2.4.2. Fourier Transform Infrared Spectroscopy (FTIR)

The presence of functional groups on the surface of the fillers and composites was verified using a PerkinElmer Spectrum Two IR spectrometer (Waltham, MA, USA). Spectra were recorded in the range of 4000 to 450 cm⁻¹ by accumulating 32 scans at a resolution of 2 cm⁻¹.

4.2.4.3. Scanning Electron Microscopy (SEM)

A Hitachi S-3500N scanning electron microscope (Tokyo, Japan), operated in a high vacuum, was used to investigate the morphology of the different types of materials and dispersion of the fillers within the polymer matrices. Cross sections of each composite sample at the fracture surface were cut and washed with an ethanol solution 70%, to eliminate surface contamination. The samples were sputter-coated with a thin layer of platinum (0.2 KÅ) by an Anatech Hummer 6.2 Sputtering system prior to analysis in order to improve their conductivity, allowed to dry and imaged.
4.2.5. Statistical analysis

Cluster analysis was done in order to group composites with similar mechanical properties. In this multivariate analysis, every sample was described by results obtained from the three different response properties: i.e. 300% modulus, tensile strength and elongation at break. Euclidian distance was used to measure the similarity between the treatments. Ward’s method was used as the linkage method. Multiple means comparison Tukey-Kramer test, at a significance level $\alpha$ of 0.05, was performed, in order to further compare the resulting groups.

4.3. Results

4.3.1. Tensile properties of composites

Considering all three properties measured, the overall results indicate that some reinforcing effects were obtained at low loadings (5 and 10 phr) of micro sized non-black fillers, especially CFA, ES and TP. Composites manufactured by partially replacing carbon black with these materials had tensile properties comparable to those of the carbon black composites. Particularly, composites made by partially replacing carbon black with TP, were reinforced similarly to carbon black alone. This is important considering the renewable character of these materials, which carbon black lacks, and their probable lower cost.

As the amount of non-carbon black fillers was increased above 10 phr, a substantial increase in elongation at break, and decrease in 300% modulus and tensile strength of the composites was observed (Table 4.3). Higher values of 300% modulus and tensile strength were achieved by composites made with micro, rather than macro,
sized particles. In general, broader particle size distributions were observed for macro particles compared to micro sized particles (Fig. 4.1). Extreme particle size values under the left side of the curve of macro size distributions were considered for the analysis of the result; however, these small portions of material do not seem to drastically affect the overall resulting properties.
Table 4.3: Tensile properties of NR composites manufactured using micro and macro sized particles obtained from different waste-derived materials. Each value is the mean of 5 samples.

<table>
<thead>
<tr>
<th>Filler Typea</th>
<th>Size</th>
<th>Waste fillerb (phr)</th>
<th>Modulus at 300% (MPa)</th>
<th>SE</th>
<th>Modulus at 300% Means comparisonc</th>
<th>Elongation at Break (%)</th>
<th>SE</th>
<th>Elongation at Break Means comparisonc</th>
<th>Tensile Strength (MPa)</th>
<th>SE</th>
<th>Tensile Strength Means comparisonc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled vulcanized</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NR</td>
<td>0</td>
<td>1.37</td>
<td>0.03</td>
<td>Q</td>
<td>1,298</td>
<td>0.23</td>
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[Continued]
Table 4.3 continued

| Filler | Type   | Amount | Mass Content (phr) | Mass Content Standard Error | Mass Content Standard Error | Carbon Black Mass Content | Carbon Black Mass Content Standard Error | Results
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aData: Carbon fly ash (CFA), Guayule bagasse (GB), Eggshells (ES), Processing tomato peels (TP)

bTable reports the amount of non-carbon black filler in the sample. Total amount of filler (carbon black plus non-carbon black), in all samples was 35 phr.

cMultiple means comparison Tukey-Kramer test, at a significance level $\alpha$ of 0.05. Samples that do not share a common letter are significantly different.

*A composite made using 35 phr of carbon black was used as the reference material.
Composites manufactured with low loading (5 phr) of CFA, ES and TP, with 30 phr carbon black, had very similar values of 300% modulus to those of composites made with carbon black alone, for both macro and micro sized particles. Furthermore, 300% modulus of composites containing 5 phr micro sized CFA, ES and TP, as well as the 10 phr micro sized TP composite, were not significantly different from the mean 300% modulus of the carbon black reference composite. Similarly, the composites with the highest tensile results were those containing 10 phr of micro sized TP and ES, and 5 phr of macro sized ES, with tensile strengths of 31.76 MPa, 30.05 MPa and 29.63 MPa, respectively. The mean tensile values of 10 phr of micro sized TP and ES, and 5 phr of macro sized ES were not significantly different from each other, but only 10 phr of micro sized TP was not significantly different from carbon black alone 34.24 MPa (Table 4.3).

As seen from the stress versus strain curves (Figs. 4.2- 4.5), for composites made with macro particle size (plot a) and micro particle size (plot b), as the amount of non-carbon black filler was increased, the composites behaved more like a unfilled vulcanized rubber, represented by the thick solid line (Figs. 4.2- 4.5). Typical strain-induced crystallization also was observed in composites containing only non-carbon black fillers at elongation greater that 700%.
Fig.4. 2: Stress vs strain curves of NR composites made with different amounts of carbon fly ash, using (a) macro size particles (b) micro size particles. Total filler loading is 35 phr. As the waste filler loading increases the carbon black filler decreases by the same amount. Waste filler loading —— 0 phr, — 5 phr, —— 10 phr, — 20 phr, —— 35 phr, Unfilled NR.
Fig. 4. 3: Stress vs strain curves of NR composites made with different amounts of guayule bagasse, using (a) macro size particles (b) micro size particles. Total filler loading is 35 phr. As the waste filler loading increases the carbon black filler decreases by the same amount. Waste filler loading \(0 \text{ phr}, \quad \cdots \cdots \quad 5 \text{ phr}, \quad \cdots \cdots \quad 10 \text{phr}, \quad \cdots \cdots \quad 20 \text{ phr}, \quad \cdots \cdots \quad 35 \text{ phr}, \quad \text{Unfilled NR.} \)
Fig. 4. Stress vs strain curves of NR composites made with different amounts of eggshells, using (a) macro size particles (b) micro size particles. Total filler loading is 35 phr. As the waste filler loading increases the carbon black filler decreases by the same amount. Waste filler loading — 0 phr, — 5 phr, —— 10 phr, —— 20 phr, —— 35 phr, — Unfilled NR.
Fig.4. 5: Stress vs strain curves of NR composites made with different amounts of processing tomato peels, using (a) macro size particles (b) micro size particles. Total filler loading is 35 phr. As the waster filler loading increases the carbon black filler decreases by the same amount. Waste filler loading ____ 0 phr, ___ 5 phr, _____ 10phr, ___ . ____ 20 phr, ____ Unfilled NR.

The high stiffness of composites containing high loadings (20 phr and 35 phr) of micro sized TP and 35 phr of macro sized TP impeded the processing of the material, compromised its integrity, and data are not shown for these unsuccessful samples.
4.3.2. FTIR Spectra Analysis

Most of the functional groups found in the rubber composites were the same as those found in unfilled vulcanized rubber, represented by the green line (Fig. 4.6). Variations in the spectra are due to changes in the concentration of the functional groups in the composites, due to the addition of fillers. A broad peak around 3390-3100 cm\(^{-1}\), possibly due to the O-H bond from stearic acid, was observed in the rubber compounds (Pal et al., 2010). Absorption bands characteristic of natural rubber were observed around 2960 – 2800 cm\(^{-1}\) due to the stretching frequency of methyl and methylene (Afiq and Azura, 2013; Pal et al., 2012). Bending vibrations of methylene and methyl bonds are represented by peaks at 1446 cm\(^{-1}\) and 1370 cm\(^{-1}\) (Afiq and Azura, 2013; Xu et al., 2015). In addition, peaks at 1016 cm\(^{-1}\) and 833 cm\(^{-1}\) may be due to C-C stretching and to isoprene double bond bending, respectively (Ali et al., 2008; Fernández-Berridi et al., 2006; Riyajan et al., 2012). On the other hand, a peak at 1091 cm\(^{-1}\), only present in CFA and CFA composites is due to Si-O vibration (Sae-Oui et al., 2002), while peaks at 1432 cm\(^{-1}\) and 875.86 cm\(^{-1}\) present in ES are due to asymmetric stretching and bending of CO\(_3\) from calcium carbonate (Engin et al., 2006; Intharapat et al., 2013). Finally, the broad band at 606 cm\(^{-1}\) observed in TP may be due to wagging of NH\(_2\) found in amides (Sumayya et al., 2008).
4.3.3. Analysis of composite morphology

Differences in interfacial interactions between natural rubber and the various types of filler were reflected in the composite morphology (Fig. 4.7). Carbon black composites (Fig. 4.7a) had a uniform surface, and neither agglomerations of the filler, nor gaps within the polymer matrix were observed. The micro sized TP composite (Fig. 4.7b) had a uniform surface similar to carbon black alone, indicating similarities between
carbon black and TP composite morphology, that further explains the resultant mechanical properties.

Fig. 4. SEM micrograph of NR composites with a) carbon black, b) processing tomato, micro, 10 phr, c) carbon fly ash, micro, 20 phr, d) eggshells, micro 20 phr, e) guayule bagasse, micro, 20 phr.
In contrast, the presence of several gaps within the composites made with the other fillers, and smooth surfaces around the fillers indicates poor interfacial adhesion of the polymer with the other fillers (Figs. 4.7c - 4.7e).

4.3.4. Statistical analysis

Five homogeneous groups with common characteristics were obtained by dividing the dendrogram obtained from cluster analysis at a distance level of 12 (Fig. 4.8). Cluster 1 includes composites made with carbon black and 10 phr micro sized TP. Samples in this cluster possessed the highest tensile strength and 300% modulus and middle values of elongation at break. Cluster 2 groups the largest number of samples. Nearly 70% of the samples in this cluster contained micro size particles at low loadings (5 and 10 phr). These samples had high tensile strength and 300% modulus (not as high as cluster 1) and middle to high values of elongation at break. Based on the mechanical properties, this cluster is more similar to cluster 1 than to the other clusters. Multiple mean comparisons performed for the response variable tensile strength indicated that there is not a significant difference between the mean tensile strength of composites in cluster 1. The analysis also showed no significant difference between the mean tensile strength of composites containing 10 phr of micro size TP and composites in cluster 2. However, there is a significant difference between the mean tensile strength of composites made with carbon black and composites in cluster 2.
Fig. 4. 8: Dendrogram obtained by hierarchical clustering analysis of 30 composite formulations.
Cluster 3 groups composites manufactured using macro size particles at high loadings (20 and 35 phr). The samples had the lowest tensile strength, relatively low modulus, and middle to high values of elongation at break. Cluster 4 and 5 gather composites that showed middle values of tensile strength, middle to low values of 300% modulus and middle to high values of elongation at break. Approximately 64% of the composites in these groups were made using 10 phr and 20 phr of macro size particles.

Although the different fillers were scattered among the different clusters, 75% of composites made with the two mineral fillers (ES and CFA), were grouped in cluster 2, and 5. The clustering of the organic materials was mostly influenced by filler loading; composites containing loadings of 5 and 10 phr were grouped in cluster 2 and 5, while composites containing 20 and 35 phr were placed in clusters 3 and 4.

4.4. Discussion

Composites made by partially replacing carbon black with TP were reinforced similarly to carbon black alone, possibly due to similarities in particle structure. At a micro scale, TP particles are in the form of agglomerates of small granules (Fig. 4.9a), similar to carbon black structure (Fig. 4.9b). This particle structure is unique to these two fillers among the fillers used in this study (Fig. 4.9), and contributes to the reinforcing of the materials due to a combination of small particle size along with a high degree of irregularity that determines the restriction of the chain motion under the applied strain. This behavior is not observed in macro sized TP particles because at this larger scale the material presents a laminar shape (Fig. 4.9c) and possesses less surface area.
Fig. 4. SEM micrograph of filler particles. (a) Micro sized processing tomato peels, (b) carbon black; (c) macro sized processing tomato peels, (d) carbon fly ash, (e) eggshells, (f) guayule bagasse.

The structure of the mineral fillers used also influenced their reinforcing effect. ES and CFA particles possess a high surface area due to roughness and porosity of the
materials (Fig. 4.9d and 4.9e). ES porosity is the consequence of naturally occurring gas exchange pores (Intharapat et al., 2013). The porosity promotes a wetting effect that provides better interfacial adhesion between the polymer and the filler. The presence of a new peak in at 1538 cm\(^{-1}\) in the spectra of ES composites (Fig. 4.6b) indicates that calcium stearate has been formed by chemical adsorption of stearic acid onto the ES calcium carbonate (Gönen et al., 2010). Surface modification of calcium carbonate with stearic acid improves the hydrophobicity of the filler (Mihajlović et al., 2009, 2013), making it more compatible with the rubber. This change in the surface chemistry of the filler leads to better polymer-filler interaction and contributes to the observed reinforcing effect of eggshells (Khan and Bhat, 2014).

In contrast, naturally occurring resins in GB (Nakayama, 2005) had an impact on the final mechanical properties of GB composites. These resins potentially add a plasticizing effect, which would increase the ductility of the material. Discrepancies in particle size distribution within a particle size range also may have contributed to the observed results. Micro sized GB had the highest proportion of larger particles, while micro sized TP, ES and CFA contained smaller particles. Bigger particles have less surface area per unit weight than smaller particles: this decreases the reinforcing effect and also generates flaws within the composite material.

It is also important to highlight the different volume fractions of fillers contained in the composites based on their bulk density. Micro sized GB possesses the lowest bulk density among the fillers used (Table 4.1) and, therefore, substantially larger volumes of material were needed for the preparation of the composites of similar weight loadings.
This implies more filler particles are enclosed within the same volume of polymer in lower density fillers compared to the higher density fillers. Filler volumes above an optimum value promote more contact between the filler particles, which favors filler-filler interaction rather than polymer-filler interaction. This condition may lead to agglomeration of the filler and also contribute to the poor reinforcing properties observed in the results.

The lower tensile strength and 300% modulus values achieved at high loadings (20 and 35 phr) of waste-derived fillers (Table 4.3) indicate a lower reinforcing effect of the non-carbon black fillers at high loadings compared to carbon black. At low filler loading the reinforcing effect of carbon black predominates in the control of the properties over the other filler, but at high loadings the reinforcing effect depends only on the non-black filler. The lower reinforcement of most of the non-black fillers is probably caused by the larger particle size compared to carbon black (lower surface area), but also may be associated with differences in surface chemistry as well as. Besides having the smallest particles (108 nm), hence more surface area, carbon black possesses a relative non-polar surface (Byers, 2001), which is more compatible with natural rubber than the more polar fillers like the cellulose in GB.

Homogeneity observed in the fracture surface of carbon black composites (Fig. 4.7a) is the result of good polymer-polymer filler interaction which, for carbon back, is mainly physical in nature (van der Waals forces) (Fröhlich et al., 2005). These weak interfacial forces allow carbon black to behave as an additional crosslinker in the natural rubber network (Chenal et al., 2007b) by restricting chain mobility and generating
stronger and harder materials. Under strain, these adhesion forces can break and relocate allowing the material to maintain flexibility while also exhibiting resistance to deformation (Byers, 2001). Given the differences in surface chemistry and particle size between the fillers studied and carbon black, this behavior is not completely matched.

The weaker polymer-filler interactions existing between some non-carbon black fillers and natural rubber is also reflected in the increased of elongation at break of composites containing high loadings of the waste derived fillers. The decrease in the carbon black portion allowed more chain mobility and so a more stretchable material is obtained. Moreover, stress vs strain curves of composites containing high loadings of non-carbon black filler resemble the behavior of unfilled vulcanized rubber (Figs. 4.2 - 4.5). In an unfilled vulcanized rubber sample, when a uniform increase in strain is applied, polymer chains are able to rearrange, and so only slight increases in stress are observed.

The partial replacement of carbon black, a nano filler, with micro sized fillers, which can be cheaply made from low cost waste materials, without loss of mechanical properties, suggests that significant cost savings may be possible by using such fillers. Nano fillers are much more difficult to manufacture at large scale than micro-fillers. It is particularly interesting that 10 phr micro-TP with 25 phr of nano-carbon black performed as well as the nano-carbon black alone.

Most of the composites manufactured from wasted-derive materials in this study meet the standard physical properties required for their application in a variety of rubber products. Potential applications for the composites include rubber gaskets for general
applications; tread components in P225/60R16 radial standard reference tires and insulating material, namely insulating line hose, covers, sleeves and gloves. Even if the smallest particle sizes in these fillers contribute to a disproportionate reinforcing effect on the properties, these fillers could potentially be used to manufacture a rubber of products with a low carbon footprint and more sustainability than conventional carbon black-filled products.

