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CHLORAMINE DEVULCANIZATION OF WASTE RUBBER

By

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May 2023

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A Dissertation Approved On

March 31, 2023

by the following Dissertation Committee:

Dr. Gerold A. Willing, Dissertation Director

Dr. R. Eric Berson

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Dr. Thomas D. Rockaway

DEDICATION

This dissertation is dedicated to my parents

Mr. Douglas Kroeger

and

Mrs. Patricia Kroeger

who always went above and beyond to ensure I had the education required to succeed

And my son Liam Kroeger

who has inspired me to not give up through this long, arduous process

ACKNOWLEDGEMENTS

I would first like to thank my professor and advisor Dr. Jerry Willing for giving me this opportunity and for being patient with me over the long haul as we slowly built this technology out of almost nothing. I would also like to thank the other committee members Dr. Eric Berson, Dr. Jim Watters, and Dr. Tom Rockaway for encouragement and support over these nearly 9 years that I have been in the program. There are so many other people who helped over the years during my time on this project. A non-exhaustive list in somewhat chronological from the pre-Arduro days includes Taylor Combs, Marcus Schwarting, Samuel Kelty, Elizabeth Peeff, Sarah Metzger, Heather Evans, and Justin Jacobson.

I would also like to thank Ian Lowe and the Arduro investors and board of directors for putting their time and money into me and an idea that started in a lab in Ernst Hall. I would like to thank all the key Arduro team members who helped me over the years including again Sarah Metzger and Heather Evans but also Brady McCauley, Michael LaRoche, Cora Grief, Blake Clark, Kirsten Waits, Sneha Nainani, Sho Takaguchi, Joe Phelan, Natalie Tuttle, Austin Wu, Evan Swofford, Phil MacLennan, Ian Byberg, Ally Stamper, and Grace Gehlhausen. Here’s to hoping that we can finish what we started when we set out to commercialize this technology.

I’d like to thank my mom and dad for putting me on this path and for my dad telling me to use my brain instead of my brawn. Dad, you are missed every day.

Finally, I’d like to thank my girlfriend, Heather Evans. She supported me through what was the most impossible time in my life and in places where I felt like I would never be able to finish this dissertation. Her love and care over the last year has made the difference.

ABSTRACT

CHLORAMINE DEVULCANIZATION OF WASTE RUBBER

Patrick Douglas Kroeger

May 13, 2023

The disposal of waste rubber, especially tire rubber, continues to be a challenge two decades into the 21st century. Devulcanization research has a rich history, yet no technology to date has had a significant impact in promoting rubber sustainability. Consequently, the majority of end-of-life tires (ELTs) are either disposed of as tire-derived fuel or in landfills. Chloramine devulcanization of waste rubber could be a solution to this rubber problem. The chloramine devulcanization process occurs at low temperature, low pressure, and with less hazardous chemicals than many other previous methods of devulcanization. Further, both chloramine recovered carbon black, CrCB, and devulcanized rubber, CdR, can be recovered as separate products which has not been demonstrated before by other devulcanization methods.

Initial analysis of CdR in this work showed that it was malleable and formable, indicating that crosslinking was no longer present in the material. The CdR was then analyzed using FTIR and NMR to determine the presence of functional groups. The spectroscopy showed evidence of alkanes, alkenes, and aromatic groups in the recovered CdR. Evidence of double bonded carbon functional groups confirmed that CdR had the capability of being revulcanized into new rubber compounds.

TGA and SEM analysis of CrCB produced by a pilot scale devulcanization process showed a particle size of 0.5-20 µm and a polymer-to-carbon black ratio reduced to 0.89 from 1.54 in the input micronized rubber. Based on this analysis, a proposed mechanism for the breakup of the micronized rubber particle into CrCB and CdR stated that chloramine diffuses into the rubber matrix between carbon black aggregates. The majority of sulfur crosslink breakage occurs in gaps between these aggregates and crack propagation causes the small 0.5-20 µm CrCB particles to break away from the larger 400 µm micronized rubber particle in solution.

Using this mechanism as a framework, the chloramine-rubber reaction was analyzed to determine whether the system is rate limiting or diffusion limiting. The analysis showed that at pH values below 7 the reaction is diffusion limiting, but at pH 8 and at a temperature of 80 °C the reaction is rate limiting with a Thiele modulus of 0.79.

CrCB was tested in ASTM standard carbon black tests and compounded in four rubber compound recipes. The CrCB analytical testing showed nitrogen surface area of 8.2 m^2/g. Physical testing of CrCB compounded in rubber in a generic natural rubber/styrene butadiene rubber compound showed a decline in reinforcement against an N550 control. However, testing in a dock fender application recipe showed that CrCB had no loss in performance versus the N650 carbon black control. These performance inconsistencies indicate that CrCB's reinforcement mechanism may differ from virgin carbon black and that sulfur crosslinking with residual polymer may be occurring in some of the tested applications. Overall, CrCB material may be appropriate to replace virgin carbon black in rubber applications where N650-N990 carbon black is used.

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CHAPTER 1 – INTRODUCTION

Rubber is ubiquitous. We encounter it every day as we drive our cars, put on our shoes, plug in our smartphones, and even cook our food. Yet, as scientists and engineers push toward making our activities and the way we interact with the world around us more sustainable, the rubber industry (producers, consumers, disposers) lags far behind in the global push for sustainability. This is not the result of a lack of effort by the industry, however. Patent filings related to waste rubber sustainability, recycling, disposal, etc. have increased steadily since the 1970s (1). In fact, the first patents on devulcanization methods were filed just 16 years after Charles Goodyear discovered the process in 1839. Rather, the lack of meaningful progress is due to the unique chemistry of vulcanized rubber, and the sulfur crosslinks present within the rubber polymer matrix. Our research to-date has shown that devulcanization of sulfur vulcanized rubber by aqueous chloramine could be a pathway to rubber sustainability.

1.1 Overview of The Rubber Problem and Current Solutions

It can be difficult to grasp the scale of the world's rubber production. The world rubber industry produced 28.8 million tons of rubber in 2019 and, despite a decrease from 2018, both production and consumption have been increasing steadily over the past seven years (2).