4.5. Conclusion

Agro-industrial residues are abundant solid wastes with heterogeneous composition. These characteristics make them promising materials for the generation of natural rubber composites with reinforcing characteristics comparable to those of carbon black. Moreover, the renewable character of agro-industrial residues could improve the sustainability of natural rubber products while adding value to these waste materials. The results open the possibility of utilizing renewable waste-derived materials to reduce the amount of non-renewable carbon black in natural rubber composites. A variety of material final properties can be tailored by modifying filler characteristics, namely type, blend, particles size and loading according to the specific requirements of each end product.
Chapter 5: High Performance Waste-Derived Filler/Carbon Black Reinforced Guayule Natural Rubber Composites

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Abstract

Guayule rubber (GNR) is an alternative source of natural rubber that does not crossreact with Type I latex allergy because it does not contain any proteins which can be recognized by antibodies raised against \textit{Hevea brasilienis} allergens. To advance the commercialization of this elastomer and diversify sources of natural rubber, efficient reinforcement of GNR is required to match the physical properties of vulcanized materials made from \textit{Hevea} natural rubber in specific products. Superior or comparable reinforcement to that of carbon black N330, was achieved by partial replacement of carbon black with 5 and 10 phr of waste-derived material. Out of several waste-derived...
fillers tested, micro sized eggshells showed remarkable reinforcing potential for GNR. Hybrid carbon black/micro sized eggshells/GNR composites (up to 20 phr micro sized eggshells), had increased tensile strength, and elongation at break, while maintaining similar values of 300% modulus and hardness to those achieved by carbon black/GNR composites. Hierarchical cluster analysis partitioned the data into six groups of composites having statistically similar properties within each group. Composites containing 5-20 phr of micro sized eggshells were clustered in a separate group due to their unique combination of high tensile strength and flexibility. The superior reinforcement may reflect a combined synergistic reinforcing effect of carbon black particles, which possess a strong polymer-filler interaction, with the formation of a unique network between the GNR and the waste-derived materials, not attained with *Hevea brasiliensis* natural rubber.

**Key words:** Natural rubber, Guayule, Waste-derived, Fillers, Reinforcing.

**5.1. Introduction**

Natural rubber (NR) is the only large scale, bio-based material among rubbers, and has a more environmentally-friendly production system than synthetic rubbers (Rasutis et al., 2015). NR possess properties, such as malleability under cold temperatures, heat dispersion and strain induced crystallization among others (Chenal et al., 2007b; Steinbüchel, 2003; Visakh et al., 2012), which cannot be matched by synthetic counterparts. In 2014, global NR consumption reached 12.159 million tons, nearly a 6.8% increase from the previous year (International Rubber Study Group IRSG, 2015), and consumption is expected to continually increase due to rising demands from
emerging economies such as China, India and Brazil. World NR consumption is expected to be 17 million metric tons by 2023 (International Rubber Study Group IRSG, 2014). Despite of being produced by over 2,500 plant species, commercial NR is obtained almost exclusively from the tropically-grown para rubber tree (*Hevea brasiliensis*) (van Beilen and Poirier, 2007).

*Parthenium argentatum* Gray, commonly known as guayule, stands out as a promising alternative source of NR (Cornish, 2001; Ray et al., 2005). This shrub, native to the Chihuahuan desert of Texas and North Central Mexico, produces high quality rubber comparable to hevea rubber (HNR) in terms of cis-1,4-polyisoprene content and molecular weight distribution (Castillo et al., 1979; Ponciano et al., 2012). However, important differences in the amount of non-rubber components have been identified between these two materials (Cornish, 2001; McMahan et al., 2015). Non-rubber constituents, such as proteins and lipids, contribute to rubber vulcanization behavior, and influence physical and chemical properties, particularly affecting the rate of crystallization when the material is under strain (Choi and Roland, 1997; McMahan et al., 2015). Differences in macromolecular structure also affect rubber compounding and product performance (Rensch et al., 1986).

GNR proteins do not crossreact with antibodies raised against Hevea latex proteins (Carey et al., 1995; Hamilton and Cornish, 2010; Siler et al., 1996; Siler and Cornish, 1995, 1994). Also, GNR possesses only 1% of the protein in HNR and 90% of these GNR trace proteins is a single protein, a nonallergenic cytochrome P450 oxidase making GNR particularly attractive for the production of elastomeric medical products.
GNR not only has lower protein content than HNR, but also contains relatively high levels of resin that can act as plasticizer and affect the resistance to deformation of the material (Schloman, 2005). The lower protein and higher resin content result in lower curing rates, lower oxidative stability and lower mechanical properties, compared to HNR, when the same cure package is used. Therefore, adjustments must be made to the vulcanization chemistry and to process parameters for GNR to achieve similar vulcanization kinetics and mechanical properties to HNR in any specific product application (Ray et al., 2010; Schloman, 2005).

Particulate materials (fillers) have been used for decades for the reinforcement, improvement of processing parameters, or dilution of NR and other elastomers (Donnet, 2003; Kohls and Beaucage, 2002). Carbon black is the oldest, and most widely used and studied, filler for rubber compounds due to its excellent reinforcing characteristics (Fröhlich et al., 2005; Kohls and Beaucage, 2002; Leblanc, 2002). However, carbon black is derived from petroleum, making this a non-renewable source. Carbon black has also been used to reinforce GNR (Porter and Stephens, 1979; Ramos-De Valle and Ramirez, 1982).

Waste-derived, bio-based materials possess a great number of potential applications, including their use as fillers in rubber composites (Bras et al., 2010; Pasquini et al., 2010). Many such materials are continuously available in high volumes, and can help to improve the sustainability of rubber products by replacing or reducing the amount of petroleum-derived carbon black (Angellier et al., 2005b; Barrera and Cornish, 2015; Gopalan Nair and Dufresne, 2003). Other potential benefits associated with the use
of waste-derived materials include valorization of these residues, reduction of disposal cost, and reduction of the final cost of polymer products.

The efficacy of the fillers depends on parameters related to their characteristics, including particle size, structure and functionality, and also parameters related to the specific rubber and processing conditions being used (Ahmadi and Shojaei, 2013; Fröhlich et al., 2005). The objective of this study was to investigate the effect of different low cost, waste-derived fillers, as partial or full replacements of carbon black, on the mechanical properties of GNR composites under constant processing conditions.

5.2. Experimental

5.2.1. Materials

GNR was obtained by drying guayule rubber latex (GNRL) for 48 hours at 50°C using a reflow oven, HVC 70 series, Conceptronic Inc. (Portsmouth, NH). Guayule rubber latex was extracted as described (Cornish, 1996), from fresh guayule shrub grown in Arizona. Compounding chemicals, namely, zinc oxide, stearic acid, sulfur, the vulcanization accelerator TBBS, and carbon black N330 (mean particle size: 108 nm, SD: 31.42 nm), were purchased from HB chemicals (Twinsburg, OH). The waste filler raw materials were generously donated as follows: eggshells (ES) by Troyer’s Home Pantry (Apple Creek, OH), carbon fly ash (CFA) by Cargill Salt (Akron, OH), processing tomato peels (TP) by Hirzel Canning Co & Farms (Toledo, OH), and guayule bagasse (GB) was generated as a co-product of latex extraction.
5.2.2. Composites Preparation

Fillers were prepared as described (Barrera and Cornish, 2015). A series of milling and sieving was used to obtain macro (diameter (d) of 300μm-38μm) and micro (d of 38μm-100nm) sized particles from the waste-derived materials. Particle size distributions were determined using a Particle size analyzer LA-950V2, Horiba Scientific (Irvine, CA). Filler bulk densities were determined by weighing a known volume of each filler and calculating the bulk density as mass/volume occupied.

The effect of different types of waste-derived fillers, particle size and filler loading, were determined using a standard compound formulation initially containing 35 phr (parts per hundred rubber) of carbon black N330 with no other filler (Table 5.1). Carbon black was gradually replaced by each specific waste-derived filler until no carbon black remained. The processing conditions for rubber compounding and curing matched those previously described (Barrera and Cornish, 2015).

Table 5.1: Compounding formulations used to prepare guayule rubber composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Guayule rubber</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black</td>
<td>35 30 25 15 0</td>
</tr>
<tr>
<td>Filler</td>
<td>0 5 10 20 35</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.5</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
</tr>
<tr>
<td>Butyl benzothiazole sulfonamide (TBBS)</td>
<td>0.75</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
</tr>
</tbody>
</table>
5.2.3. Materials Characterization

5.2.3.1. Mechanical Properties

Tensile properties were measured according to ASTM D412 (ASTM International, 2013b), along the grain direction with a crosshead speed of 500 mm/min at 23°C. Tensile test was done using a tensiometer, Model 3366, Instron (Norwood, MA), with the Bluehill v. 2.26 software package. Five dumbbell specimens of each composite, cut using ASTM D412 Die C, were tested. The samples were conditioned at 23±2°C and at a relative humidity of 50±5% for at least 24 hours prior to assessment of tensile properties. The resulting properties of these composites (300% modulus, tensile strength and elongation at break) were compared. Hardness was determined according to ASTM D 2240 (ASTM International, 2010a), using a Shore A, Ergo style durometer, model 408, PTC Instruments, (Los Angeles, CA) with an operating stand type 2. A mass of one kg, securely affixed to the durometer and centered on the axis of the indentor was used in order to improve repeatability.

5.2.3.2. Scanning Electron Microscopy (SEM)

The morphology of the different materials and dispersion of the fillers within the polymer matrices was investigated using a Hitachi S-3500N scanning electron microscope (Tokyo, Japan), operated under high vacuum. After tensile testing, cross sections of each composite sample at the fracture surface were cut and washed with a 70% aqueous ethanol solution, to eliminate surface contamination. The samples were sputter-coated with a thin layer of platinum (0.2 KÅ) by an Anatech Hummer 6.2
Sputtering system prior to analysis in order to improve their conductivity, allowed to dry, and then imaged.

5.2.3.3. Swelling Properties

Swelling measurements were performed on samples of 10mm x10mm x2 mm. The initial weight of the dry samples was recorded to an accuracy of 0.1 mg. Samples were immersed in toluene and kept at 25°C. The samples were periodically removed from the test bottles, weighed and immediately replaced in the bottles. This procedure was continued until no change in sample weight was noted. The swelling ratio of the samples was calculated as follows:

\[
\text{Swelling ratio} = \frac{(W_t - W_0)}{W_0}
\]

Where \( W_0 \) and \( W_t \) are the weights of the samples before and after a time \( t \) of immersion, respectively. The value of swelling ratio of each composite was the average of three specimens. Crosslink density of the sample was calculated using the Flory-Rehner equation (ASTM International, 2013a).

\[
v_e = \frac{-[\ln(1 - V_r) + V_r + x_1V_r^2]}{[V_1(V_r^{1/3} - V_r)/2]}
\]

Where \( x_1 \) is the polymer-solvent interaction parameter (0.393) and \( V_1 \) is the molar volume of the solvent (106.2 cm\(^3\)/g mole) (Sheehan and Bisio, 1966). \( V_r \) is the volume fraction of polymer in a swollen network in equilibrium with solvent, and was calculated as (ASTM International, 2013a):

\[
v_r = \frac{W_r/\rho_r}{W_r/\rho_r + W_s/\rho_s}
\]
Where \( W_r \) and \( W_s \) are weights of the dried sample and solvent absorbed by the sample, respectively. \( \rho_r \) and \( \rho_s \) are the density of the rubber compound and solvent respectively. \( \rho_r \) was calculated as described (ASTM International, 2013a).

5.2.4. Statistical Analysis

Statistical significance of the independent variables, i.e. filler type, particle size, and filler loading was determined by analysis of variance (ANOVA) with a significance level \( \alpha \) of 0.05 using the software JPM v.11 from SAS. Multiple means comparison Tukey-Kramer tests, at a significance level \( \alpha \) of 0.05, were performed, to determine statistical differences between composites properties.

Composites with similar mechanical properties were grouped through cluster analysis using Vegan package (Vegan v. 2.3-0) implemented in R (R Core Team, 2014). In this multivariate analysis, every sample was described by results obtained from the four different response properties: i.e. 300% modulus, tensile strength, elongation at break, and hardness number. Euclidian distance was used to measure the similarity between the treatments. Ward’s method was used as the linkage method. The data were standardized so that the variation extent of each response variable had an equivalent contribution to the formation of the classification.

5.3. Results

5.3.1. Characterization of Fillers

Significant differences were observed among the bulk densities of the waste-derived fillers. GB possessed the lowest bulk density among the fillers used, both at the macro and micro scale, while ES particles possessed the highest (Table 5.2). In general,
macro sized particles had a higher bulk density than the micro sized material. Carbon black’s bulk density was significantly different from the bulk density of all other fillers, except the micro sized GB. Filler loading in the composites was measured based on weight of the materials, therefore, substantially larger volumes of material were needed for the preparation of the composites with lower bulk density for similar weight loadings.

Table 5.2: Filler bulk densities.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Size</th>
<th>Density (g/cm$^3$)</th>
<th>Means comparison*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black</td>
<td></td>
<td>0.42 ± 0.01</td>
<td>E</td>
</tr>
<tr>
<td>CFA</td>
<td>macro</td>
<td>0.74 ± 0.02</td>
<td>B</td>
</tr>
<tr>
<td>CFA</td>
<td>micro</td>
<td>0.57 ± 0.01</td>
<td>D</td>
</tr>
<tr>
<td>GB</td>
<td>macro</td>
<td>0.53 ± 0.02</td>
<td>D</td>
</tr>
<tr>
<td>GB</td>
<td>micro</td>
<td>0.36 ± 0.07</td>
<td>E</td>
</tr>
<tr>
<td>ES</td>
<td>macro</td>
<td>1.32 ± 0.02</td>
<td>A</td>
</tr>
<tr>
<td>ES</td>
<td>micro</td>
<td>0.79 ± 0.05</td>
<td>B</td>
</tr>
<tr>
<td>TP</td>
<td>macro</td>
<td>0.69 ± 0.02</td>
<td>BC</td>
</tr>
<tr>
<td>TP</td>
<td>micro</td>
<td>0.60 ± 0.02</td>
<td>CD</td>
</tr>
</tbody>
</table>

* Multiple means comparison Tukey-Kramer test, at a significance level $\alpha$ of 0.05.

Samples that do not share a common letter are significantly different.

Variations in particle size distributions also were observed among the different materials (Fig. 5.1). The largest mean particle size and broadest distribution was in the GB fillers for both size ranges. CFA had the smallest mean particle size for both macro and micro size ranges. These discrepancies have important implications in the final characteristics of the composites. Particles in the size range of 38 µm or smaller were present in the
macro sized particle distributions and were considered in the interpretations of the results. However, these small portions of material did not seem to drastically affect the overall composite properties.

Fig. 5. 1: Macro —— and micro —— sized fillers’ particle size distribution. a) Carbon fly ash; macro (median: 76.20 µm, mean: 89.32 µm, SD: 61.94 µm), micro (median: 11.25 µm, mean: 12.12 µm, SD: 4.93 µm), b) eggshells; macro (median: 230.33 µm, mean: 241.46 µm, SD: 111.01µm), micro (median: 16.07 µm, mean: 23.19 µm, SD: 20.79 µm), c) guayule bagasse; macro (median: 243.10 µm, mean: 279.33 µm, SD: 188.56 µm), micro (median: 49.09 µm, mean: 54.75 µm, SD: 30.63 µm), d) tomato peels; macro (median: 170.70 µm, mean: 179.02 µm, SD: 154.91 µm), micro (median: 23.08 µm, mean: 26.95 µm, SD: 17.00 µm).
A variety of particle shapes and complex structures were identified among the fillers. TP presented different particle structure at the macro and micro size scale. At a micro scale, TP particles (Fig. 5.2a) were agglomerates of small granules similar to the carbon black structure (Fig. 5.2b). In contrast, macro sized TP had a laminar shape (Fig. 5.2c). CFA and ES (Figs. 5.2d, 5.2e) both were block like particles with irregular contours; however, CFA particles had a more porous structure than the ES particles. The GB filler particles had the elongated, cylindrical shape characteristic of cellulosic fibers (Fig. 5.2f).
Fig. 5.2: SEM micrographs of filler particles. (a) Micro sized processing tomato peels; (b) carbon black; (c) macro sized processing tomato peels, (d) micro sized carbon fly ash; (e) micro sized eggshells; (f) micro sized guayule bagasse.
5.3.2. Mechanical properties of composites

Filler loading, filler type and particle size, had significant effects on all the measured mechanical properties of GNR composites. Superior or comparable mechanical properties to those of carbon black filled composites were achieved by partial replacement of carbon black with low loadings (5 and 10 phr) of all waste-derived fillers (Fig. 5.3). Remarkably, the micro sized ES particles, in combination with carbon black, showed reinforcement beyond carbon black alone. The addition of micro sized ES up to 20 phr (57% replacement of carbon black in the composite), improved tensile strength and elongation while maintaining similar values of 300% modulus and hardness to those achieved by carbon black alone. In addition, 5 phr of micro sized TP and CFA and 5 phr of macro sized GB had tensile strength of 25.79 ± 0.08 MPa, 24.05 ± 0.26 MPa and 26.28 ± 0.41 MPa respectively, significantly higher than composites manufactured with carbon black alone (21.3 ± 0.75 MPa).
Fig. 5. 3: Mechanical properties of guayule rubber composites manufactured using micro and macro sized particles obtained from different waste-derived materials. Total amount of filler (carbon black plus waste-derived filler), in all samples was 35 phr. As the waste filler loading increases the carbon black filler decreases by the same weight amount as represented by the double X axis.

Composites containing 5 phr of macro sized CFA, TP and GB, 10 phr of macro sized GB and TP, or 5 phr of micro sized CFA, had significantly higher 300% modulus than composites with carbon black alone. Nearly 94% of composites containing 5 and 10
phr of macro and micro sized waste-derived fillers had significantly higher hardness numbers that the carbon black composites.

In general, as the amount of waste-derived filler in the composite increased above 5 phr and the amount of carbon black in the composites decreased below 30 phr, tensile strength, 300% modulus and hardness decreased while elongation at break increased (Fig. 5.3). However, the mechanical properties of unfilled vulcanized GNR were considerably improved with the incorporation of the different waste-derived fillers alone (Fig. 5.4). All the composites made with 35 phr of waste-derived fillers (no carbon black), except those made with 35 phr of macro sized TP and GB, had significantly higher tensile strength than unfilled vulcanized rubber (7.07±0.41 MPa). Furthermore, composites manufactured with 35 phr of micro sized GB and ES presented significantly higher values of 300% modulus, while significantly higher values of hardness were obtained for composites containing 35 phr of micro sized GB.
Composites made only with waste-derived fillers had significant lower 300% modulus, tensile strength and hardness than carbon black filled composites (Fig 5.4). Nonetheless, composites containing 35 phr of micro sized TP had the highest tensile strength (18.7MPa) among the 35 phr waste-derived composites, only 12% lower than carbon black composites. In addition, elongation at break of 35 phr micro sized TP was
0.6 times higher than elongation of carbon black composites and very close values of hardness.

5.3.3. Composite Morphology

The SEM’s of composite morphology (Fig. 5.5) indicate that, upon fracture, particles remained embedded in the rubber, especially in ES and TP composites (Fig. 5.5b and 5.5d). Polymer strings connecting the filler to the rubber matrix, uneven polymer surfaces around the filler and roughness of the particles suggest relatively good interfacial adhesion between some of the fillers and GNR. Furthermore, uniform dispersion of the fillers within the composites, without agglomeration, was attained at all loadings including 35 phr (Fig. 5.5) (SEM’s for lower loadings are not shown).
5.3.4. Swelling behavior

All the composites had a rapid weight gain during the first 3 h in toluene, but then the sorption rate decreased reaching a plateau (Fig. 5.6) (swelling curves of composites containing 10 and 20 phr of waste-derived fillers are not shown). Variations of swelling ratio at equilibrium and crosslink density were observed among the different guayule rubber compounds (Table 5.3). Composites containing 5 phr of waste-derived fillers had very similar swelling behavior to composites containing only carbon black.
Fig. 5.6: Guayule rubber composites swelling behavior. Unfilled –○–, carbon black –●–, carbon fly ash 5phr –▲–, carbon fly ash 35phr –△–, eggshells 5phr –□–, eggshells 35phr –▲–, guayule bagasse 5phr –●–, guayule bagasse 35phr –○–, processing tomato peels 5phr –■–, processing tomato peels 35phr –□–. (a) Composites containing micro particles and (b) composites containing macro particles.
Table 5.3: Swelling ratio at equilibrium and crosslink density ($v_e$) of guayule rubber composites.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Swelling ratio at equilibrium (%)</th>
<th>$v_e$ ($10^{-3}$ mol/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unfilled compound (no filler)</td>
<td>337.71</td>
<td>0.395</td>
</tr>
<tr>
<td>35 phr carbon black</td>
<td>199.69</td>
<td>1.151</td>
</tr>
<tr>
<td>35 phr tomato peel micro</td>
<td>269.98</td>
<td>0.622</td>
</tr>
<tr>
<td>20 phr tomato peel micro</td>
<td>262.95</td>
<td>0.656</td>
</tr>
<tr>
<td>10 phr tomato peel micro</td>
<td>244.98</td>
<td>0.758</td>
</tr>
<tr>
<td>5 phr tomato peel micro</td>
<td>243.02</td>
<td>0.770</td>
</tr>
<tr>
<td>35 phr tomato peel macro</td>
<td>257.00</td>
<td>0.687</td>
</tr>
<tr>
<td>20 phr tomato peel macro</td>
<td>238.05</td>
<td>0.803</td>
</tr>
<tr>
<td>10 phr tomato peel macro</td>
<td>216.80</td>
<td>0.973</td>
</tr>
<tr>
<td>5 phr tomato peel macro</td>
<td>208.53</td>
<td>1.053</td>
</tr>
<tr>
<td>35 phr carbon fly ash micro</td>
<td>348.30</td>
<td>0.371</td>
</tr>
<tr>
<td>20 phr carbon fly ash micro</td>
<td>233.76</td>
<td>0.834</td>
</tr>
<tr>
<td>10 phr carbon fly ash micro</td>
<td>211.60</td>
<td>1.022</td>
</tr>
<tr>
<td>5 phr carbon fly ash micro</td>
<td>197.62</td>
<td>1.175</td>
</tr>
<tr>
<td>35 phr carbon fly ash macro</td>
<td>329.58</td>
<td>0.415</td>
</tr>
<tr>
<td>20 phr carbon fly ash macro</td>
<td>236.22</td>
<td>0.816</td>
</tr>
<tr>
<td>10 phr carbon fly ash macro</td>
<td>200.05</td>
<td>1.146</td>
</tr>
<tr>
<td>5 phr carbon fly ash macro</td>
<td>184.08</td>
<td>1.359</td>
</tr>
<tr>
<td>35 phr guayule bagasse micro</td>
<td>320.20</td>
<td>0.440</td>
</tr>
<tr>
<td>20 phr guayule bagasse micro</td>
<td>320.03</td>
<td>0.440</td>
</tr>
<tr>
<td>10 phr guayule bagasse micro</td>
<td>244.22</td>
<td>0.763</td>
</tr>
<tr>
<td>5 phr guayule bagasse micro</td>
<td>236.82</td>
<td>0.812</td>
</tr>
<tr>
<td>35 phr guayule bagasse macro</td>
<td>411.41</td>
<td>0.266</td>
</tr>
<tr>
<td>20 phr guayule bagasse macro</td>
<td>265.39</td>
<td>0.644</td>
</tr>
<tr>
<td>10 phr guayule bagasse macro</td>
<td>217.60</td>
<td>0.965</td>
</tr>
<tr>
<td>5 phr guayule bagasse macro</td>
<td>200.25</td>
<td>1.144</td>
</tr>
<tr>
<td>35 phr eggshell micro</td>
<td>275.62</td>
<td>0.596</td>
</tr>
<tr>
<td>20 phr eggshell micro</td>
<td>235.78</td>
<td>0.819</td>
</tr>
<tr>
<td>10 phr eggshell micro</td>
<td>193.35</td>
<td>1.229</td>
</tr>
<tr>
<td>5 phr eggshell micro</td>
<td>223.77</td>
<td>0.912</td>
</tr>
<tr>
<td>35 phr eggshell macro</td>
<td>270.79</td>
<td>0.618</td>
</tr>
<tr>
<td>20 phr eggshell macro</td>
<td>221.43</td>
<td>0.931</td>
</tr>
<tr>
<td>10 phr eggshell macro</td>
<td>199.51</td>
<td>1.153</td>
</tr>
<tr>
<td>5 phr eggshell macro</td>
<td>197.81</td>
<td>1.173</td>
</tr>
</tbody>
</table>

*Total amount of filler (carbon black plus waste-derived filler), in all samples was 35 phr.
Replacement of carbon black with waste-derived filler in the composites led to an increase in swelling ratio and a decrease in crosslink density. The largest swelling ratios were achieved by unfilled guayule compound and composites containing 35 phr of waste-derived filler as full replacement of carbon black. Nevertheless, the addition of macro and micro sized TP and ES up to 35 phr (no carbon black) significantly reduced the swelling of the guayule rubber compounds (Table 5.3). Most of the composites containing micro sized filler had higher swelling ratio than macro sized composites at the same loading with the same filler.

5.3.5. Cluster analysis

Analysis of overall properties led to the classification of the composites into six groups with different characteristics (Fig. 5.7). Composites made with 35 phr of waste-derived fillers, and the unfilled vulcanized rubber sample, were grouped within clusters 1 and 2. Each property cluster was then plotted as a radar plot (Fig. 5.8). Composites in cluster 1 (Fig. 5.8 first row, left) included composites with relatively low values of 300% modulus (less than 1.7 MPa), low hardness (hardness number less than 40), medium values of elongation at break (1550% - 1820%), and the lowest tensile strength among the composites. Composites grouped in cluster 2 (Fig. 5.8 first row, right) possessed the lowest values of 300% modulus, the lowest hardness, the highest elongation at break, and low tensile strength (less than 13 MPa). Based on the mechanical properties, these clusters are more similar to each other than to any of the other clusters (Fig. 5.7), and these composites achieved the lowest performance properties of any of the composite groupings.
Fig. 5. 7: Dendrogram obtained from hierarchical cluster analysis of 34 formulations. Composite labels represent the amount of waste-derived filler in the sample, filler type and particle size. Total amount of filler (carbon black plus waste-derived filler), in all samples was 35 phr. Filler type: carbon fly ash (CFA), guayule bagasse (GB), eggshells (ES), processing tomato peels (TP).
Fig. 5. 8: Radar chart representing mechanical properties of composites in each of the cluster obtained from hierarchical cluster analysis of 34 formulations. Composite labels represent the amount of waste-derived filler in the sample, filler type and particle size. Total amount of filler (carbon black plus waste-derived filler), in all samples was 35 phr. Filler type: carbon fly ash (CFA), guayule bagasse (GB), eggshells (ES), processing tomato peels (TP).
Cluster 3 (Fig. 5.8 second row, left) is the largest group of samples with similar performance properties and contains mostly composites manufactured with 5 phr waste derived fillers. Composites in this group had the highest 300% modulus, the greatest hardness, the lowest elongation at break, and high tensile strength (more than 21 MPa). Overall properties of composites in this cluster are different from all the other clusters, and were distinct from carbon black, which fell in cluster 6. However, mechanical properties of the composites in cluster 3 are more similar to composites in clusters 4, 5 or 6 than to clusters 1 or 2 (Fig. 5.7). Cluster 4 (Fig. 5.8 second row, right) contains composites manufactured by partially replacing carbon black with 5, 10 and 20 phr of micro sized ES. This group of composites possesses relatively high 300% modulus (greater than 2.3 MPa), medium hardness (hardness number 40 - 45), high elongation at break (greater than 1820%), combined with the highest tensile strength of all the clusters. Composites gathered in cluster 5 (Fig. 5.8 third row, left) present a balance of all properties, with medium values of 300% modulus (1.7 - 2.3 MPa), medium hardness, medium elongation at break, and medium tensile strength (13 - 21 MPa). This cluster groups six of the composites made with 20 phr of waste derived fillers. Finally, cluster 6 (Fig. 5.8 third row, right) groups the carbon black reference composite and most of the composites manufactured with 10 phr of waste derived fillers. This group of composites had high 300% modulus, high hardness (hardness number greater than 45), low elongation at break (less than 1550%), and medium tensile strength. Based on the mechanical properties, cluster 6 is more similar to cluster 5 than to cluster 4 or 3 (Fig. 5.7).
5.4. Discussion

Waste-derived fillers, ES, TP, CFA and GB effectively reinforced GNR (Figs. 5.4 and 5.8), due to good polymer-filler interfacial adhesion, as reflected in the composite morphology (Fig. 5.5). However, this hypothesis is based on SEM evaluation of composites, and requires deeper analysis. Filler dispersion within the polymer also contributed to the good performance properties. Uniform dispersion of the particles and relative good interfacial interaction between the particles and the polymer allows efficient stress transfer, leading to improved tensile strength and resistance to deformation compared to unfilled vulcanized GNR. Composites made with micro waste-derived fillers, without carbon black, performed better than those made with macro sized particles (Fig. 5.4). This is unsurprising, because bigger particles have less surface area per unit weight than smaller particles, and so have less interaction with the polymer, and also can generate flaws within the composite material. Micro sized particles had a lower bulk density than macro sized particles. This is probably due to the broader particle size distribution of the macro sized particles, which allowed better packaging by fitting the smallest particles in between the spaces of the bigger particles.

Composites made with 5 phr of waste-derived particles as co-fillers with 30 phr carbon black, showed higher tensile strength and elongation to break compared to composites manufactured solely with carbon black. Interaction between these waste-derived filler particles, as well as interactions between the particles and the rubber, may be the cause of such reinforcement. The waste-derived fillers studied are more polar than carbon black but less polar than silica or commercial calcium carbonate due to their
complex compositions. Therefore, hydrophobic components of the waste-derived fillers allow affinity to the rubber.

Filler-filler interactions existing between particles with polar surfaces, are mainly due to hydrogen bonding (Byers, 2001; Kato et al., 2014). This type of interaction is stronger than those of non-polar fillers, such as carbon black, in which filler-filler interactions are due to van der Waals forces (Fröhlich et al., 2005). When filler volume reaches the percolation threshold, this strong filler-filler interaction promotes the formation of a percolation network that contributes to the overall reinforcement of the material by restricting chain mobility. The linear chain structure of GNR allows it to flow more easily into the filler network than HNR, which has a branched structure (Rensch et al., 1986). Thus, when stress is applied to the materials, entanglement of polymer chains in this filler network allows better load transfer between the filler and the polymer than in HNR (Barrera and Cornish, 2015).

The percolation threshold is dependent on the aspect ratio (length to diameter ratio) of the filler and the degree of dispersion (Bandyopadhyay-Ghosh et al., 2015; Peddini et al., 2014), and varies among the different fillers used. Rod shaped particles, such as GB (Fig. 5.2f), have a higher aspect ratio than the other fillers (Fig. 5.2). Uniformly dispersed fillers with high aspect ratio require lower volumes of material to form the percolation network (Angellier et al., 2005b; Bandyopadhyay-Ghosh et al., 2015). GB also had the lowest bulk density among the waste derived fillers (Table 5.2), and so had larger volumes of particles in composites with similar weight loadings. As the volume of filler increases beyond the percolation threshold, interfacial interaction
between filler particles are favored over polymer-filler interactions. Filler-filler interactions are less effective than polymer-filler interactions at supporting stress transfer through the material and hence a lower tensile strength was achieved at high loadings of GB compared to the other waste-derived fillers (Fig. 5.4).

Hybrid carbon black/waste-derived filler/GNR composites made with 10 phr of waste-derived particles had similar properties to those of composites manufactured solely with carbon black. At low loadings of waste-derived fillers (5 phr), carbon black predominates the reinforcement of the material, and the waste-derived fillers further enhanced the reinforcement. Carbon black not only has a good interfacial interaction with the polymer, but also the smallest particle size (108 nm). Small particle size together with high loading (30 phr of carbon black and only 5 phr of waste-derived filler in the composites), generate a larger interfacial contact area for polymer-filler interaction and good reinforcement. However, as the amount of carbon black decreased below 30 phr the overall reinforcement was also decreased.

Composites made with high loading (20 and 35 phr) of most of the waste-derived fillers, had lower values of tensile strength and 300% modulus than carbon black composites (Fig. 5.3), reflecting a lower reinforcing effect of the non-carbon black fillers. Despite the relative good polymer-filler interaction observed between GNR and the waste-derived fillers (Fig. 5), and the contribution of the filler network to the reinforcement of the materials, these interactions are not as strong as the interaction of the polymer with carbon black. By increasing the waste-derived filler and reducing the carbon black fraction, the interfacial interaction between the matrix and non-carbon black
filler may fail, creating voids in the composite. These voids concentrate the stress and result in composite fracture.

Strong interfacial interaction between GNR and carbon black was also reflected by the swelling of the composites. Composites containing low loadings (5 phr) of waste-derived filler and those containing only carbon black had the lowest swelling and the highest crosslink density (Table 5.3). Rubber-filler interaction is dependent on the surface activity of the filler. Carbon black possesses a relative non-polar surface (Byers, 2001), which is more compatible with natural rubber than more polar fillers. The strong carbon black-rubber interaction is mainly physical in nature (van der Waals forces) (Fröhlich et al., 2005). These weak interfacial forces allow carbon black to behave as an additional crosslinker in the NR network (Chenal et al., 2007b) by restricting chain mobility and generating stronger and harder materials.

Composites made solely with TP and ES had higher crosslink density than composites made with GB or CFA (Table 5.3) and unfilled compound. Solvent absorption measurements yield an apparent crosslink density that can be explained by sum of both chemical crosslinks and physical crosslink, such as entanglement of polymer chain within the filler network (Lee et al., 1994). Higher crosslink density leads to the better mechanical properties, particularly modulus and tensile strength, attained by TP and ES /GNR composites.