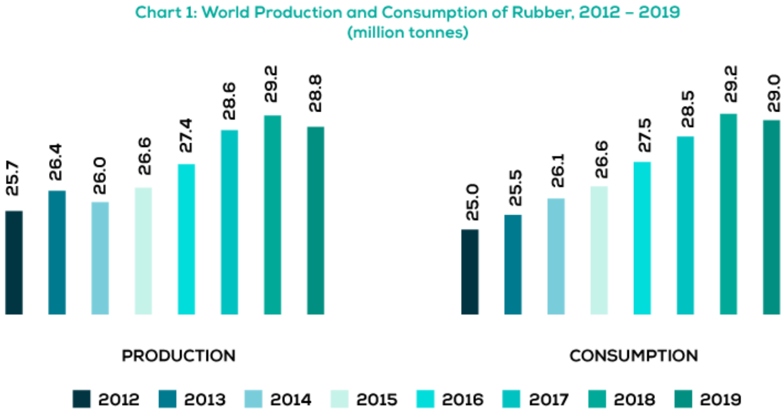


Figure 1 - World Rubber Production 2012-2019

Rubber production is not homogenous, but rather, consists of many types designed for use in a wide range of applications. Natural rubber (polysisoprene), styrene butadiene rubber, polybutadiene rubber, neoprene rubber, nitrile rubber, EPDM rubber, and halobutyl rubber are a few of the types of rubber that are used in applications ranging from tires to gloves. For each rubber type however, there is a commonality; virtually all will either be burned or landfilled when they reach end-of-life (3).

1.1.1 Waste Rubber – End of Life Tires

While it is true that all rubber products, regardless of rubber type, lack suitable pathways for sustainable disposal or re-use, end-of-life tires (ELTs) are the premier example of rubber waste and no discussion on rubber sustainability is complete without addressing them. Over 1 billion ELTs are generated each year and there are an estimated 4 billion ELTs currently landfilled worldwide. In 2005, 292 million ELTs were generated in the US, with 53% of those tires burned for energy recovery, 33% shredded or modified to use as filler in civil engineering projects or subjected to post processing, and 14% sent to landfill. Of course, not all disposal methods are inherently negative. Like most solutions, there are positives (tires that are burned replace oil or coal that would have been mined) and negatives (the air emissions from burned tires are as dirty as coal). However, none of these current solutions can keep pace with the relentless growth rate of the tire and rubber industry, in general (4). Without comprehensive and sustainable solutions, the quantity of tires, and rubber products in general, disposed using non-sustainable methods will continue to increase.

1.2 Scope of this Research

The chloramine devulcanization technology has the potential to be part of the solution to the world's rubber problem, but development and maturation of this field of research will take time. Most sustainable methods of rubber recycling reviewed as part of this work, including devulcanization and pyrolysis, needed 20 to 50 years of development to have an impact and have also seen development work completed by numerous different parties in both academia and industry. As such, the purpose of this research is not to answer all questions regarding chloramine devulcanization, but rather provide the foundation for the long-term development of the chloramine devulcanization technology. Consequently, this research focuses on the following areas:

1. Efficacy – Prior work showed that chloramine caused rubber degradation and that there was the potential to recover high molecular weight material from solutions of chloramine that had been exposed to rubber (5; 6). The first part of this work expands on that initial research and examines the efficacy of chloramine devulcanization and analyzes the condition of material recovered from the devulcanization process.

2. Physical Mechanism and Rate – Building on the findings from the chapter on efficacy, the second part of this work analyzes the recovered carbon black (referred to as chloramine recovered carbon black or CrCB) and devulcanized rubber (referred to as chloramine devulcanized rubber or CdR) material produced from chloramine devulcanization and proposes a physical mechanism for the devulcanization and breakup of the vulcanized rubber particle. Additionally, the rate of chloramine devulcanization is analyzed to assess whether the reaction is rate limited or diffusion limited.
3. Recovered Materials Analysis – The third part of this work analyzes the materials recovered from the chloramine devulcanization process. The value of a devulcanization technology is directly tied to the value of the materials that can be produced from it. CrCB is the focus but the status of testing on CdR is also covered. CrCB is first analyzed using industry standard carbon black tests and then its reinforcement capability in several rubber compounds is evaluated against virgin carbon black.

1.3 Organization of this Work

The research portion of this dissertation, Chapters 3-5, consists of three separate research projects conducted over the course of approximately 8 years. Chapter 3 covers the research on chloramine devulcanization efficacy that was completed in 2013-2015. Chapter 4 is the product of research and development conducted from 2016-2022 that focused on scaling the lab scaled devulcanization to a pilot scale. The last 3 years of this development (2019-2022) occurred in partnership with Arduro Sustainable Rubber Inc., the startup that has licensed chloramine devulcanization technology from the University of Louisville. Much of the analysis in this section is the direct result of prototyping and refining manufacturing unit operations to devulcanize and then separate out the resulting devulcanization products. Finally, Chapter 5 covers work done in 2021-2022 to test the CrCB and CdR that has been produced by the pilot scaled chloramine devulcanization process. Prior to Chapters 3-5, Chapter 2 thoroughly introduces rubber chemistry, rubber compounding and testing, current methods of rubber recycling and reuse, aqueous chloramine, and the prior work to understand the effect of chloramine on sulfur crosslinked rubber.

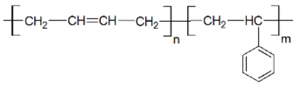
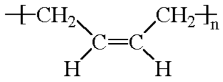
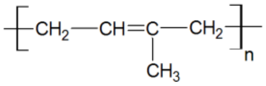
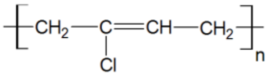
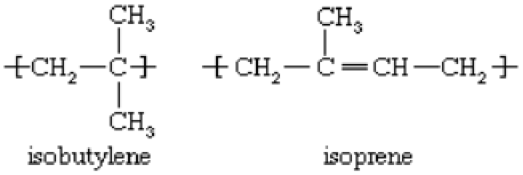
CHAPTER 2 – BACKGROUND

2.1 Rubber Chemistry, Compounding, And Physical Properties

2.1.1 Rubber Types and Vulcanization

Rubber is not monolithic. The chemistry of specific elastomeric polymers used in rubber applications vary widely but are all high molecular weight amorphous hydrocarbon polymers. Table 1 shows the chemical formula for the repeat unit of a few common types of rubber. Average molecular weights for these polymer types can vary but are usually within the range between 10^4 and 10^6 g/mol. For example, a 2002 patent from The Goodyear Tire and Rubber company reported that “a high molecular weight version of styrene butadiene rubber (SBR) has a weight average molecular weight which is within the range of about 1,000,000 to about 1,500,000; and wherein the low molecular weight styrene-butadiene rubber has a weight average molecular weight which is within the range of about 120,000 to about 260,000” (7).

Table 1 - Chemical Composition of a Few Base Rubber Types

Polymer	Repeat Unit
Styrene Butadiene Rubber	
Polybutadiene Rubber	
Polyisoprene (Natural Rubber)	 $\left[\mathrm{CH_2-CH=C(CH_3)-CH_2}\right]_n$
Chloroprene (Neoprene Rubber)	 $\left[\mathrm{CH_2-C(Cl)=CH-CH_2}\right]_n$
Isobutylene-isoprene (Butyl Rubber)	 $\mathrm{-[CH_2-C(CH_3)_2]-}$ $\mathrm{-[CH_2-C(CH_3)=CH-CH_2]-}$

Although the elastomeric polymer molecules have high molecular weight, they do not form a crystalline structure like many thermoplastic polymers and each molecule can move independently on a molecular scale, with respect to the other polymer molecules in the rubber compound. This causes rubber in its virgin state to be sticky and malleable with properties not suitable for use in many applications. This issue is solved by vulcanization, where sulfur is added to the rubber polymer and heated to temperatures of 140-160 °C (8). During vulcanization, the sulfur atoms are rearranged to form mono, di, and polysulfidic crosslinks between polymer molecules at carbon-carbon double bond sites, creating a dense matrix where every polymer molecule is connected to every other polymer molecule. It is through the creation of this interconnected network that the rubber gains the physical properties that make it suitable in applications such as tires.

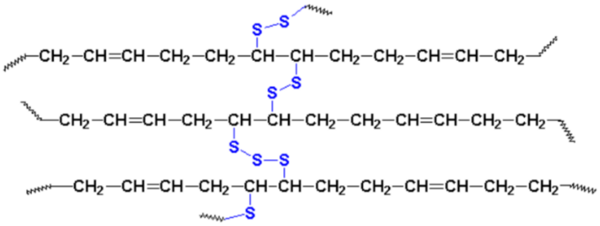


Figure 2 - Sulfur Vulcanization of Rubber

Although this interconnected polymer matrix is essential for giving rubber useable properties, it also makes it impossible to recycle using conventional methods applied to thermoplastic polymers. Thermoplastic polymers, such as polyethylene and polypropylene, that can be found in everyday items such as water bottles and plastic bags do not have crosslinking present, but rather form a crystalline structure that provides resilience. Without crosslinking present, the thermoplastic polymer can be melted and reformed into another product after the initial product has been recycled. Vulcanized elastomeric polymers, however, cannot be melted and reformed. The crosslinking restricts the movement of polymer molecules, not allowing them to move freely when heated and enter the melt phase (3). As additional heat is added, carbon-carbon bonds begin to break, destroying the polymer structure, and, in cases where an oxygen atmosphere is present, burn. This unique chemistry is the source of the world’s rubber problem and despite 150 years of research on devulcanization the problem has not been adequately solved. However, there is more complexity to rubber recycling than just breaking the sulfur crosslinks. The many components found in a rubber compound formulation add further complexity and are introduced in the next section.

2.1.2 Rubber Compound Formulations

The rubber products that you use daily are composed of what is called a rubber compound, consisting of 2 primary ingredients (elastomeric polymers and reinforcing fillers) and usually 5-7 secondary ingredients (vulcanizing agents, antioxidants, antiozonants, etc.). Table 2 shows an example of a basic compound. This rubber compound recipe was produced by the Ashtabula Rubber Company for the AWWA's chloramine degradation research.

Table 2 - Basic Rubber Compound Formulation

Ingredient	Function	PHR
SBR 1502	Base Polymer	100
SRF N762	Filler (Carbon Black)	90
Sun 4240	Extending Oil	10
Sulfur	Vulcanizing Agent	1
Zinc Oxide	Zinc Oxide	5
Stearic Acid	Stearic Acid	1
Santocure	Accelerant	1

The relationship between the elastomeric polymer and reinforcing filler is analogous to the relationship between concrete and steel rebar, but it is so much more than that. Although separately, polymer resists tensile stress well and filler resists compressive stress well, the polymer-filler interactions that occur on a molecular level give tensile reinforcement to the rubber compound that is greater than the sum of the individual parts. There are thousands of different rubber compound formulations, and no two rubber compound formulas are alike. Many applications, including tires, are composed of multiple different compound formulations and most are more complex than the recipe shown in Table 2. Figure 3 is a visual representation of the different rubber compounds in a tire.

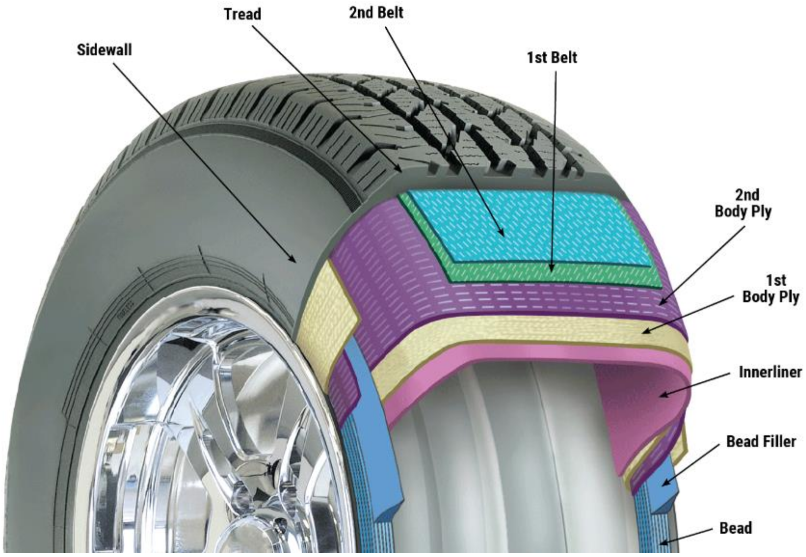
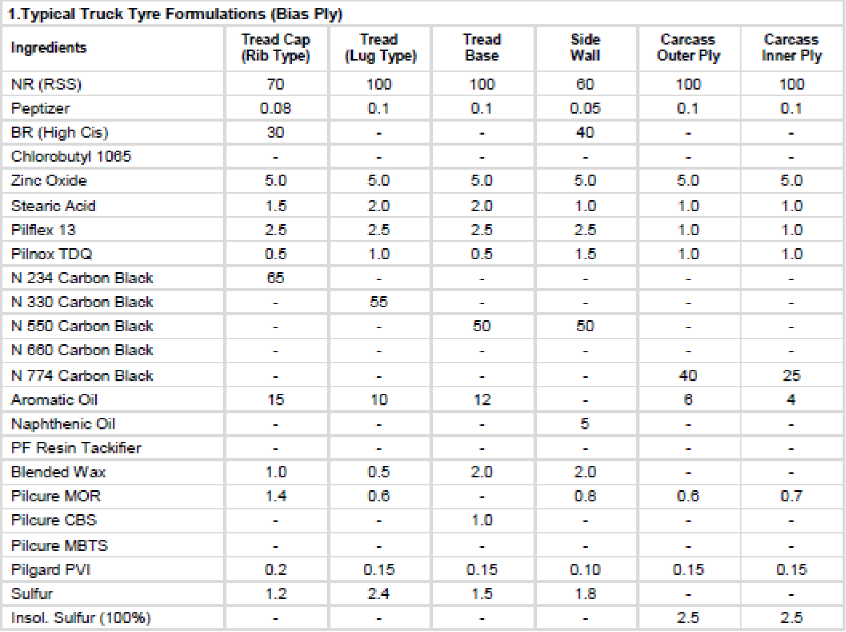