Particle structure played an important role in the performance of the different composites. The micro sized TP structure (Fig. 5.2a) is similar to carbon black (Fig. 5.2b). This complex aggregate structure, along with the small particle size, allows the
material to provide better reinforcement due to high degree of irregularity of the filler that limits the mobility of polymer chain under strain (Fröhlich et al., 2005), leading to increased stress at equivalent strain. This behavior is not observed in macro sized TP particles because, at this larger scale, the material has a laminar shape (Fig. 5.2c) and less surface area.

Although distinctly different from carbon black and micro sized TP, the ES and CFA particle structures provide high surface area due to roughness and porosity of the materials (Fig. 5.2d and 5.2e). ES porosity is the consequence of naturally occurring gas exchange pores (Intharapat et al., 2013) in eggshells which allow oxygen to pass from the atmosphere to the developing chick embryo. High surface area allows large contact interface between the polymer and the filler creating good interfacial adhesion.

Despite similarity in particle morphology, better performance properties were achieved by ES composites compared to CFA composites probably due to differences in their chemical composition. CFA is mainly composed of alumino-silicate (>50%) (Kutchko and Kim, 2006). Silanol groups can react with rubber compounding ingredients, and can lead to slower curing (Byers, 2001). ES on the other hand, is over 95% calcium carbonate (Intharapat et al., 2013), which can contribute to faster curing rates than silicate fillers due to alkalinity of the material (Byers, 2001). Given that processing conditions for all the composites were the same, slower curing rate may lead to lower crosslink density (Table 5.3), which translates into lower performance properties.
Increase in 300% modulus and/or tensile strength often leads to a decrease in elongation at break (Angellier et al., 2005b; Gerspacher and Wampler, 2001); however, this was not the case for the waste-derived fillers (Fig. 5.4). This confirms that the interfacial interaction is not the result of chemical bonding such as those achieved by coupling agents. Under strain, the adhesion forces can break and relocate allowing the polymer chains to rearrange while effectively transferring stress. This characteristic generated materials which maintained flexibility while also exhibiting resistance to deformation.

The reinforcement of GNR with waste-derived fillers as co-fillers with carbon black, offer the potential to engineer materials with a varied combination of properties (Fig. 5.8). These combinations result from the modification of waste-derived filler/carbon black ratio in the composite, as well as the type of waste-derived filler and its particle size. Consequently, these fillers can be added not only to reduce cost, but to target specific performance requirements for elastomeric products. Potential applications for composites in cluster 1 and 2 include rubber bands, insulating rubber tapes and any other rubber products that require really flexible materials with medium to low values of tensile strength, hardness and 300% modulus. Composites in these two clusters surpass requirements for tensile strength and elongation at break specified in ASTM D4388 (ASTM International, 2013c) for insulating rubber tapes. Flexible composites made with lightweight materials such as GB, can also be good candidates for sponges and expanded rubber products.
Composites in cluster 3 possess high tensile strength, 300% modulus and hardness, making these composites good candidates for more demanding applications such as tire components. Potential uses for composites in cluster 4 include rubber surgical drainage tubes, due to the combination of high elongation, high modulus and tensile strength exhibited by these composites. These composites exceed requirements for tensile strength and elongation at break specified in ASTM D3579 (ASTM International, 2010b) for rubber surgical drainage tube, penrose type. Insulating materials, namely insulating line hose, blankets, sleeves and gloves are some of the potential usage of composites grouped in Cluster 5. Composites in cluster 6 exceed tensile strength, elongation at break and hardness requirements for elastomeric seals for joining concrete structures as specified in ASTM C1619 (ASTM International, 2011).

Partial replacement of carbon black with waste-derived fillers in GNR composites enhanced overall reinforcement, leading to stronger composites than those made solely with carbon black. This outstanding reinforcement was not attained for HNR composites made with the same waste-derived fillers in a previous study (Barrera and Cornish, 2015), due to differences in rubber structure and composition (non-rubber components). The macromolecular structure of HNR is branched (Tanaka, 2001), making it bulkier than the linear GNR, and this may impede the polymer filler network which can be established especially with the porous fillers. Non-rubber components, such as proteins and phospholipids are involved in the branched structure of HNR, by serving as reactive groups for the formation of branch-points (Sakdapipanich et al., 1999). The marked differences between the interactions of the two NRs with the fillers is most evident for
the TP-derived fillers: GNR composites containing 35 phr of micro sized TP had the highest tensile strength (18.7± 0.47 MPa) among the 35 phr waste-derived composites. Moreover, tensile strength of GNR composites made with 20 phr of micro sized TP and 15 phr of carbon black, was not significantly different from the tensile strength of composites containing carbon black alone. However, in HNR, 35 phr and 20 phr of micro-sized TP could not even be mixed in to generate a cohesive composite (Barrera and Cornish, 2015).

Waste-derived materials have a lower carbon footprint than petroleum-derived materials such as carbon black. Additionally, reductions in carbon black production capacity in North America are expected by 2020 (Rubber and Plastic News, 2014) due to increasing regulation by the U.S. Environmental Protection Agency (EPA) because of different pollutants, namely sulfur dioxide, nitrogen oxide and particulate matter, generated during its manufacture. Reinforcement of GNR by partially or completely replacing carbon black with these micro sized fillers, can improve the sustainability of rubber industry and mitigate potential carbon black shortfalls in the future. Solid wastes such as ES and TP are continuously generated in large volumes. In 2012, 12 million tons of processing tomatoes were harvested in the United States (Thornsbury et al., 2013) generating a processing waste of 437,574 metric tons of skins, while 95.176 billion eggs were produced in the United States 2013 (United States Department of Agriculture, 2014) generating 596,754 metrics tons of shells. Economics of GNR production and other industries also could be improved by the use of these waste-derived fillers, which not
only can be cheaply made but also entail significant savings for cost associated to disposal of these residues.

It is particularly interesting that low loadings of micro sized waste-derived fillers, especially ES as co-filler with nano-carbon black, performed as well as the nano-carbon black alone. The use of nano sized waste-derived fillers could potentially result in better properties than those achieved with micro sized filler. However, nano fillers are much more difficult and expensive to manufacture at large scale than micro-fillers. Unique properties of GNR, such as malleability at extreme cold temperatures (Cornish and Wood, 2002), along with the high performance achieved by the addition of waste-derived fillers, offer the possibility to use this rubber for value-added products and markets that are not possible even for HNR.

5.5. Conclusion

Waste-derived fillers can improve guayule rubber performance while reducing the amount of petroleum-derived carbon black in the final product. Flexible materials with comparable tensile strength to 100% carbon black composites were achieved by low loading of micro sized waste-derived fillers, particularly those made from eggshells and tomato peels as co-filler with carbon black. This is important considering the renewable character of these materials, and possible applications for these composites in which these new combination of mechanical properties can be exploited. Moreover, remarkable improvement of tensile strength and elongation at break beyond those achieved by carbon black alone was achieved by micro sized eggshell composites up to 20 phr of eggshell and only 15 phr of carbon black. Thus, eggshells are a promising reinforcing filler for the
manufacturing of high performance rubber products. The superior reinforcement obtained may reflect a synergistic reinforcing effect of carbon black particles with the formation of a unique network between the guayule rubber and the waste-derived materials, not attainable with *Hevea brasiliensis* natural rubber. Moreover, hybrid carbon black/waste-derived filler/guayule composites presented crosslink densities similar to that of carbon black. This is consistent with crosslink density being an extremely important factor controlling the physical properties of vulcanized rubber. Partial replacement of carbon black with these cheaply made particles could alleviate future carbon black shortages.
Chapter 6: Prediction of Mechanical Properties of Natural Rubber Composites

Using Statistical Models

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Abstract

Practical statistical models were developed to quantify individual contributions from characteristics of conventional and non-conventional fillers and predict resulting mechanical properties of rubber composites. Filler characteristics were used as explanatory variables in multiple linear regression analyses. Principal component analysis was used to evaluate correlations among explanatory variables and to transform them into a new set of independent variables, which were then used to generate reliable regression
models. Surface area, dispersive component of surface energy, carbon black and waste-derived filler loading were found to have almost equal importance in the prediction of composite properties. However, models developed for ultimate elongation poorly explained variability, indicating the dependence of this property on other variables. Agro-industrial residues could potentially serve as more sustainable fillers for polymer composites than conventional fillers. This new modeling approach for polymer composites allows the performance of a wide range of different waste-derived fillers to be predicted with minimum laboratory work facilitating the optimization of compound recipes to address specific product requirements.

**Key words**: Natural rubber, Composite properties, Statistical modelling, Fillers characteristics.

### 5.1. Introduction

Over 50,000 different products used on a daily basis worldwide are made with natural rubber (Priyadarshan, 2011), most of them containing fillers. Fillers are commonly used in the rubber industry either as diluents, or for the improvement of processing parameters and enhancement of properties such as modulus, tear strength, abrasion resistance, tensile and compressive strength (Donnet and Custodero, 2013; Fröhlich et al., 2005; Samsuri, 2013). The reinforcement of rubber by fillers has been extensively studied for decades (Bradley, 1956; Payne, 1962; Samsuri, 2013; Watson, 1956). However, most of the research has focused on carbon black and silica fillers.

Different theories have been formulated to explain the mechanisms of reinforcement of natural rubber by fillers (Samsuri, 2013), most of them based on the
evaluation of performance properties affected by modifying a single filler characteristic, particularly surface area, thought to be the most important morphological characteristic affecting filler reinforcing potential (Donnet and Custodero, 2013; Khan and Bhat, 2014; Leblanc, 2002). Surface area and filler loading (amount of filler in the composites) determine the available interfacial area between the filler and the polymer (Fröhlich et al., 2005).

Filler structure also contributes to the reinforcing capability of the fillers by restricting polymer chain motion (Fröhlich et al., 2005; Kohls and Beaucage, 2002). Filler particles can aggregate into complex tri-dimensional objects due to bonding forces between the particles (Leblanc, 2002). Random spatial arrangement of the primary particles generates different degrees of irregularity that define the structure of the filler (Fröhlich et al., 2005). Complex filler structure also can result from naturally occurring pores and surface roughness. However, unlike surface area, this filler characteristic is difficult to measure quantitatively. Also, different structures may coexist in a sample of the same filler due to the random aggregation, filler type and production method (Donnet and Custodero, 2013).

In general, filler characteristics govern the final mechanical properties of composites by determining the interaction between polymer and filler, and the filler-filler interactions (Fröhlich et al., 2005; Kohls and Beaucage, 2002). Surface activity must also be an important filler characteristic influencing rubber reinforcement because surface activity determines the ability of the filler to interact with the polymer. Differences in surface activity have been related to chemical groups on the surface of the particles.
(Byers, 2001; Fröhlich et al., 2005), but may also result from structural heterogeneities (Leblanc, 2002). These differences result in variations of surface free energy, a parameter that describes the interaction potential of a given surface (Cordeiro et al., 2011a; Nardin et al., 1990). Wetting experiments such as contact angle have been used for the evaluation of surface free energy of solid particles. However, these methods have been designed for macroscopic flat surfaces, and the accuracy of the measurements is limited by the size of the particles, surface roughness, chemical heterogeneity (Hole et al., 2011; Riedl and Matuana, 2006). Inverse gas chromatography (IGC) has proven to be a useful technique to characterize surface of small particles (Cordeiro et al., 2011b; Mohammadi-Jam and Waters, 2014; Strzemiecka et al., 2014).

A complete understanding of the relationships between filler characteristics and macroscale mechanical properties of polymer composites has not been achieved. Furthermore, only limited attempts have been made to quantitatively estimate the contribution of each individual filler characteristic on the final composites properties and generate practical models to predict mechanical properties of rubber composites from filler characteristics. Generally determining the extent to which different fillers reinforce a specific type of rubber requires extensive lab work. Molecular-level simulations require detailed information about the forces acting between the atomic centers, which is often not available. Furthermore, simulations performed at the atomic level are usually confined to relatively short oligomers (Allegra et al., 2008) and cannot be applied effectively to rubber composites.
A statistical modelling approach is proposed to quantify the contribution of filler characteristics on mechanical properties of rubber composites, and to establish functional relationships between these variables. We have developed data-driven models that best represent the relationship between the characteristics of different low cost, waste-derived, alternative fillers and mechanical properties of natural rubber composites.

5.2. Experimental

5.2.1. Materials

Four waste-derived materials namely, eggshells (ES), carbon fly ash (CFA), processing tomato peels (TP), and guayule bagasse (GB) were used. These materials were generously donated as follows: ES by Michael Foods (Gaylord, MN) and Troyer’s Home Pantry (Apple Creek, OH); CFA by Cargill Salt (Akron, OH); TP by Hirzel Canning Co & Farms (Toledo, OH). GB was generated as a co-product of latex extraction at our facility from guayule shrubs donated by PanAridus (Casa Grande, AZ). Waste-derived materials were separately ground and sieved as described (Barrera and Cornish, 2015) to obtain macro (diameter (d) of 300 μm-38 μm) and micro (d of 38 μm-100 nm) sized particles. Carbon black N330 (mean particle size: 108 nm, SD: 31.42 nm), was purchased from HB Chemicals (Twinsburg, OH).

Probes used for particles’ surface characterization, included non-polar n-alkanes of different carbon chain length (C₅-C₉), and the polar probes, ethyl acetate and dichloromethane. All probes were chromatographic grade and were purchased from Sigma–Aldrich (St. Louis, MO). Physical constants of the probes were taken from the

100
literature (Table 6.1) (Strzemiecka et al., 2014). High purity methane purchased from Praxair Technology, Inc. (Akron, OH), was used as a non-interacting probe.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Cross-sectional area $(a) \times 10^{19}$ m$^2$</th>
<th>Surface tension $(\gamma_l^D)$ J/m$^2$</th>
<th>Electron acceptor parameter $(\gamma_i^+)$ J/m$^2$</th>
<th>Electron donor parameter $(\gamma_i^-)$ J/m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>4.92</td>
<td>0.0155</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Hexane</td>
<td>5.15</td>
<td>0.0179</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Heptane</td>
<td>5.73</td>
<td>0.0203</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Octane</td>
<td>6.30</td>
<td>0.0213</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Nonane</td>
<td>6.90</td>
<td>0.0227</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>2.45</td>
<td>0.0245</td>
<td>0.0052</td>
<td>0</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>3.30</td>
<td>0.0196</td>
<td>0</td>
<td>0.0192</td>
</tr>
</tbody>
</table>

5.2.2. Filler characterization

5.2.2.1. Inverse gas chromatography (IGC)

The fillers’ surface energies were characterized by IGC, using a packed column gas chromatograph GC-2014 equipped with flame-ionization detector (FID), Shimadzu Scientific Instruments (Columbia, MD). Approximately 0.5–1.5 g of each filler were packed by mechanical vibration into stainless steel columns (50 cm long with inside diameter of 2.1 mm), and the two ends were plugged with silane-treated glass wool. The columns were shaped in a smooth “U” to fit the detector/injector geometry of the
instrument. To minimize pressure drop across the GC column only macro sized particles were used for the waste-derived materials. Carbon black was used as received.

The packed columns were preconditioned at 105°C with 10 ml/min helium sweep for 12 h. After conditioning the columns, pulse injections were done with 0.04 µl for each of probes. Retention times were determined at 50 and 100 °C, with the injector and detector kept at 180°C and 200°C, respectively. Helium was used as carrier gas. The flow rate was 20 ml/min for ES, TP and GB, 40 ml/min for CB and 60 ml/min for CFA. The retention times were determined from the median values of the elution peaks. Three columns were prepared for each material.

5.2.2.2. IGC Theoretical background and calculations

The ability of a surface to interact with another surface depends on their individual surface energies. Surface free energy ($\gamma_S$) is the result of dispersive, $\gamma_S^{D}$, and specific components, $\gamma_S^{SP}$ (Voelkel et al., 2009):

$$\gamma_S = \gamma_S^{D} + \gamma_S^{SP}$$  \hspace{1cm} (1)

IGC uses the relationship between the retention volume of the probes in contact with the filler surface and the thermodynamic parameters to determine these surface properties. This relation is given by the Gibbs free energy change equation (Mohammadi-Jam and Waters, 2014):

$$\Delta G_{ad}^0 = \Delta G_{de}^0 = RT\ln V_N + C$$  \hspace{1cm} (2)

Where $\Delta G_{ad}^0$ and $\Delta G_{de}^0$ are the standard molar Gibbs free energy changes of adsorption and desorption, $R$ is the gas constant (8.314 J/K*mol), $T$ is absolute
temperature and C is the integration constant. $V_N$ is the net retention volume of the probe, and is calculated as:

$$V_N = J F_c (t_R - t_0)$$

Where $J$ is the James-Martin compressibility correction factor, $F_c$ is the temperature corrected flow rate of the carrier gas, $t_R$ is the retention time of the probe, and $t_0$ is the dead time determined from the retention time of a non-interacting probe (methane). $V_N$ can be divided by the mass and surface area of the particles to obtain a specific retention volume (Rückriem et al., 2010).