Figure 3 - Rubber Formulations in a Tire (9)

Each of the nine components listed in Figure 2 represents a unique rubber formulation and some include non-rubber reinforcing materials like nylon, steel, and Kevlar. Styrene butadiene rubber (SBR), butadiene rubber (BR), and natural rubber (NR) are typically used however the innerliner, responsible for preventing air leakage from inside the tire, is typically composed of halobutyl rubber (9).



1.Typical Truck Tyre Formulations (Bias Ply)

Ingredients	Tread Cap (Rib Type)	Tread (Lug Type)	Tread Base	Side Wall	Carcass Outer Ply	Carcass Inner Ply
NR (RSS)	70	100	100	60	100	100
Peptizer	0.08	0.1	0.1	0.05	0.1	0.1
BR (High Cis)	30	-	-	40	-	-
Chlorobutyl 1065	-	-	-	-	-	-
Zinc Oxide	5.0	5.0	5.0	5.0	5.0	5.0
Stearic Acid	1.5	2.0	2.0	1.0	1.0	1.0
Pilflex 13	2.5	2.5	2.5	2.5	1.0	1.0
Pilnox TDQ	0.5	1.0	0.5	1.5	1.0	1.0
N 234 Carbon Black	65	-	-	-	-	-
N 330 Carbon Black	-	55	-	-	-	-
N 550 Carbon Black	-	-	50	50	-	-
N 660 Carbon Black	-	-	-	-	-	-
N 774 Carbon Black	-	-	-	-	40	25
Aromatic Oil	15	10	12	-	6	4
Naphthenic Oil	-	-	-	5	-	-
PF Resin Tackifier	-	-	-	-	-	-
Blended Wax	1.0	0.5	2.0	2.0	-	-
Pilcure MOR	1.4	0.6	-	0.8	0.6	0.7
Pilcure CBS	-	-	1.0	-	-	-
Pilcure MBTS	-	-	-	-	-	-
Pilgard PVI	0.2	0.15	0.15	0.10	0.15	0.15
Sulfur	1.2	2.4	1.5	1.8	-	-
Insol. Sulfur (100%)	-	-	-	-	2.5	2.5

Figure 4 - Truck Tire Formulations (10)

Figure 4 further illustrates the significant complexity across the multiple sections of a truck tire. Different mixtures of NR and SBR, multiple grades of carbon black filler, and slight differences in the additives and curing package are all designed to slightly modify properties. The breakdown of different formulations in a tire shown in Figure 3 and Figure 4 conveys both the complexity of some rubber products and the challenge that many rubber recyclers face. When a mix of passenger and truck tires across multiple manufacturers is recycled, especially in the case of devulcanization, the material produced from that contains a mixture of all types of rubber, all grades of carbon black, and all fillers that were added. A mixed recycled product, devulcanized rubber for example, has less value inherently since it is attempting to displace a specific target blend of pure virgin rubber. As a result, that devulcanized rubber needs an application that is insensitive enough to base rubber type, and that is not considering the loss of physical properties that are inherent to all recycled/reused products. Further, even a recycled material from a singular rubber source with residual fillers and vulcanization agents can make that new rubber compound perform differently than virgin material during the curing (vulcanization) process and alter characteristics of the final product. The importance and the impact of the primary rubber filler, carbon black, is explored in more detail in the following section.

2.1.3 Carbon Black

The purpose of rubber fillers is to enhance the properties of rubber products. Fillers and the effect they have on vulcanized rubber properties can vary widely but can be generally classified as reinforcing or non-reinforcing. Non-reinforcing fillers, clays for example, are typically used in small quantities, if at all, and are included as a cost saving measure. Generally, non-reinforcing filler enhancements of rubber properties are insignificant.

Reinforcing fillers are of considerably more interest when discussing rubber properties. Unfilled vulcanized rubber typically exhibits significantly lower tensile strength, tear resistance, and abrasion resistance among other physical properties of importance. This behavior can be seen in Figure 5 where the unfilled rubber is stretched easily to break at ~2 MPa tensile strength. The CB reinforced material on the other hand shows a significant increase in strength compared to the unfiled material with a tensile strength of 25 MPa, and significantly less strain (elongation %) at break (11).

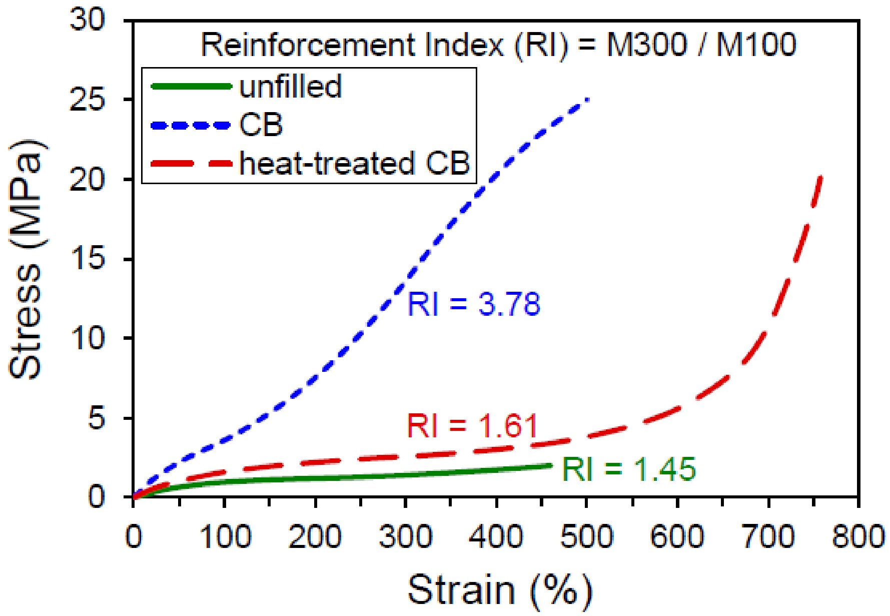


Figure 5 - Stress vs Strain Curves for Unfilled, CB filled, and heat-treated CB filled rubber

Carbon black is by far the most prevalent filler used in rubber compounding. Global carbon black production capacity was approximately 16 million metric tons per year in 2017 with approximately 93% of that going to the rubber industry. Unsurprisingly, of that 93% used in rubber products, 73% was used in tires (11).

Carbon black is a nuanced material and the mechanism of its reinforcement with rubber is complex. The paper *Nature of Carbon Black Reinforcement of Rubber: Perspective on the Original Polymer Nanocomposite* by Robertson et. al is a comprehensive review of over 100 papers studying the morphology of carbon black and its effect on rubber properties (11). The information presented here is taken primarily from that source. Carbon black is comprised of aggregates of small spherical carbon particles. TEM images of both the primary particle and the aggregates are seen in Figure 6.

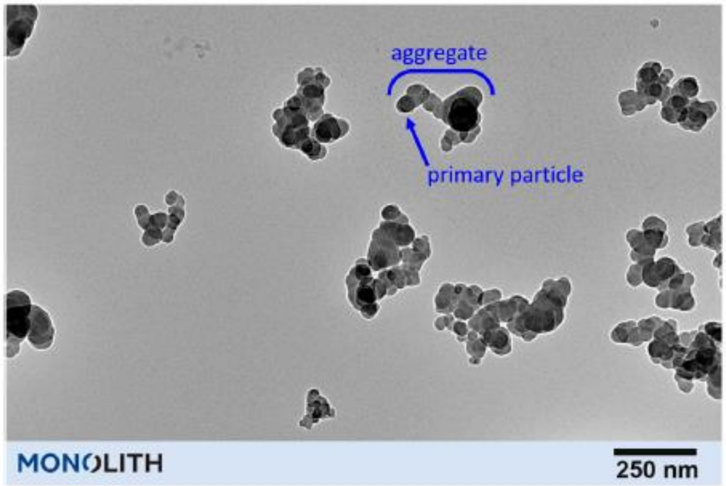
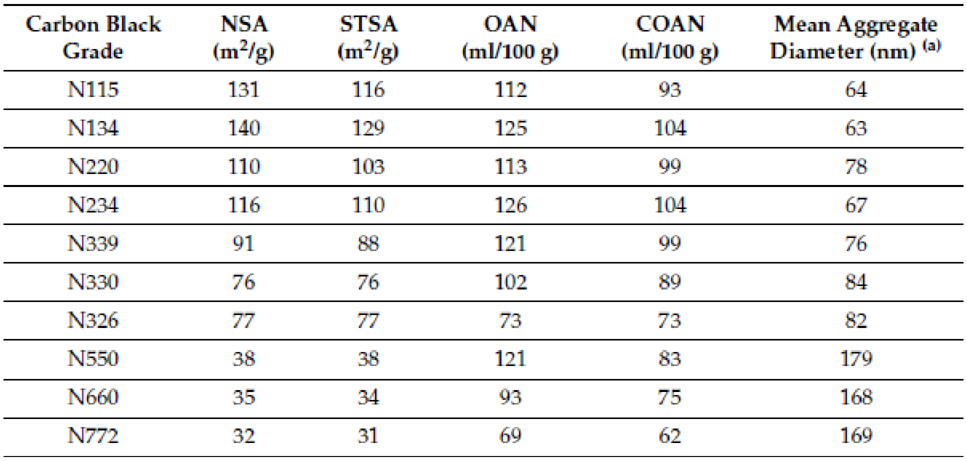


Figure 6 - Carbon Black Aggregates and Particles for an N660 Carbon Black

The size of the primary particle and aggregate are the primary driver of carbon black reinforcement. In general, increased carbon black surface area per unit mass leads to more reinforcement in rubber and the smaller the aggregates and primary particles the greater the surface area per unit mass. Carbon black is graded by manufacturers between N100-N900 types based on the overall reinforcement capability of the material. Hence, higher grades of carbon black (N100-N300) typically have smaller aggregates and primary particles than lower grades (N500-N900).



Carbon Black Grade	NSA (m^2/g)	STSA (m^2/g)	OAN (ml/100 g)	COAN (ml/100 g)	Mean Aggregate Diameter (nm) [(a)]
N115	131	116	112	93	64
N134	140	129	125	104	63
N220	110	103	113	99	78
N234	116	110	126	104	67
N339	91	88	121	99	76
N330	76	76	102	89	84
N326	77	77	73	73	82
N550	38	38	121	83	179
N660	35	34	93	75	168
N772	32	31	69	62	169

Figure 7 - Mean Aggregate Diameter Across Different Carbon Black Grades

Figure 7 shows a breakdown of mean aggregate diameter for a range of carbon black grades. The data is also displayed against parameters designed to evaluate both the particle and aggregate size. Nitrogen surface area (NSA) and statistical thickness surface area (STSA) (calculated from NSA) are a measure of primary particle size. Oil adsorption number (OAN) and compressed oil adsorption number (COAN) are a measure of the aggregate structure and size. As seen above, the values for all four tests increase as mean aggregate diameter decreases.

Primary particle size and surface area are not the only factors affecting reinforcement. The second element of the reinforcement mechanism of carbon black is chemical surface activity. The carbon black primary particle is not an amorphous monolith of carbon atoms but rather a “quasi-crystalline structure”. The interior of this structure consists of amorphous carbon surrounded by an exterior of 1.5 nm x 1.5 nm x 1.5 nm cubic graphene sheets. Typically, a primary particle consists of hundreds or thousands of these graphene sheets arranged in a spherical pattern. Figure 8 shows a detailed look at the structure of the carbon black primary particle.