Non-polar probes such as n-alkanes only will interact through London dispersive forces (Belgacem et al., 1995), even when they come into contact with polar surfaces. This characteristic has been used to quantify the dispersive component of the surface of solids. The dispersive component can be calculated using the method proposed by Schultz and Lavielle (Mohammadi-Jam and Waters, 2014; Rückriem et al., 2010; Voelkel et al., 2009):

$$RT \ln V_N = 2Na \sqrt{\gamma_s^D \times \gamma_L^D} + C$$

Where $a$ is the cross-sectional area of the probe, $N$ is Avogadro’s number ($6.023 \times 10^{23}$/mol), and $\gamma_s^D$ and $\gamma_L^D$ are the dispersive components of surface free energy of the solid and the probe, respectively. For a series of n-alkanes, $\gamma_s^D$ is calculated from the slope of $RT \ln V_N$ Vs $a \sqrt{\gamma_L^D}$.

Unlike non-polar probes, which only interact with the solid surface through dispersive forces, polar probes can interact with a solid surface through both dispersive
and specific interactions. Therefore, the standard molar Gibbs free energy changes of adsorption for the interaction of the polar probe and the surface under investigation (Das et al., 2011; Mohammadi-Jam and Waters, 2014) is:

$$
\Delta G^0_{ad} = \Delta G^D_{ad} + \Delta G^{SP}_{ad}
$$

(5)

Where $\Delta G^D_{ad}$ and $\Delta G^{SP}_{ad}$ are the dispersive and specific free energies of adsorption. $\Delta G^{SP}_{ad}$ has been described in terms the tendency of a surface to behave as either an electron acceptor or an electron donor. These surface characteristics can be calculated using the Good-van Oss equation (Das et al., 2011):

$$
\Delta G^{SP} = 2Na\left(\sqrt{\gamma^+_I \times \gamma^-_S} + \sqrt{\gamma^-_I \times \gamma^+_S}\right)
$$

(6)

Where $\gamma^+_S$ and $\gamma^-_S$ are the electron acceptor and electron donor parameters of the solid surface, and $\gamma^+_I$ and $\gamma^-_I$ are the electron acceptor and electron donor parameters of the probe. Monopolar acidic and basic probes such as dichloromethane and ethyl acetate are used to measure $\gamma^+_S$ and $\gamma^-_S$, which allows the calculation of the specific component of the surface of solid ($\gamma^{SP}_S$) (Das et al., 2011; Strzemiecka et al., 2014):

$$
\gamma^{SP}_S = 2\sqrt{\gamma^+_S \times \gamma^-_S}
$$

(7)

Evaluation of surface energy through IGC is based on the assumption that adsorption and desorption equilibrium conditions between adsorbent and adsorbate are achieved. This condition is satisfied by injecting very low concentrations of probes, which result in linear adsorption isotherms and symmetrical chromatographic peaks. This chromatographic condition is known as infinite dilution. Due to the limited amount of probe, interaction occurs only with the high-energy sites on the surface and no probe to
probe interactions are expected, enabling an accurate and reproducible calculation of the retention volume (Charmas and Leboda, 2000; Mohammadi-Jam and Waters, 2014; Thielmann, 2004).

5.2.2.3. *Surface area and pore size distribution*

Surface area and pore size distribution of the waste-derived fillers were determined from nitrogen adsorption-desorption isotherms at 77K. The samples were analyzed using a Tristar II 3020 analyzer, Micromeritics Instrument Corporation (Norcross, GA). The particles were degassed at room temperature for 12 h prior to analysis. Surface area was calculated using the Brunauer-Emmett-Teller (BET) method (Brunauer et al., 1938), while pore size distribution was calculated using Barrett-Joyner-Halenda (BJH) method (Barrett et al., 1951). Carbon black surface area was obtained from the specification provided by the supplier.

5.2.3. Statistical analysis

5.2.3.1. *Data*

Mechanical properties for the guayule and hevea rubber composites used in this study were determined in previous work (Barrera and Cornish, 2016, 2015). These data include mechanical properties of vulcanized composites manufactured by partially and fully replacing carbon black with different waste-derived fillers, composites made solely with carbon black, and unfilled rubber compounds.

Data normality and constant variance assumptions were tested using the Shapiro-Wilk normality test (Shapiro and Wilk, 1965), and visualized by histograms. The variables were categorized into response variables ($Y_i$) which represent the different
mechanical properties of the composites, and explanatory variables \( (X_i) \), which represent filler characteristics (Table 6.2). The data were standardized by subtracting the mean and dividing by the standard deviation before statistical analysis.

Table 6.2: Notation of different experimental data used for statistical analyses.

<table>
<thead>
<tr>
<th>Variable Notation</th>
<th>Experimental Data for Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Y_1 )</td>
<td>300% Modulus (MPa)</td>
</tr>
<tr>
<td>( Y_2 )</td>
<td>Ultimate Elongation (%)</td>
</tr>
<tr>
<td>( Y_3 )</td>
<td>Tensile Strength (MPa)</td>
</tr>
<tr>
<td>( X_1 )</td>
<td>Total filler surface area (m(^2))</td>
</tr>
<tr>
<td>( X_2 )</td>
<td>Dispersive component of filler surface free energy (mJ/m(^2))</td>
</tr>
<tr>
<td>( X_3 )</td>
<td>Specific component of filler surface free energy (mJ/m(^2))</td>
</tr>
<tr>
<td>( X_4 )</td>
<td>Carbon black loading (phr)</td>
</tr>
<tr>
<td>( X_5 )</td>
<td>Waste-derive filler loading (phr)</td>
</tr>
</tbody>
</table>

5.2.3.2. Principal component analysis (PCA)

Principal component analyses (PCA) were used to evaluate correlations among the variables based on their correlation matrices and to transform correlated explanatory variables. In order to produce reliable probabilistic models, all explanatory variables should be completely independent. However, this is rarely the case in biological and
engineering systems. PCA is used to transform all the correlated explanatory variables into uncorrelated sets of new variables that account for the majority of the original variance (principal component scores) (Abdul-Wahab et al., 2005; Çamdevýren et al., 2005; Jolliffe, 2002; Plappally et al., 2011). This is done by using a procedure that applies a matrix method as an essential mathematical tool. The new standardized uncorrelated explanatory variables are given by equation 8.

\[
[PC] = [X][T]
\]  

(8)

Where \([PC]\) corresponds to the value of the principal components, \([T]\) is the matrix of principal component loadings that multiplies the standardized original explanatory variables \([X]\) (Jolliffe, 2002; Soboyejo, 2011). PCA was performed using the Stats package implemented in R (R Core Team, 2014). Principal component (PC) scores were used as independent variables in multiple linear regression analysis to predict mechanical properties of the composites.

5.2.3.3. Multiple linear regression (MLR)

MLR analysis was used to develop models using JMP 11 Statistical Analysis Software (SAS Institute Inc., Cary, NC). Two different approaches were applied for model development. In the first approach, filler characteristics were used as explanatory variables (Table 6.2) to predict the composites’ mechanical properties, whereas in the second approach, PC scores obtained from PCA of filler characteristics, were used to predict tensile properties.

The standard format for the regression models is represented by Equation 9.
\[ Y = f(X_1, X_2 ... X_k) = a + \sum_{i=1}^{k} b_i X_i \] (9)

Where \( Y \) is the response variable, \( X_1, X_2, ..., X_k \) are the predictor variables, and \( a, b_i \) for \( i = 1, 2, ..., k \) are the model constants (Soboyejo, 2011). Non-significant terms were excluded from the models. Model adequacy was evaluated based on residuals analysis. Coefficient of determinations (\( R^2 \)) and adjusted \( R^2 \), were reported.

5.3. Results and Discussion

5.3.1. Filler Characterization

Carbon black had the highest specific surface area among all the fillers (Table 6.3). This is due to its small particle size (108 ± 31 nm). In general, specific surface area of all the waste-derived fillers increased with decreasing particle size, except in the case of GB. For this filler, the micro sized particles had a lower surface area than the macro, possibly due to a decrease in aspect ratio. Grinding of the GB not only reduced the diameter of the fiber but also the length. CFA had the largest specific surface area, both for macro and micro sized particles, due to its small particle size and high porosity. CFA had the smallest mean particle size for both the macro (89.32 ± 61.94 \( \mu m \)) and micro (12.12 ± 4.93 \( \mu m \)) (Barrera and Cornish, 2016), and the highest pore volume (Table 6.3).
Table 6. 3: Fillers’ surface area and pore volume.

<table>
<thead>
<tr>
<th>Filler</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore volume (mm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon black N330</td>
<td>80.2$^a$</td>
<td>--</td>
</tr>
<tr>
<td>Carbon fly ash micro</td>
<td>10.440</td>
<td>21.391</td>
</tr>
<tr>
<td>Carbon fly ash macro</td>
<td>4.241</td>
<td>5.961</td>
</tr>
<tr>
<td>Eggshells micro</td>
<td>1.075</td>
<td>5.368</td>
</tr>
<tr>
<td>Eggshells macro</td>
<td>0.224</td>
<td>0.676</td>
</tr>
<tr>
<td>Guayule bagasse micro</td>
<td>0.482</td>
<td>0.730</td>
</tr>
<tr>
<td>Guayule bagasse macro</td>
<td>0.716</td>
<td>1.108</td>
</tr>
<tr>
<td>Tomato peels micro</td>
<td>0.852</td>
<td>1.409</td>
</tr>
<tr>
<td>Tomato peels macro</td>
<td>0.016</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$Cetyl trimethyl ammonium bromide (CTAB) surface area
$^b$Barrett-Joyner-Halenda (BJH) adsorption cumulative pore volume.

Variations in filler surface energy were observed among the different materials (Table 6.4), due to differences in energy sites where the interaction between the filler and the adsorbate occurs. These sites correspond to chemical and structural heterogeneities in the surface of the material (Papirer et al., 1999). Carbon black had the highest dispersive component ($\gamma_D^S$) among the fillers used. Also, this was the only filler with a higher dispersive than specific component ($\gamma_S^{SP}$) of surface energy. All the waste-derived fillers had a higher specific than dispersive component. A low specific component indicates that the contribution of specific interactions in the adsorption of the filler is small and the surface of the material is mostly only capable of interaction through London type interactions (Papirer et al., 1988; Strzemiecka et al., 2014). Given the non-polar character of natural rubber, dispersive forces play the main role in the interaction with the filler. Therefore, composites containing fillers with high specific components have been
associated with weak polymer-filler interactions and strong filler-filler interactions (Leblanc, 2002).

Table 6.4: Fillers’ surface properties.

<table>
<thead>
<tr>
<th>Filler</th>
<th>50°C</th>
<th></th>
<th>100°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\gamma_S^D$ (mJ/m²)</td>
<td>$\gamma_S^{SP}$ (mJ/m²)</td>
<td>$\gamma_S$ (mJ/m²)</td>
<td>$\gamma_S^D$ (mJ/m²)</td>
</tr>
<tr>
<td>Carbon black</td>
<td>162.273</td>
<td>80.357</td>
<td>242.630</td>
<td>128.564</td>
</tr>
<tr>
<td>Carbo fly ash</td>
<td>119.594</td>
<td>--</td>
<td>108.474</td>
<td>126.787</td>
</tr>
<tr>
<td>Eggshells</td>
<td>21.035</td>
<td>53.318</td>
<td>74.353</td>
<td>11.454</td>
</tr>
<tr>
<td>Guayule bagasse</td>
<td>42.430</td>
<td>120.832</td>
<td>163.262</td>
<td>26.151</td>
</tr>
<tr>
<td>Tomato peels</td>
<td>46.136</td>
<td>216.174</td>
<td>262.310</td>
<td>29.276</td>
</tr>
</tbody>
</table>

$\gamma_S^D$: Dispersive component of surface energy
$\gamma_S^{SP}$: Specific components of surface energy
$\gamma_S$: Total surface free energy

Carbon black surface energy can be explained by its particular chemical composition and structure. Carbon blacks are mainly elemental carbon in the form of graphitic crystallites with some amorphous regions. However, they also contain small quantities of other components namely, hydrogen, oxygen and sulfur (Gerspacher and Wampler, 2001; Leblanc, 2002). CFA had both high dispersive and specific components and overall the highest total surface energy ($\gamma_S$). CFA has varies amount of unburned carbon (20%-1 %), but it is mainly amorphous alumino-silicate (over 50%) and also possess large quantities of iron, calcium, potassium, magnesium, sodium and sulfur.
compounds (Kutchko and Kim, 2006; Sombatsompop et al., 2004). These polar groups on the surface of the CFA are able to exchange both dispersive and specific interaction.

GB and TP both had high specific components and relatively low dispersive components (Table 6.4). This can be attributed primarily to the presence of large number of polar groups such as hydroxyl and carboxyl groups. However, both GB and TP are a complex assembly of biopolymers in which structural heterogeneities also contribute to their surface energy. TP consists of a thin cuticle layer, attached to the epidermal cell wall by a pectinaceous layer (Kolattukudy, 1980; Wang et al., 2014). The cell wall is composed of cellulose and hemicellulose, structural proteins, and other non-polysaccharide components such as phenolics (Wang et al., 2014). The cuticle layer is composed mostly of cutin, which is a polyester rich in hydroxyl and epoxy fatty acids (Fameau et al., 2013; Kolattukudy, 1980), overlaid with wax. GB is a ligno-cellulosic residue and also contains approximately 10% terpene resin (Nakayama, 2005; Rasutis et al., 2015).

ES had the lowest dispersive and specific components among all the fillers, due to its crystalline structure. ES is 95% calcium carbonate crystals (Guru and Dash, 2014; Intharapat et al., 2013). Surface energy of the solid is not only dependent on the chemical composition, but also the accessibility to high energy sites which is determined by arrangement and orientation of chemical groups in the surface (Cordeiro et al., 2011b). Materials containing an amorphous fraction present a higher surface energy than well crystalized materials (Burry and Keller, 2002). Other components in ES include
magnesium carbonate, calcium phosphate and organic matter (Intharapat et al., 2013; Tsai et al., 2006).

Both dispersive and specific components decreased with increasing temperature for all the fillers tested. This is likely due to desorption of surface impurities that contribute to the surface energy at lower temperatures. Very broad peaks were obtained when ethyl acetate was injected as a polar probe in CFA columns at 50°C, which made it impossible to accurately determine the peak maximum. Therefore, surface properties at 100°C were used for the statistical analysis.

5.3.2. Statistical analysis

5.3.2.1. Analysis of the data

Tensile strength and 300% modulus were highly positively correlated with total filler surface area, dispersive component and carbon black loading, and negatively correlated with waste-derived filler loading, in both guayule and hevea composites (Fig. 6.1, Table 6.5). PCA biplots show graphically the correlation among variables (Fig. 6.1). Each vector represents a variable, and the correlation between any pair of variables is determined by the angle between them. Vectors orthogonal to each other (90° angle) are independent from each other. If the angle between two vectors is close to 0° these variables are highly positively correlated but if the angle is close to 180° the pair of variables are highly negatively correlated.
Fig. 6. 1: Biplot generated by principal component analysis. a) Hevea composites, b) Guayule composites. PC1 is the first principal component and PC2 is the second principal component. Y1: 300% modulus, Y2: ultimate elongation, Y3: tensile strength, X1: total filler surface area, X2: dispersive component of surface energy, X3: specific component of surface energy, X4: carbon black loading, X5: waste-derive filler loading.
Table 6.5: Correlation matrix.

<table>
<thead>
<tr>
<th></th>
<th>Total filler surface area</th>
<th>$\gamma_D$</th>
<th>$\gamma_S$</th>
<th>Carbon Black loading</th>
<th>Waste-derived filler loading</th>
<th>300% Modulus</th>
<th>Ultimate Elongation</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hevea composites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total filler surface</td>
<td>1.000</td>
<td>0.837</td>
<td>0.068</td>
<td>0.997</td>
<td>-0.856</td>
<td>0.937</td>
<td>-0.667</td>
<td>0.884</td>
</tr>
<tr>
<td>area</td>
<td>$\gamma_D$</td>
<td>1.000</td>
<td>0.170</td>
<td>0.830</td>
<td>-0.619</td>
<td>0.721</td>
<td>-0.503</td>
<td>0.737</td>
</tr>
<tr>
<td></td>
<td>$\gamma_S$</td>
<td>1.000</td>
<td>-0.069</td>
<td>0.290</td>
<td>-0.041</td>
<td>0.215</td>
<td></td>
<td>-0.108</td>
</tr>
<tr>
<td>Carbon Black loading</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste-derived filler loading</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>300% Modulus</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Ultimate Elongation</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Guayule composites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total filler surface</td>
<td>1.000</td>
<td>0.839</td>
<td>0.036</td>
<td>0.997</td>
<td>-0.867</td>
<td>0.955</td>
<td>-0.453</td>
<td>0.866</td>
</tr>
<tr>
<td>area</td>
<td>$\gamma_D$</td>
<td>1.000</td>
<td>0.284</td>
<td>0.832</td>
<td>-0.646</td>
<td>0.745</td>
<td>-0.401</td>
<td>0.698</td>
</tr>
<tr>
<td></td>
<td>$\gamma_S$</td>
<td>1.000</td>
<td>0.033</td>
<td>0.159</td>
<td>-0.005</td>
<td>-0.256</td>
<td></td>
<td>-0.187</td>
</tr>
<tr>
<td>Carbon Black loading</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Continued
Table 6.5 Continued

<table>
<thead>
<tr>
<th></th>
<th>Waste-derived filler loading</th>
<th>300% Modulus</th>
<th>Ultimate Elongation</th>
<th>Tensile Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
<tr>
<td>300% Modulus</td>
<td>-0.849</td>
<td>-0.476</td>
<td>-0.011</td>
<td></td>
</tr>
<tr>
<td>Ultimate Elongation</td>
<td>0.486</td>
<td>0.858</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>-0.732</td>
<td>0.858</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\gamma_s^D$: Dispersive component of surface energy

$\gamma_s^{SP}$: Specific components of surface energy
The results obtained are in agreement with existing literature about the reinforcement of natural rubber by fillers. The enhancement of these properties by filler is generally attributed to strong polymer-filler interactions (Samsuri, 2013). Non-polar elastomers like natural rubber will mainly interact through dispersive forces and carbon black has a higher dispersive component of surface energy than the waste-derived fillers studied (Table 6.4). Filler surface area determines the available contact area for these interactions to occur. Negative correlations of tensile strength and 300% modulus and waste-derived filler loading are due to particular characteristics of the filler studies and reflects general trend among the different fillers.