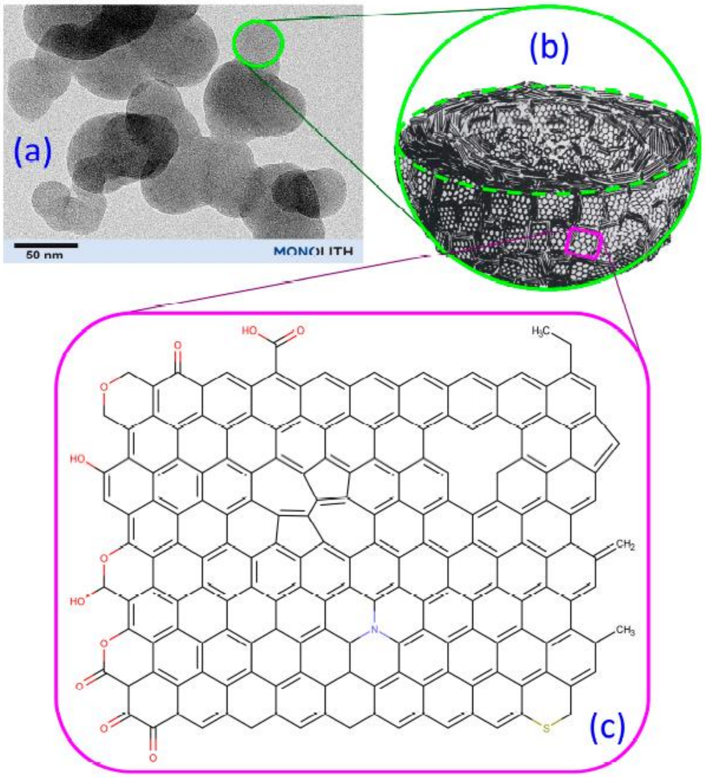


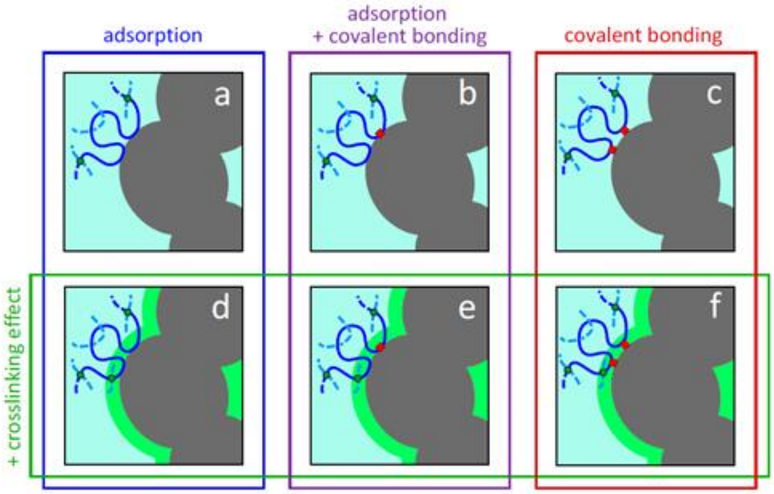
Figure 8 - Molecular Structure of Carbon Black

Within and throughout this structure are functional groups consisting of oxygen, hydrogen, nitrogen, and sulfur atoms. Further, reactive unconjugated double bonds are present intermittently. This overall chemical structure including the additional function groups aid in reinforcement in rubber compounds. Covalent bonds are formed between these active sites during the rubber compound mixing and vulcanization process. Although physical adsorption and van der Waals interactions dominate reinforcement and occur at an estimated 10-100x frequency, a single covalent bond has the same bond energy as approximately 30 physical interactions and thus contributes significantly to reinforcement. Elimination of these functional groups via heat treatment at 900-1200 °C was shown to reduce reinforcement capability of the carbon black in a rubber compound when the primary particle and aggregate structures were observed to be unchanged. The

Figure 5 performance shows a significant loss of reinforcement properties in the heat-treated carbon black versus the non-heat-treated version.

The third significant mechanism of carbon black reinforcement is related to sulfur crosslink density. Typically, virgin carbon black, regardless of grade, contains 1-2% sulfur and it has been shown that sulfur can directly bond with carbon black. Blokh and Melamed showed that after direct reaction of sulfur with carbon black at vulcanization temperatures of 145 °C, the sulfur could not be removed even after 25 days of benzene extraction (12). It is thought that because of sulfur content within the carbon black and its mechanism of bonding with both carbon black and rubber that there is higher sulfur crosslink density at the rubber-carbon black interface than at other places in the rubber matrix.

Roberston et. al presented 6 different reinforcement mechanisms (shown in Figure 9) and states that out of all the possible reinforcement mechanisms, schematic e is most likely.



Possible polymer–filler interaction/reaction scenarios for crosslinked elastomer reinforced with nano-structured filler aggregates. A portion of filler aggregate is illustrated (gray) with one full primary particle shown that is fused to two other primary particles. The solid blue line represents a polymer network chain between crosslinks (green dots). Covalent polymer–filler bonds are indicated with red squares. The green halo surrounding the filler aggregate in (**d**–**f**) signifies a region of increased crosslink density due to proximity to filler, with an additional crosslink (green dot) therein compared to (**a**–**c**).

Figure 9 - Roberston et. al Possible Polymer Filler Interactions (11)

In schematic e, reinforcement is a combination of (1) physical adsorption of the polymer on the carbon black surface, (2) covalent bonding between the surface-active sites and polymer, and higher sulfur crosslink density at the carbon black-rubber interface. In addition to the sulfur cross linkage mechanism, this physical and chemical mechanism of reinforcement both enables and enhances vulcanized rubber properties and makes it challenging to recycle. The current landscape for waste rubber recycling and reuse is discussed in the following section.

2.2 Rubber Recycling

A report titled “Managing End-of-Life Tires” produced by the World Business Council for Sustainable Development in 2007 states that approximately 1 billon end-of-life tires (ELTs) are generated globally each year and as of 2007 an estimated 4 billon ELTs were found in landfills and stockpiles (4). Essentially one passenger tire per person is discarded each year in the developed world. Although these figures may seem bleak, significant progress has been made in re-routing tires from landfills over the last 50 years.

The primary destination for non-landfilled ELTs is tire-derived fuel (TDF). The same 2007 study showed that more tires in the US are sent to TDF than all other recycle/reuse methods combined. TDF is a better solution than sending tires to landfills, but as a fuel source is not altogether different than coal. With more focus on sustainable energy and greenhouse gas reduction, major players in the rubber industry continue to look for better methods of sustainable tire recycling and reuse.

	Millions of ELTs generated per year (excluding export and retread)	Of those tires that do not go to export or retread, they are destined for:			Specific reuse/ disposal/ recovery data not available	Year	Sources
		Energy recovery (%)	Civil engineering uses or material recovery (%)	Landfill, stockpiled, discarded waste or other (%)			
USA	**292**	53	33	14	n/a	2005	Estimates based on data from Rubber Manufacturers Association (RMA)
Europe	**250**	41	43	16	n/a	2006	Estimates based on data from European Tyre & Rubber Manufacturers' Association (ETRMA) Europe (EU 27 plus Norway and Switzerland)
China	**112**	n/a	n/a	n/a	100		Various newspaper articles including Recycling Today and Hong Kong Trade Development Council
Japan	**80**	70	15	15	n/a	2006	Estimates based on data from Japan Automobile Tyre Manufacturers Association Inc. (JATMA)
Mexico	**30**	0	90	10	n/a	2004	"Mexico pays cement industry to burn scrap tires" www.ecoamericas.comm/en/story/.aspx?id=569
Brazil	**27**	69	13	18	n/a		Associação Nacional da Indústria de Pneumáticos (ANIP), Instituto Brasileiro de Geografia e Estatística (IBGE)
South Korea	**23**	77	16	7	n/a	2003	Korea Tire Manufacturers Association (KOTMA)
Canada	**22**	20	75	5	n/a	2003	Pehlken A. and E. Essadiqi, Scrap Tire Recycling in Canada, 2005.
Australia	**20**	22	8	70	n/a	2006	URS, Market Failure in End-of-Life Tyre Disposal, report for the Department of Environment and Heritage, September 2006 (see also www.environment.gov.au/settlements/waste/tyres/index.html).
Malaysia	**14**	n/a	n/a	n/a	100		What to do with old tires? Lim J.
South Africa	**12**	n/a	n/a	n/a	100	2003	"Fixing a Tyred Environment", Die Burger, 6 April 2003
Iran	**10**	n/a	n/a	n/a	100	2006	Iran daily newspaper online (/www.iran-daily.com/1385/2586/html/focus.htm)
Israel	**7**	n/a	n/a	n/a	100	2003	Ministry of the Environment, Israel "Waste Tires : A Case Study", Environmental e-bulletin September 2003, Issue 2 (see also www.sviva.gov.il)
New Zealand	**4**	0	15	85	n/a		Estimates taken from "Product Stewardship Case Study for End-of-Life-Tyres" by URS for the Ministry of the Environment (NZ) 2006

For USA, Europe and Japan, ELTs destined for export and/or retread are excluded from the volume of ELTs generated per year.

Figure 10 - Global ELT Disposal Methods 2007

Other methods of waste rubber and ELT disposal are civil engineering projects, ground rubber applications, pyrolysis, and devulcanization. The strength of whole tires makes it extremely suitable for projects such as creating embankments, backfill for walls, field drainage, and crash barriers, among other civil engineering uses and ground up rubber has been used in asphalt, running tracks, sports fields, and playground mulch. However, pyrolysis and devulcanization are focused on here since those methods seek to reuse the components of waste rubber in new rubber applications with the goal of creating a circular, sustainable economy.

2.2.1 Pyrolysis for Recovery of Carbon Black

Pyrolysis is a thermal decomposition process where high molecular weight molecules (i.e. polymers) decompose into lower molecular weight molecules in an inert atmosphere. Typically, this is seen as a two-step process where first the polymer decomposes and then the resulting low molecular weight material evaporates and separates from non-evaporative material. When a vulcanized rubber compound is pyrolyzed, the base polymer, whether NR, SBR, BR or other, decomposes and evaporates along with the extending oils and leaves carbon black, inorganic compounds such as zinc, steel, silica, and calcium, and a small amount of carbonaceous residue behind (13). Revisiting Table 2 and further breaking out the formula by weight percent shows that approximately 52% of the rubber would decompose and evaporate under pyrolysis leaving the remaining 47% of carbon black, zinc and other non-volatile inorganic compounds. This compound in Table 3 contains slightly more carbon black than the average tire compound. The ratio of pyrolytic oil to carbon black residue in tire samples is usually closer to 57/43.

Table 3 - Weight % of Components of a Rubber Compound

Ingredient	Function	PHR	Wt %
SBR 1502	Base Polymer	100	48.1
SRF N762	Carbon Black	90	43.3
Sun 4240	Extending Oil	10	4.8
Sulfur	Vulcanizing Agent	1	0.5
Zinc Oxide	Zinc Oxide	5	2.4
Stearic Acid	Stearic Acid	1	0.5
Santocure	Accelerant	1	0.5

The low molecular weight oil recovered from tire pyrolysis is typically of low value and is often used by pyrolysis manufacturers to fuel the pyrolytic furnaces. The carbon black recovered from tire pyrolysis (PrCB), is more valuable, however.

Typically, PrCB has lower reinforcement capability than virgin carbon blacks (vCB) in rubber applications. PrCB is composed of a mix of vCB grades and contains an irregular distribution of primary particle sizes and larger aggregate sizes than vCB. Two studies looking at PrCB particle size and structure found that primary particles were found in 3 distributions (80-115 nm, 212-253 nm, and 418-474 nm) and the average aggregate size of 10 μm was much larger than for N770 vCB (2 μm) (14) (15). The study by Huang et. al also found that the additional inorganic residue and carbonaceous material cause the surface of the PrCB to have “lower graphite-like character when compared with commercial carbon black (14). Surface activity is also affected by the heat treatment. Robertson noted in *Nature of Carbon Black Reinforcement of Rubber* that heat treated carbon blacks have lower reinforcement properties and concluded it was likely due to loss of surface activity. All these factors contribute to PrCB having lower reinforcement capability. This loss of reinforcement is usually observed as loss of modulus performance when compounded in rubber. A 2022 study showed that even though the tensile strength of PrCB was comparable to N660 and N770 vCBs, the 100% and 300% modulus and elongation % at break were significantly worse than the vCB.

The pyrolysis of tire rubber is often completed in industrial kilns and ovens at temperatures between 500-800 °C. A 2004 paper by Li et. al described the continuous production of PrCB from scrap tires in a rotary kiln dryer. This process showed that oil yield and conversion of waste rubber into products was maximized at 500 °C with PrCB yield of 39.8% weight based on the input rubber. That manufacturing process produced a

PrCB with a relatively high NSA of 89.1 m^2/g (16).