Although ultimate elongation was correlated to the same filler characteristics as tensile strength and 300% modulus the magnitude of the correlation coefficients were generally lower (Table 6.5). Overall, filler characteristics had an opposite effect on ultimate elongation than 300% modulus and tensile strength.

Two-way interaction plots also were made to check for interactive effects among the different response variables (Figs. 6.2 and 6.3). Due to the high correlation between waste-derived filler loading and carbon black loading, only waste-derived filler loading was used in the analyses. Fillers’ dispersive and specific surface energy components were combined into filler type, and particle size range was used instead of the surface area. In the two-way interaction plot, interactive effects between two explanatory variables on the response variables are indicated if the plotted lines are not parallel to each other.
Fig. 6. 2: Interaction of waste-derived filler loading with particle size (a,c,e) and waste-derived filler type (b,d,f) on mechanical properties of hevea composites. Particle size: macro –○–, micro –●–; waste-derived filler type: Carbon fly ash —, eggshells ——, guayule bagasse –– –, tomato peels ——.
Fig. 6. 3: Interaction of waste-derived filler loading with particle size (a,c,e) and waste-derived filler type (b,d,f) on mechanical properties of guayule composites. Particle size: macro —○—, micro —●—; waste-derived filler type: Carbon fly ash —, eggshells —――, guayule bagasse ——, tomato peels ——. 
Interactive effects were observed particularly between waste-derived filler loading and type of filler, for both hevea and guayule composites. These interactions indicate that the effect of one predictor variable on the response variable is different at different values of the other predictor variable. Interactive effects between filler characteristics are understandable in rubber composites due to the complexity of these systems. The contribution of the filler network to final composite properties is an example of these interactive effects. A specific volume of particles, known as the percolation threshold, is required in order to form this network. The percolation threshold depends on the filler used. Different fillers will have different percolation thresholds due to differences in aspect ratio (Bandyopadhyay-Ghosh et al., 2015; Barrera and Cornish, 2016). This means that the effect of the filler type will be different depending on whether the loading is above or below the percolation threshold. Hence, interactive effects between filler characteristics were included in the regression models.

5.3.2.2. Multiple regression analysis

Regression models were developed for each of the response variables both for hevea and guayule composites based on the explanatory variables and their interactions (Table 6.6). These models excluded variables that were found not significant (p>0.05). Coefficients of determination indicate the proportion of the variability explained by the model.
### Table 6.6: Regression models using the standardized original independent variables.

<table>
<thead>
<tr>
<th>Regression Equation</th>
<th>$R^2$</th>
<th>Adjusted $R^2$</th>
<th>Equation number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hevea composites</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Y_1 = -0.541 + 4.759X_1 + 3.924X_5 + 2.765X_1X_4$ $+ 2.536X_4X_5$</td>
<td>0.922</td>
<td>0.910</td>
<td>(10)</td>
</tr>
<tr>
<td>$Y_2 = -0.714 - 16.092X_3 - 0.692X_4 + 0.536X_5$ $- 10.722X_3X_4$</td>
<td>0.743</td>
<td>0.705</td>
<td>(11)</td>
</tr>
<tr>
<td>$Y_3 = -0.404 - 9.177X_3 + 0.589X_4 - 6.065X_3X_4$</td>
<td>0.835</td>
<td>0.817</td>
<td>(12)</td>
</tr>
<tr>
<td><strong>Guayule composites</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Y_1 = (-2.94e - 16) - 0.175X_2 + 1.106X_4$</td>
<td>0.931</td>
<td>0.927</td>
<td>(13)</td>
</tr>
<tr>
<td>$Y_2 = (5.14e - 16) - 0.342X_3 + 0.540X_5$</td>
<td>0.350</td>
<td>0.308</td>
<td>(14)</td>
</tr>
<tr>
<td>$Y_3 = 0.082 + 0.540X_3 - 0.817X_5 - 0.533X_3X_5$</td>
<td>0.820</td>
<td>0.802</td>
<td>(15)</td>
</tr>
</tbody>
</table>

The models proposed account for over 90% of the variability observed in the 300% modulus response, for both guayule and hevea composites (equations 10 and 13). In contrast, the models fitted for ultimate elongation accounted for 74% of the variability in hevea composites and only 35% in guayule composites (equations 11 and 14). Approximately 83% and 82% of the variability in tensile strength for hevea and guayule composites, respectively, was explained by the proposed models (equations 12 and 15). The low portion of variability explained by the models proposed for ultimate elongation, particularly for guayule composites; indicate that other effects not considered have a significant influence on this particular property.

Differences in variable combinations and the magnitude of model parameters between models generated for hevea and guayule composites for the same response variable also were found. These differences are mostly due to chemical and structural differences between these two natural rubbers, and the way they interact with the fillers.
However, they are also a consequence of multicollinearity within the data. Filler characteristics used as explanatory variables were strongly correlated among each other (Table 6.5). The presence of such strong multicollinearity makes the models obtained with the original explanatory variables unable to determine the real effect of the filler characteristics on the response variables.

Regression models were developed using PC scores that resulted from the transformation of explanatory variables using PAC (Table 6.7). Nearly 90% of the variability in the 300% modulus response was explained by the regression model (equations 16 and 19) for both hevea and guayule composites (Fig. 6.4a and 6.4b), whereas the models generated for tensile strength (equations 18 and 21) accounted for approximately 80% of the variability observed for both rubbers (Fig. 6.4e and 6.4f). Common variables in all of these models are PC$_1$ and PC$_4$. These two components’ main contribution are attributed to total filler surface area, and carbon black and waste-derived filler loading (Table 6.8). For both 300% modulus and tensile strength, PC$_1$ had a positive effect on the response while PC$_4$ has a negative impact as indicated by the sign of the coefficients (Table 6.7). This means that a total increase in total filler surface area and carbon black loading will generate an increase in the responses proportional to their contribution in the model. On the other hand, an increase in waste-derived filler loading would adversely affect these two responses for both guayule and hevea.
Table 6.7: Regression models using principal component scores.

<table>
<thead>
<tr>
<th>Regression Equation</th>
<th>$R^2$</th>
<th>Adjusted $R^2$</th>
<th>Equation number</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hevea composites</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Y_1 = (-5.09e-7) + 0.481PC_1 - 0.810PC_4 - 2.475PC_5$</td>
<td>0.896</td>
<td>0.885</td>
<td>(16)</td>
</tr>
<tr>
<td>$Y_2 = (-4.573e-7) - 0.366PC_1$</td>
<td>0.471</td>
<td>0.454</td>
<td>(17)</td>
</tr>
<tr>
<td>$Y_3 = (-6.254e-7) + 0.456PC_1 - 0.765PC_4$</td>
<td>0.792</td>
<td>0.778</td>
<td>(18)</td>
</tr>
<tr>
<td><strong>Guayule composites</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Y_1 = (-8.047e-7) + 0.497PC_1 - 0.623PC_4$</td>
<td>0.914</td>
<td>0.909</td>
<td>(19)</td>
</tr>
<tr>
<td>$Y_2 = (2.258e-7) - 0.256PC_1$</td>
<td>0.232</td>
<td>0.208</td>
<td>(20)</td>
</tr>
<tr>
<td>$Y_3 = (-8.447e-7) + 0.446PC_1 - 0.210PC_2 - 0.662PC_4$</td>
<td>0.800</td>
<td>0.780</td>
<td>(21)</td>
</tr>
</tbody>
</table>
Fig. 6. 4: Standardized observed vs values predicted by regression models using principal component scores. (a) 300% Modulus, (c) Ultimate elongation and (e) Tensile strength of hevea composites; (b) 300% Modulus, (d) Ultimate elongation and (f) Tensile strength of guayule composites. The red solid line represents the regression line; the red dashed lines indicate the 95% confidence intervals; and the horizontal blue dashed line represents the mean response observation.
Table 6. 8: Principal component loadings.

<table>
<thead>
<tr>
<th></th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
<th>PC4</th>
<th>PC5</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hevea composites</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total filler surface area</td>
<td>0.526</td>
<td>0.026</td>
<td>0.037</td>
<td>-0.482</td>
<td>-0.699</td>
</tr>
<tr>
<td>$\gamma^D_S$</td>
<td>0.462</td>
<td>0.309</td>
<td>-0.701</td>
<td>0.446</td>
<td>0.015</td>
</tr>
<tr>
<td>$\gamma^{SP}_S$</td>
<td>-0.053</td>
<td>0.917</td>
<td>0.394</td>
<td>0.038</td>
<td>-0.011</td>
</tr>
<tr>
<td>Carbon black loading</td>
<td>0.526</td>
<td>0.022</td>
<td>0.083</td>
<td>-0.454</td>
<td>0.714</td>
</tr>
<tr>
<td>Waste-derived filler loading</td>
<td>-0.479</td>
<td>0.251</td>
<td>-0.587</td>
<td>-0.601</td>
<td>0.032</td>
</tr>
<tr>
<td>Eigen value</td>
<td>3.520</td>
<td>1.133</td>
<td>0.243</td>
<td>0.100</td>
<td>0.003</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.876</td>
<td>1.065</td>
<td>0.493</td>
<td>0.317</td>
<td>0.051</td>
</tr>
<tr>
<td>Proportion of variance</td>
<td>0.704</td>
<td>0.227</td>
<td>0.049</td>
<td>0.020</td>
<td>0.001</td>
</tr>
<tr>
<td>Cumulative proportion</td>
<td>0.704</td>
<td>0.931</td>
<td>0.979</td>
<td>0.999</td>
<td>1.00000</td>
</tr>
</tbody>
</table>

Continued
### Guayule composites

<table>
<thead>
<tr>
<th></th>
<th>0.524</th>
<th>-0.032</th>
<th>0.007</th>
<th>-0.482</th>
<th>-0.701</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total filler surface area</td>
<td>0.470</td>
<td>0.272</td>
<td>-0.702</td>
<td>0.461</td>
<td>0.016</td>
</tr>
<tr>
<td>$\gamma^D_S$</td>
<td>0.037</td>
<td>0.925</td>
<td>0.379</td>
<td>-0.006</td>
<td>-0.007</td>
</tr>
<tr>
<td>$\gamma^{SP}_S$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon black loading</td>
<td>0.525</td>
<td>-0.039</td>
<td>0.049</td>
<td>-0.463</td>
<td>0.712</td>
</tr>
<tr>
<td>Waste-derived filler loading</td>
<td>-0.477</td>
<td>0.262</td>
<td>-0.601</td>
<td>-0.585</td>
<td>0.027</td>
</tr>
<tr>
<td>Eigen value</td>
<td>3.541</td>
<td>1.126</td>
<td>0.227</td>
<td>0.103</td>
<td>0.002</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>1.882</td>
<td>1.061</td>
<td>0.477</td>
<td>0.321</td>
<td>0.050</td>
</tr>
<tr>
<td>Proportion of variance</td>
<td>0.708</td>
<td>0.225</td>
<td>0.045</td>
<td>0.021</td>
<td>0.001</td>
</tr>
<tr>
<td>Cumulative proportion</td>
<td>0.708</td>
<td>0.933</td>
<td>0.979</td>
<td>0.999</td>
<td>1.00000</td>
</tr>
</tbody>
</table>

$\gamma^D_S$: Dispersive component of surface energy
$\gamma^{SP}_S$: Specific components of surface energy
PC: Principal component

PC$_5$ was found to have a significant effect for 300% modulus in hevea composites (equation 16), but not in guayule composites (equation 19). However, due to the low percentage of the portion of the variance in the filler characteristics explained by PC$_5$ (<0.1%) (Table 6.8), the removal of this effect from the model (equation 16) will only slightly reduce the $R^2$ to 0.880. PC$_2$ was included as a significant factor for the prediction of tensile strength for guayule composites (equation 21), but was not significant for the
same response in hevea composites (equation 18) and so was not included here. Unlike
the models fitted for modulus, the removal of PC$_2$ will have a greater impact on the
prediction of tensile strength ($R^2$ decreased from 0.80 to 0.75) for guayule composites
due to the larger portion of the variance in filler characteristics explained by PC$_2$ (>22%)
(Table 6.8).

PC$_2$ had a negative effect on the tensile strength of guayule rubber composites.
This component is heavily influenced by specific components of surface energy, which
indicates that this filler characteristic is important in predicting the tensile strength of
guayule composites, but not of hevea composites. This is due to the impact that this filler
characteristic has on the vulcanization of the rubber. A high specific component results
from a more chemically active surface. These highly active surfaces can interact with
compounding ingredients, affecting the cure kinetics, and lead to differences in crosslink
density that affect mechanical properties (Byers, 2001). Given that the same curing
system was used for all composites, this variable is more important in guayule than hevea
because of differences in vulcanization behavior. Guayule rubber has lower curing rates
due to different non-rubber components than hevea (Ramos-de Valle, 1981; Schloman,
2005).

Contrary to 300% modulus and tensile strength, the variability explained by the
models generated for ultimate elongation was lower than 50% (Fig. 6.4c and 6.4d)
(equation 17 and 20). This means that other, unmeasured, variables contribute to the
observed ultimate elongation. Filler structure is an example of an unaccounted variable.
Filler structure has been associated with changes in ultimate elongation in carbon black
composites (Gerspacher and Wampler, 2001; Leblanc, 2002). Fillers with highly irregular surfaces due to branched aggregates and/or porosity restrict chain motion under applied strain and contribute to physical crosslinking of rubber. Chemistry related variables such as the pH of the fillers also may affect crosslink density, and hence properties such as ultimate elongation. Alkaline fillers like ES can cause faster curing rates which can lead to higher crosslink density (Barrera and Cornish, 2016; Byers, 2001). Finally the presence of terpene resins, such as those in GB, can also have an effect on resulting composite properties. These resins can act as plasticizers, which would increase ductility of the materials (Barrera and Cornish, 2015).

It is important to notice that PC1 is a common variable in all the models (Table 6.7). This is because this component alone accounts for over 70% of the total variation in the original explanatory variables (Table 6.8). PC1 is also slightly influenced by the dispersive component of surface energy and the waste-derived filler loading.

Despite of the lower $R^2$ for the models developed with the transformed explanatory variables (Table 6.7), these models are more reliable than the models developed with the original explanatory variables (Table 6.6), which were highly correlated. Multicollinearity does not reduce the overall predicting power of the model, but it drastically affects the calculation of regression equation. In regression models containing correlated explanatory variables, the variances of the regression coefficients can become very large (Jolliffe, 2002). This compromises the model’s ability to accurately identify real contributions of the filler characteristic on a given response variable.

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5.4. Conclusions

The statistical modelling approach employed proved to be an efficient tool for the estimation of individual contributions of different filler characteristics on the properties of both guayule and hevea natural rubber composites. This is important considering the complexity of these systems and the wide range of possible alternative fillers that remain unexplored. Furthermore, this modelling approach can be used to predict properties in different polymer composites based on specific polymer and filler characteristics, compounding formulations and processing conditions. Filler surface area and loading were found to be important variables contributing to composite properties, particularly for 300% modulus and tensile strength. However, the new models demonstrate that a single variable cannot predict all properties of rubber composites due to their complexity. Therefore, a combination of two or more filler characteristics is required to provide a good fit. The identification of the contribution of each filler characteristic to particular properties makes it easier to target a particular material or combination of materials as potential fillers for a given composite application based on the desired performance properties. This modelling method can facilitate the screening of a large number potential non-conventional fillers and hybrid filler composites and the optimization of properties.
Chapter 7: Processing and Mechanical Properties of Natural Rubber/Waste-derived Nano Filler Composites compared to Macro and Micro Filler Composites.

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Abstract

Nano-sized fillers produced from renewable materials can generate high performance natural rubber (NR) composites while reducing dependency on petroleum. We made NR composites, with both hevea and guayule NR, containing nano-scale waste-derived fillers as complete and partial replacements of carbon black. The effect of nano-filler type and loading on composite mechanical properties was analyzed and compared to previous results with micro and macro fillers. Also, processability of the compounds was investigated. Reinforcement of both NRs was achieved by nano-sized waste-derived
Fillers, even with complete replacement of carbon black. Better relative reinforcement was obtained in guayule than in hevea rubber due to different rubber macromolecular structure and the strength of the rubber-waste filler interactions. Composites containing waste-derived fillers as co-fillers with carbon black displayed uncommon combinations of properties not achieved with single conventional reinforcing fillers. Furthermore, significant reductions in power consumption during mixing were obtained even by replacement of a small portion of carbon black in the composites. Despite increased interest in nano-sized particles, micro-sized fillers are effective reinforcing fillers when used as partial replacements of carbon black, and can be produced at a much lower cost than nano-sized particles.

**Keywords:** Natural rubber, Nanocomposites, Waste-derived fillers, mechanical properties, processability.

### 7.1. Introduction

Fillers are extensively used polymer additives, considered essential to attainment of product performance (Leblanc, 2002). Currently the main two commercially used reinforcing fillers are carbon black and silica. Since the early 1900s, carbon black has been the most widely used and studied reinforcing filler for rubber composites (Fröhlich et al., 2005; Tohsan and Ikeda, 2014). However, carbon black is a non-renewable resource derived from petroleum. Furthermore, increased tire production along with reductions in carbon black production capacity due to increasing environmental regulations in North America and Europe, is likely to lead to carbon black shortfalls and price rises by 2020 (Moore, 2015; Pourriahi, 2016).
Silica has gained increasing attention as a reinforcing filler since the early 1990s, particularly in the tire industry due to improvements it confers in dynamic-mechanical properties such as lower rolling resistance at equal wear resistance and improved wet grip compared to carbon back composites (Rattanasom et al., 2007; Stöckelhuber et al., 2010). The use of silica in rubber compounds also has positive impact on the sustainability of the tire industry, due to increased fuel economy and decreased CO$_2$ emissions achieved as result of tires’ low rolling resistance. Nevertheless, the production of silica requires the use of harsh chemicals and high temperatures (Byers, 2001). Moreover, compounding natural rubber with silica requires the use of expensive coupling agents to overcome unacceptably strong filler-filler interactions and improve compatibility with natural rubber (Choi et al., 2003; Kato et al., 2014; Murakami et al., 2003). Furthermore, 36% of the silica demand is related to non-rubber products (Notch consulting Inc., 2015), which limits current availability for the rubber industry.

New fillers are desired that can offer similar or better reinforcing and processing properties to carbon black but be derived from more sustainable sources. Increasingly, research is focusing on the utilization of waste-derived, renewable materials as alternative fillers for elastomers (Abraham et al., 2013a; Barrera and Cornish, 2016, 2015; Gopalan Nair and Dufresne, 2003; Intharapat et al., 2013; Ishak and Bakar, 1995; Pasquini et al., 2010; Visakh et al., 2012). This field of research is driven by concerns about environmental footprint, sustainability in manufacturing, and the rising cost of treatment and disposal of high volume waste materials.
Particle size is an important morphological characteristic affecting the utility of alternate fillers as reinforcing agents (Leblanc, 2002). Smaller particles have more surface area per unit weight than bigger particles. Greater surface area facilitates more interfacial contact between the filler and the polymer, which increases the effectiveness of reinforcement (Bandyopadhyay-Ghosh et al., 2015; Szeluga et al., 2015). However, the strength and nature of this interaction is dependent on other filler characteristics such as surface activity (Kohls and Beaucage, 2002). Moreover, big particles act as localized stress points, generating flaws within the composite that can initiate failure (Byers, 2001; Samsuri, 2013). Hence, research efforts on alternative filler sources have focused on nanoparticles for the manufacture of high performance polymer composites (Angellier et al., 2005a; Bitinis et al., 2013; Visakh et al., 2012).

Nevertheless, important drawbacks have been associated with the use of nanoparticles, including the complexity and high cost of their production compared to macro and micro size particles, and composite processability issues (Abraham et al., 2011; Byers, 2001; Fang et al., 2014; Peddini et al., 2014). The mixing of rubber is a very complex operation. Despite advancements in composites technology, the dispersion of nanoparticles in the polymer matrix remains a challenge, particularly for non-carbon black composites. The higher surface area and active surfaces of these particles, favor interaction between the particles leading to agglomeration that reduces composite performance (Chao and Riggleman, 2013; Donnet and Custodero, 2013; Kueseng and Jacob, 2006). To achieve homogeneous dispersion of nanoparticles in rubber, complex
mixes are required that often involve high power consumption, increasing processing costs (Szeluga et al., 2015).

The aim of this study was to evaluate power consumption during mixing of different waste-derived fillers with hevea and guayule rubber, and compare resultant mechanical properties of the nanocomposites to composites made with carbon black, and micro and macro sized waste-derived particles.

7.2. Experimental

7.2.1. Materials

Hevea natural rubber (grade SMR-20), and natural rubber latex (NRL) purchased from Centrotrade (Chesapeake, Virginia) were used for the manufacture of hevea rubber composites. Guayule rubber was obtained by drying guayule natural rubber latex (GNRL) extracted as described (Cornish, 1996). Guayule rubber and GNRL were used to prepare guayule rubber composites. Compounding chemicals, namely zinc oxide, stearic acid, sulfur, the vulcanization accelerator butyl benzothiazole sulfonamide (TBBS), and carbon black N330 (mean particle size: 108 nm, SD: 31.42 nm), were purchased from HB chemicals (Twinsburg, OH). The waste filler raw materials were generously donated as follows: eggshells (ES) by Michael Foods (Gaylord, MN), carbon fly ash (CFA) by Cargill Salt (Akron, OH), processing tomato peels (TP) by Hirzel Canning Co & Farms (Toledo, OH), and guayule bagasse (GB) was generated as a co-product of latex extraction from shrub generously donated by PanAridus LLC, (Casa Grande AZ).
7.2.2. Preparation of waste-derived nano-fillers

Raw materials were dried and ground to macro particle size (300μm>d>38μm) as described (Barrera and Cornish, 2015). Nano-sized ES, TP and CFA particles were made by wet-milling the macro sized particles using a five liter ball mill, U.S. Stoneware (East Palestine, OH) for 5-8 days. Nano-sized GB particles were prepared by wet-milling with simultaneous hydrolyzation using a sulfuric acid solution (40%) at room temperature for 2-3 days. The GB dispersion was then centrifuged at 8,000 rpm for 10 min using a J2-MC high speed centrifuge, Beckman Coulter (Indianapolis, IN). The acid was decanted and the precipitated particles re-suspended in deionized water. Centrifugation and resuspension was repeated three times to quench hydrolysis.

Aqueous dispersions (1:3 w:v) of each filler were sonicated for 30 min at 35% amplitude using a high intensity ultrasonic processor VCX750, Sonics & Materials (Newtown, CT) to break apart aggregates. Intervals of 10 sec on and 5 sec off were used to avoid over-heating. Particle size distributions were determined using a Particle size analyzer LA-950V2, Horiba Scientific (Irvine, CA).

7.2.3. Rubber nanocomposites manufacture

Aqueous filler dispersions were added to latex (NRL or GNRL) (1:1 v:v) under constant mixing using a magnetic stirrer. Latex coagulated during the mixing process was collected and allowed to rest overnight, during which time the rubber exuded most of the entrained water. The coagulated rubber with nano fillers dispersed throughout, were then passed once through a two-roll EEMCO lab mill, roll diameter 15.24 cm and 33.02 cm face width, Rubber City Machinery Corporation (Akron, OH), and dried at 50°C. The
resulting materials were used as master batches for compounding with various amounts of unfilled solid rubber (guayule or hevea) and carbon black to achieve specific waste-derived filler concentrations (5, 10, 20 or 35 phr) (parts per hundred rubber). Total combined filler loading (carbon black plus waste-derived nano filler) was 35 phr. A standard compounding formulation was used for all the composites (Table 7.1). Composites containing 35 phr of carbon black N330 with no other filler were used as reference materials for both natural rubbers, and unfilled compounded rubber was used as a second reference.

Table 7.1: Compounding formulation used to prepare natural rubber composites.

<table>
<thead>
<tr>
<th>Material</th>
<th>Quantity (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>Carbon black</td>
<td>35 30 25 15 0</td>
</tr>
<tr>
<td>Filler</td>
<td>0 5 10 20 35</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3.5</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>5</td>
</tr>
<tr>
<td>Butyl benzothiazole sulfonamide (TBBS)</td>
<td>0.75</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
</tr>
</tbody>
</table>

Carbon black and compounding ingredients were mixed into the rubber composites through mastication using a Farrel BR lab mixer, Rubber City Machinery Corporation (Akron, OH). The mixing protocol can be summarized in three steps: (1) rubber was added into the mixer and allowed to knead; (2) fillers and stearic acid were added in the mixing chamber. In this two first steps roto speed was 6.3 rad/s; (3) sulfur
and remaining compounding ingratiates were added, and rotor speed was increased to 9.4 rad/s. Power required for the mixing of each rubber composite in the lab mixer was recorded using a Pro-server Ex software v 1.3., Pro-face Digital Electronics Corporation (Osaka, Japan). The hot mix was discharged from the mixer, then milled and cured. The processing conditions for rubber compounding and curing were as previously described (Barrera and Cornish, 2015).

7.2.4. Materials Characterization

7.2.4.1. Mechanical properties

Tensile properties and tear strength were measured according to ASTM D412 and ASTM D624 respectively (ASTM International, 2013b, 2012), along the grain direction at a crosshead speed of 500 mm/min at 23°C. Testing was performed using a tensiometer (Model 3366, Instron Norwood, MA), with the Bluehill v. 2.26 software package. Specimens were cut using an ASTM D412 Die C for tensile tests, while samples for tear strength tests were cut using an ASTM D624 Die B. Five replicates were used for each test. The samples were conditioned at 23±2°C and at a relative humidity of 50±5% for at least 24 hours prior to assessment of their properties. The properties of these composites (300% modulus, tensile strength, elongation at break and tear strength) were compared.

7.2.4.2. Microscopic analysis

The morphology of the different nanofillers was investigated using a Hitachi H-7500 transmission electron microscope (Tokyo, Japan). Imaging of the nanoparticles was done with an accelerating voltage of 80 kV. Aqueous dispersions containing the nanofiller were deposited on a copper grid bearing a carbon film and excess liquid was
removed by blotting with filter paper. The samples were then stained with 2% uranyl acetate solution, blotted with filter paper to remove excess staining solution and allowed to dry.

A Hitachi S-3500N scanning electron microscope (Tokyo, Japan), operated in a high vacuum, was used to investigate the morphology of the different composites at the fracture surface and distribution of the fillers within composites. After tensile testing cross sections of each composite were cut and washed with 70% aqueous ethanol, to eliminate surface contamination. The samples were sputter-coated with a thin layer of platinum (0.2 KÅ) by an Anatech Hummer 6.2 Sputtering system prior to analysis in order to improve their conductivity, allowed to dry and imaged.

7.2.5. Statistical Analysis

Cluster analysis was done in order to group composites with similar mechanical properties. The data were standardized so the extent of the contribution of each response variable in the classification was not affected by differences in scale. Cluster analysis was performed using Vegan package (Vegan v. 2.3-0) implemented in R (R Core Team, 2014). Euclidian distance was used to measure the similarity between the treatments. Ward’s method was used as the linkage method. Multiple means comparison Tukey-Kramer tests (p < 0.05) was used to detect significant differences in the mechanical properties of composites obtained with different formulations.
7.3. Results

7.3.1. Filler characterization.

Variations in particle size distribution were observed among the different materials (Fig. 7.1). Nano sized ES particles had the narrowest distribution. Broader distributions and larger mean particle size of the other materials reflected higher tendency to agglomerate and limitations of the instrument to identify individual particles. However, all of the waste-derived fillers had elementary particles with nano size dimensions (Fig. 7.2). Variations in particle morphology were also observed (Fig. 7.2). CFA, ES and TP present more irregular particle contours, while GB had rod-like particles.
Fig. 7. 1: Nano sized fillers’ particle size distribution. a) Guayule bagasse (median: 1.370\(\mu\)m, mean: 1.585\(\mu\)m), b) carbon fly ash (median: 0.218\(\mu\)m, mean: 1.109\(\mu\)m), c) eggshells (median: 0.125\(\mu\)m, mean: 0.757\(\mu\)m), d) tomato peels (median: 0.386\(\mu\)m, mean: 7.711\(\mu\)m).
7.3.2. Composites mechanical properties

Considerable enhancement of vulcanized rubber mechanical properties were obtained at all loadings for most of the waste-derived fillers studied (Fig. 7.3). The addition of waste-derived fillers, alone or in combination with carbon black, increased tensile strength of hevea from 9.96 MPa (unfilled) up to 29.38 MPa and tensile strength
of unfilled guayule from 7.07 MPa (unfilled) up to 24.72 MPa (Fig. 7.3). Modulus (300%) of unfilled compounds was also significantly increased with the addition of the different waste-derived fillers. In general, as the amount of waste-derived nano filler was increased above 5 phr, a decrease in 300% modulus was observed (Fig. 7.3). However, higher values of 300% modulus than those of unfilled vulcanizates were achieved at all loadings of nano-sized waste-derived fillers, including composites containing 35 phr of waste-derived fillers (no carbon black), both for guayule and hevea rubber (Fig. 7.3).
Fig. 7. 3: Mechanical properties of hevea and guayule natural rubber nano composites and unfilled compounds. Total filler (carbon black plus waste-derived filler), in all composites was 35 phr. As the waste filler loading increases the carbon black filler decreases by the same weight amount.
Most of the composites manufactured by partial replacement of carbon black with 5 phr to 20 phr of nano-sized ES, CFA and TP had very similar values of elongation at break to unfilled Vulcanizates for both rubbers used (Fig. 7.3). Significantly higher values of elongation at break to those of unfilled rubber were obtained at 35 phr of ES for both guayule and hevea nano composites. Tear strength of all waste-derived fillers/hevea composites was between 0.21 and 1.82 times higher than tear strength of unfilled hevea compounds (Fig. 7.3), except for composites made with 20 phr of TP (with 15phr of carbon black). Likewise, tear strength of all waste-derived fillers/guayule composites were between 0.4 – 1.31 times higher than tear strength of unfilled guayule compounds (Fig. 7.3), except the composite containing 20 phr of GB (with 15phr of carbon black).

Based on the four properties measured, reinforcement comparable to that of carbon black alone was obtained by partial replacement of carbon black with low loading (5 and 10 phr) of ES, TP and CFA (Fig. 7.3). Nano-sized ES particles, showed outstanding reinforcing potential among the waste-derived fillers used, particularly for guayule rubber composites. Guayule composites containing 5 phr of nano-sized ES had significantly higher tensile strength and not significantly different 300% modulus, elongation at break and tear strength than carbon black composites. Furthermore, there was no significant difference between the tensile strength of guayule composites manufactured with 10, 20 and 35 phr of nano-sized ES particles and guayule composites made solely with carbon black. Hevea composites containing 10 phr nano-sized ES (with 25phr of carbon black) had the highest tensile strength (29.38 MPa) among hevea composites containing waste-derived fillers, only 14% lower than carbon black.
composites (Fig. 7.3), but lower 300% modulus and tear strength compared to hevea composites made with 5 phr of TP and CFA. In general, hevea composites containing 5 phr of TP and CFA had the highest overall values of tensile, tear strength and 300% modulus among hevea composites containing waste-derived fillers.

Due to the low bulk density of GB, large volumes of material are required for 35 phr composites. It was impossible to prepare a master batch containing this amount of GB. Data are not shown for these unsuccessful samples.

7.3.3. Composites morphology

Scanning electron microscopy (SEM) of composite fracture surfaces revealed different composite morphology resulting from differences between the natural rubbers and their interfacial interaction with the waste-derived fillers (Figs. 7.4 and 7.5). Both hevea and guayule rubber composites made with 35 phr carbon black had micro scale particles in the fracture surface (Figs. 7.4a and 7.5a), which are most likely aggregates of carbon black or compounding ingredients. In general, greater surface roughness was observed in guayule composites that hevea composites, due to a more ductile fracture of guayule.
Fig. 7. 4: SEM micrograph of hevea rubber nano composites with (a) 35 phr carbon black; (b) 35 phr carbon fly ash; (c) 35 phr eggshells; (d) 20 phr guayule bagasse; (e) 35 phr processing tomato peels
In general, even distribution of the waste-derived fillers throughout both natural rubbers was achieved at all loadings including 35 phr, but there was some agglomeration.
of the nano particles (Figs. 7.4 and 7.5) (SEM of composites at lower loadings of waste-derived fillers are not shown). Nevertheless, upon fracture, most of the particles remained embedded in both types of rubber.

Problems with uneven drying of master batches containing nano-sized CFA and GB particles were revealed by SEM. Composites made with these two fillers had a high prevalence of voids that probably resulted from the exit of residual water during curing of the materials. This problem was more obvious in guayule that hevea composites. Despite the presence of voids in CFA composites, most of the particles remained embed in the rubbers (Figs. 7.4b and 7.5b). GB nanoparticles were hardly distinguishable in hevea composites (Fig. 7.4d), but bundles of the particles were observed intertwined within the guayule rubber (Fig. 7.5d).

7.3.4. Cluster Analysis

Cluster analysis of composite mechanical properties led to classification of the composites into four groups with different characteristics for hevea composites and three groups for guayule composites (Fig. 7.6). Composites with the highest tensile and tear strength, high 300% modulus and elongation at break were grouped in cluster 2 for hevea composites and cluster 3 for guayule composites. These clusters included composites made with 35 phr with carbon black, 5 and 10 phr of waste-derived nano-sized fillers, except composites made with 10 phr of GB, which were classified into a different group of composites.
Fig. 7. 6: Dendrograms obtained from hierarchical cluster analysis of (a) hevea and (b) guayule rubber formulations. Composite labels represent the amount of waste-derived filler in the sample, filler type and particle size. Total amount of filler (carbon black plus waste-derived filler), in all samples was 35 phr. Filler type: carbon fly ash (CFA), guayule bagasse (GB), eggshells (ES), processing tomato peels (TP).
Hevea composites in cluster 1 (Fig. 7.6a) and guayule composites in cluster 2 (Fig. 7.6b) possessed high tensile strength and elongation at break, but medium values of tear strength and low 300% modulus. These clusters mainly grouped composites made with 20 phr and 35 phr of ES and 20 phr of CFA.

Unfilled compounds, composites made with 35 phr of TP and CFA, and composites containing 10 phr and 20 phr of nano-sized GB, were gathered in cluster 4 for hevea composites and cluster 1 for guayule composites. These composites had lower overall performance properties compared to previously described clusters both for hevea and guayule composites. Finally, hevea composites manufactured with 20 phr of TP had the lowest tensile strength, elongation at break and tear strength, but high modulus, and was grouped in cluster 3 (Fig. 7.6a).

7.3.5. Power consumption during mixing

The power required for the compounding of hevea and guayule rubber with different nano-sized waste-derived fillers and carbon black was compared to power consumption during mixing of macro and micro sized composites at equal filler loadings (Figs. 7.7-7.14). Due to the lower bulk viscosity of guayule rubber (Schloman, 2005), mixing identical formulations required higher power for hevea than for guayule rubber compounds.
Fig. 7. Power consumption during mixing of hevea rubber composites with carbon fly ash. Unfilled compound (gray), 35 phr carbon black composite (black), 5 phr waste filler composite (light green), 10 phr waste filler composite (red), 20 phr waste filler composite (blue), 35 phr waste filler composite (dark green). Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. Panels represent the steps in the mixing protocol.
Fig. 7.8: Power consumption during mixing of hevea rubber composites with eggshells. Unfilled compound (gray), 35 phr carbon black composite (black), 5 phr waste filler composite (light green), 10 phr waste filler composite (red), 20 phr waste filler composite (blue), 35 phr waste filler composite (dark green). Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. Panels represent the steps in the mixing protocol.
Fig. 7.9: Power consumption during mixing of hevea rubber composites with guayule bagasse. Unfilled compound (gray), 35 phr carbon black composite (black), 5 phr waste filler composite (light green), 10 phr waste filler composite (red), 20 phr waste filler composite (blue), 35 phr waste filler composite (dark green). Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. Panels represent the steps in the mixing protocol.
Fig. 7. 10: Power consumption during mixing of hevea rubber composites with processing tomato peels. Unfilled compound (gray), 35 phr carbon black composite (black), 5 phr waste filler composite (light green), 10 phr waste filler composite (red), 20 phr waste filler composite (blue), 35 phr waste filler composite (dark green). Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. Panels represent the steps in the mixing protocol.
Fig. 7.11: Power consumption during mixing of guayule rubber composites with carbon fly ash. Unfilled compound (gray), 35 phr carbon black composite (black), 5 phr waste filler composite (light green), 10 phr waste filler composite (red), 20 phr waste filler composite (blue), 35 phr waste filler composite (dark green). Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. Panels represent the steps in the mixing protocol.
Fig. 7.12: Power consumption during mixing of guayule rubber composites with eggshells. Unfilled compound (gray), 35 phr carbon black composite (black), 5 phr waste filler composite (light green), 10 phr waste filler composite (red), 20 phr waste filler composite (blue), 35 phr waste filler composite (dark green). Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. Panels represent the steps in the mixing protocol.
Fig. 7. 13: Power consumption during mixing of guayule rubber composites with guayule bagasse. Unfilled compound (gray), 35 phr carbon black composite (black), 5 phr waste filler composite (light green), 10 phr waste filler composite (red), 20 phr waste filler composite (blue), 35 phr waste filler composite (dark green). Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. Panels represent the steps in the mixing protocol.
Fillers were added to the rubber during the second step in the mixing protocol. Partial and full replacement of carbon black with waste-derived filler reduced the power required in this step (panel 2 from left to right Figs. 7.7-7.14), even when nano-sized waste-derived filler particles were used. In general, upon addition of the filler, a
progressive increase in power consumption was observed as the amount of waste-derived filler loading decreased and carbon black loading increased for both natural rubbers. However, this trend was clearer in guayule than hevea composites.

Power consumption increased during the second step in the mixing procedure (panel 2 from left to right Figs. 7.7-7.14), as the particle size of the waste-derived fillers in the composite decreased. However, this trend was clearest for composites containing 35 phr of waste-derived fillers (no carbon black).

In the last step of the mixing protocol (panel 3 from left to right Figs. 7.7-7.14), the presence of carbon black in the formulation was the main factor affecting the power consumption. As the amount of carbon black in the compound increased, power consumption also increased for most of the formulations. However, for hevea composites, power consumption of compounds containing waste-derived fillers was very close to that of compounds containing carbon black alone. The minor substitution of only 5 phr CB with waste-derived fillers, reduced power consumption by 0.9% -10.5% in hevea composites and 0.8-19.7 % in guayule in guayule composites, with the greatest power savings achieved with ES and GB in hevea and CFA and ES in guayule.

7.4. Discussion

Reinforcement of guayule and hevea natural rubber achieved by nano-sized waste-derived fillers can be attributed to different factors, including high surface area offered by nano-sized particles and good dispersion as depicted by SEMs of surface fracture (Figs. 7.4 and 7.5). The high surface area of the nano-sized particles combined with uniform distribution throughout the material, allowed sufficient contact between the
fillers and the polymers to limit chain movement, which results in increased polymer resistance to deformation and molecular separation, which can lead to failure (Hamed, 2000; Samsuri, 2013). This is reflected by the increased tear and tensile strength of composites compared to unfilled vulcanizates (Fig. 7.3).

Filler-filler networks and polymer-filler interactions are likely also significant contributions in the reinforcement (Fig. 7.4 and 7.5) especially for the guayule rubber composites, as has been indicated in macro and micro composites (Barrera and Cornish, 2016, 2015). The formation of a filler network within the rubber can considerably enhance mechanical properties (Bandyopadhyay-Ghosh et al., 2015; Samsuri, 2013) by interlocking the rubber chains within the filler network. Such filler networks are very strong in waste-derived filler particles because of stronger filler-filler interactions in these polar fillers caused by hydrogen bonds and ionic bonds, which do not occur in carbon black particles which interact by dispersive forces (Byers, 2001; Jong, 2014). By using co-filler systems, in this case carbon black with waste-derived fillers at low loadings, the greater strength of waste-derived filler networks complements the carbon black-mediated reinforcement. Hence composites retained or even enhanced mechanical properties obtained with carbon black alone (Fig. 7.3). These synergistic effects were more pronounced in guayule than hevea rubber (Fig. 7.3), due to differences in rubber structure and composition (non-rubber components). Hevea rubber is a branched macromolecule while guayule has a more linear chain structure (Rensch et al., 1986), which allows it to flow more easily into the filler network. Furthermore non-rubber components such as
resins in guayule rubber that are not present in hevea rubber could act as compatibilizers between the rubber and the fillers.

Filler-filler interactions compete with the polymer-filler interactions within the composite (Sarkawi et al., 2014). Carbon black possesses a non-polar surface more compatible with non-polar poly-isoprene chains in natural rubber than the more polar waste-derived fillers (Leblanc, 2002), thus stronger polymer-filler interaction. Adsorption of rubber into the carbon black surface acts as an additional crosslinks (Chenal et al., 2007b), which translate to stronger materials. At high loadings, reinforcement achieved through filler-filler interaction is not comparable to the reinforcement obtained from polymer-filler interactions between carbon black and the natural rubber (Barrera and Cornish, 2016; Jong, 2014), hence a decrease in properties is observed (Fig. 7.3). However, some of the waste-derived fillers, namely ES and TP, retained high values of tensile and tear strength at loadings as high as 35 phr for guayule composites and 10 phr for hevea composites (Fig. 7.3). This indicates differences in the strength of polymer-filler interaction among the waste-derived fillers due to differences in chemical and structural composition of the filler.

Despite the lower particle size, nano-sized waste-derived fillers did not improve mechanical properties much beyond the micro-sized particles previously studied (Barrera and Cornish, 2016, 2015) (Figs 7.15 and 7.16). In general, composites containing micro-sized waste-derived fillers as co-fillers with carbon black performed as well or better than composites containing equivalent combination with nano-sized waste-derived fillers.
Furthermore, mixing of micro-sized particles into compounds required less power than nano-sized particles (Figs. 7.7-7.14).
Fig. 7.15: Mechanical properties of hevea rubber composites manufactured using various particle size particles obtained from different waste derived materials. Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. As the waste filler loading increases the carbon black filler decreases by the same weight amount.
Fig. 7. 16: Mechanical properties of guayule rubber composites manufactured using various particle size particles obtained from different waste derived materials. Total amount of filler (carbon black plus waste-derived filler), in all composites was 35 phr. As the waste filler loading increases the carbon black filler decreases by the same weight amount.
The similar or lower reinforcement and the higher power consumption of nano-sized waste-derived filler composites, compared to micro-composites, are due to increased attraction between the particles caused by their smaller size. Exposure of polar functional groups, changes in crystallinity and increases in surface area that result from mechanical and/or chemical treatment (Gamble et al., 2012; Paul et al., 2007) increase the interaction between waste-derived fillers particles. Despite the dispersion method used, agglomerates of the nano-sized waste-derived fillers may form during drying due to this strong inter-particle interaction. This would result in lower final particle surface area and increase the energy required for uniform dispersion in the compound.

Other factors that influenced the mechanical properties and processability of hevea and guayule composites include structure, particles size distribution, filler alkalinity and reactivity with curing chemicals (Barrera and Cornish, 2016, 2015). Waste-derived fillers like ES and CFA possess unique and complex porous structures at the micro-scale (Fig. 7.17), that increase effective surface area and contribute to the observed reinforcement (Barrera and Cornish, 2016). These structural features maybe lost at the nano-scale. Broad particle size distribution of micro fillers allows better packing of the particles in the rubber, which generates compounds with lower viscosity than nano composites. Furthermore, high compound viscosity is obtained with the addition of highly branched aggregate structures of nano-sized particles (Gerspacher and Wampler, 2001; Khan and Bhat, 2014). Hence higher power was required to mix into the rubber carbon black and nano-sized waste-derived fillers compared to larger filler. Also, the
presence of terpene resins, such as those in GB, can act as plasticizers, which would increase ductility of the materials (Barrera and Cornish, 2015)

Fig. 7. 17: SEM micrographs of waste-derived filler particles. (a) Carbon fly ash; (b) eggshells

Given that curing conditions were the same for all the composites, pH and active surface of waste-derived fillers result in different performance properties particularly for guayule due to slower curing rate compared to hevea. Alkaline fillers like ES can cause faster curing rates and increased crosslink density which can improve modulus, tensile and tear strength (Barrera and Cornish, 2016; Byers, 2001). In contrast, the silanol groups found in CFA can react with the compounding ingredients and decrease the curing rate of the compound (Byers, 2001).
Although composites manufactured with GB required low mixing power, overall mechanical properties of composites containing loadings greater than 5 phr of GB were lower than other waste-derived fillers used. Furthermore, the amount of GB that could be incorporated into the master batch was limited, due to the low density of this material, which required higher volume fractions to obtain the same weight loadings. Currently there are other alternatives to generate added-value products from this residue such as the production of bio-oil through pyrolysis of the material (Boateng et al., 2010, 2009). Composites manufactured with nano-sized GB and CFA also higher moisture retention than ES or TP, due to their hydrophilic nature.

Different combinations of composite properties achieved with these co-filler systems are not usually achieved with a single conventional reinforcing filler. Enhancement of natural rubber tensile strength by carbon black for instance, is generally paired with a decrease in flexibility of the material. Composites with higher flexibility at comparable strength were obtained with some of the waste-derived fillers used. In addition decreases in power consumption were obtained even with the replacement of a small fraction of carbon black in the composite. This could really benefit the economics and sustainability of large scale rubber product manufacture.

Many researchers have focused on biobased nano-sized particles due to the inherent benefits of large surface area of the particles and lower carbon footprint (Angellier et al., 2005a; Bitinis et al., 2013; Bras et al., 2010; Visakh et al., 2012). However, commercial application of these nano fillers is still restricted by their limited availability, high production cost and strong tendency to agglomerate (Abraham et al.,
2011; Angellier et al., 2005b; Szeluga et al., 2015). The partial replacement of carbon black with micro-sized waste-derived fillers, which can be made at a lower cost than nano-sized particles, without loss of mechanical properties, suggests a potential added-value for these highly abundant materials.

7.5. Conclusion

Partial replacement of carbon black with waste-derived fillers can generate material with performance characteristics suitable for commercial applications while adding value to agro-industrial residues and offering low cost and a sustainable alternative source of fillers for natural rubber products. Such fillers would supplement increasing demand for fillers and mitigate projected shortages. Positive impacts on overall manufacturing costs of rubber products may be achieved through the use of micro-sized fillers that can be cheaply made and also decrease power consumption during rubber compounding. Furthermore, optimization of curing profiles for each rubber and surface modification of the filler may result in materials with properties superior to those so far achieved.
Chapter 8: Conclusion

The main goals of this research were to improve the sustainability of natural rubber products, strengthen commercialization efforts of alternative natural rubber sources through development of composites containing agro-industrial residues as reinforcing fillers, and valorize wastes. Reinforcement of unfilled hevea and guayule rubber compounds was obtained at all loadings of most of waste-derived fillers, particularly composites containing micro and nano sized particles, including composites made without carbon black.

Some of the composites made by partial replacement of petroleum-derived carbon black with waste-derived fillers had superior or similar mechanical properties than those solely containing carbon black. Furthermore, the use of waste-derived/carbon black co-filler systems generated materials with unusual combinations of properties. An example of this was the higher flexibility at comparable strength of some of the composites containing micro sized eggshells and tomato peels. These combinations of properties are not usually achieved with a single conventional reinforcing filler, and reflect different physico-chemical interactions between the fillers and among the fillers and rubber. In addition, positive impacts in the overall manufacturing costs of rubber products may also be achieved from decreased power consumption during compounding of the rubber containing these alternative fillers.
Currently most research efforts on bio-based fillers have focused on the evaluation of nano sized particles due to their inherent benefit of large surface area per unit volume. However, commercial application of these nano-fillers is still restricted by their limited availability, high production cost and strong tendency to agglomerate. In this study, nano sized waste-derived fillers did not improve mechanical properties much beyond the micro sized particles. Furthermore, statistical analyses proved the contributions of various filler characteristics to the observed reinforcement. These results highlight the importance not only of high surface area, but combined mechanisms of reinforcement arising from the structural and chemical heterogeneities of the agro-industrial residues used. Micro sized fillers can be cheaply made from low cost waste materials and significant cost savings may be possible using such fillers. Nano-fillers are much more difficult and expensive to manufacture at a large scale than micro-fillers.

The reinforcement of hevea and guayule rubber with waste-derived fillers as co-fillers with carbon black, offers the potential to engineer materials with a varied combination of properties through modification of filler type, size and carbon black/waste derived filler ratio in the composite. Consequently, these fillers can be added not only to reduce cost, but to target specific performance requirements for elastomeric products. Moreover, waste-derived fillers represent a more sustainable, low cost source of fillers for natural rubber composites and could help alleviate increasing demand for fillers in the rubber industry, while reducing dependency in petroleum derivatives.
Chapter 9: Future Studies

This research highlights the potential of agro-industrial residues as alternative filler sources for natural rubber composites and provides a starting point for the development of new natural rubber composites. In addition, it demonstrated the importance of the contribution of filler characteristics in the overall reinforcement. Nevertheless further assessment of these complex systems is required to validate their functionality for commercial applications. This includes the evaluation of curing behavior for the optimization of crosslinking package for each formulation. In this study a standard compounding formulation was used for all composites. Characterization of polymer-filler interaction and filler-filler interaction are also required in order to gain further understanding of these systems. Combinations of different waste-derived filler in composites and/or surface functionalization could also lead to improvements in the performance observed and possibly allow further decrease of the carbon black fraction in the composite while retaining desired properties. Finally, additional material characterization, including degradability studies, analysis of dynamic properties and aging resistance need to be performed.
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