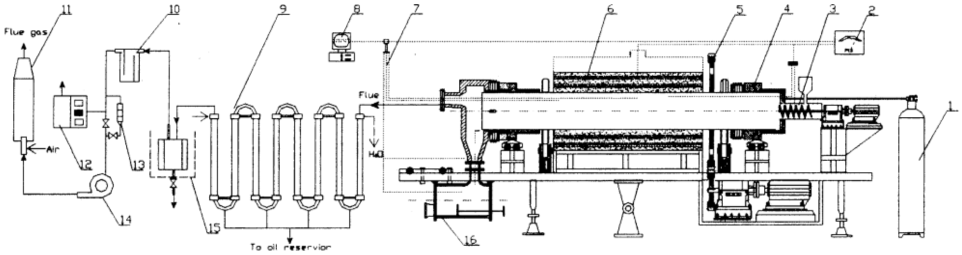


Figure 1. Schematic of a pilot-scale continuous rotary kiln pyrolysis reactor: 1, purge-gas tank; 2, PID controller; 3, supply and screw feed; 4, mechanically frictional seal; 5, gear wheel; 6, external electric heater; 7, thermocouples; 8, computer; 9, primary packed condenser; 10, filter; 11, postcombustor; 12, gas sampling; 13, gas flowmeter; 14, induced fan; 15, secondary condenser with ice−water mixture; 16, collector of solid residue.

Figure 11 - Schematic of a Waste Rubber Pyrolysis Reactor

Other reactor styles such as fluidized bed reactors or batch ovens have also been used. A significant technical challenge with pyrolysis is maintaining an even temperature throughout the reactor and throughout the rubber within the reactors. Further, the pyrolysis process produces poly-aromatic hydrocarbons, which are known to be carcinogenic, and efforts are underway globally to reduce production and emission of those compounds.

As of Q4 2022, the PrCB industry is a growing space with some significant players in the US market specifically. Boulder Industries, Delta Energy, Contec, and Pyrolyx are all manufacturers in the recovered carbon black space. Boulder claims that their PrCB has been shown to reinforce rubber like N600-N700 carbon blacks and is “used in over 300 products today” (17). In 2019, TireReview.com reported that Bridgestone Americas had begun the first at-scale use of PrCB in the tire industry after partnering with Delta Energy. As of the reporting date of November 26, 2019, Bridgestone had purchased 235 metric tons of CB and planned to use more in the coming years. Bridgestone was using D-E PrCB in tire compounds for both passenger and agricultural applications (18).

The PrCB product is an example of a successful method of recycling tires and creating valuable products. The pyrolysis drawback, aside from the performance and manufacturing challenges, is the relatively low yield of 40% that is inherent to its process. The chloramine devulcanization process seeks to produce both a recovered carbon black (CrCB) and a devulcanized rubber product from waste tires. Devulcanization is covered in the next section, including a brief look at the history of efforts to reuse waste rubber material.

2.2.2 Devulcanization

2.2.2.1 History of Devulcanization

Although Mesoamericans achieved it in 1600 BCE and Thomas Hancock submitted a patent for the process 8 weeks prior to him, Charles Goodyear is generally considered the father and inventor of the sulfur vulcanization of rubber (19) (20). Like many other discoveries in history, vulcanization was discovered in 1839 by accident after Goodyear dropped a mixture of rubber and sulfur on a hot stove and noticed that it hardened instead of melting. Unfortunately, Goodyear did not profit from his invention and died in 1860 with significant debts. However, he did leave a detailed account of his experiments on rubber and his discovery of devulcanization in a two volume 500+ page work called *Gum-Elastic and Its Varieties* (21) (22).

The ink had barely dried on Goodyear’s *Gum-Elastic* when other inventors and scientists were trying to reverse the vulcanization process. One of the first patents to use the term devulcanization, awarded in May 1855, claims that the inventor had developed “a process for treating india-rubber and gutta-percha or their compounds after those have been cured or vulcanized with sulphur, that treatment having for its object the restoring of the said gums to a condition or state whereby they may be again worked, either as a substitute for the original or native material or in combination or mixture with it.” This early process used a turpentine solvent to swell the rubber and a high concentration lye solution as the devulcanizing agent (23).

Despite these early efforts, it is difficult to think of a topic with more research and less meaningful outcomes than devulcanization. A google patent search for “devulcanization” uncovers just over 6000 patents on the subject and yet an effective method of devulcanizing rubber still has not found widespread use. The Goodyear Tire and Rubber Company currently holds 28 of their own patents for devulcanization and yet as of the end of 2019 no meaningful amount of devulcanized rubber was being used in their tires (24). The reason for this is simple; no current devulcanization process has proven capable of producing a devulcanized rubber product that, when compounded, meets the physical testing requirements of the majority of rubber products, including tires. Devulcanized rubber typically has a lower molecular weight than virgin rubber and consequently has significantly lower tensile strength, elastic modulus, and drum abrasion, some of the most critical parameters in defining the performance of rubber, than virgin rubber across many different applications. In fact, devulcanized rubber can only completely replace virgin rubber (as opposed to being mixed with virgin rubber in a low percentage in the rubber compound) in the lowest of performance applications such as floor mats.

Despite all the negative outcomes over the past 160 years, the search for the elusive process devulcanization process continues. The next section gives an overview of a few devulcanization methods that have been developed over the last 20 years.

2.2.2.2 Overview of Devulcanization Methods

Devulcanization methods typically fall within one of the following categories (25):

1. Chemical
2. Mechanical
3. Biological
4. Microwave
5. Ultrasonic

The common feature of these methods is the goal of breaking the sulfur crosslinks while maintaining the carbon-carbon single and double bonds in the rubber backbone and thus a high molecular weight. The following sections review one method in each category presented above.

2.2.2.2.1 Chemical Devulcanization

Chemical devulcanization methods use a variety of techniques to achieve devulcanization. Organic solvents, molten sodium, and supercritical CO_2 are a few among the plethora of chemical techniques that have been explored. A devulcanization via 2-butanol was developed by The Goodyear Tire and Rubber Company and patented (US Pat US5891926A) in 1998. The patent describes a process where vulcanized rubber is reacted in a bath of 2-butanol at 230-260 °C at a pressure of 3400 kPAa (493 psia). The reaction is carried out for 10-20 minutes and then subsequently cooled to below 100 °C. The resulting liquid contained a slurry of devulcanized rubber and other filler materials from the rubber compound including carbon black. The devulcanized rubber could be separated from the solvent and fillers using decantation, filtration, centrifugation, and other separation operations. The patent claims that “this devulcanization technique does not significantly change the microstructure of the rubber and it can accordingly be used in the same types of applications as was the original rubber.” Although the authors do not report the performance of the devulcanized rubber in a re-vulcanized compound, they do show that on average the molecular weight of the polymer was reduced by about 50% (26).

Goodyear allowed the patent on the 2-butanone process to expire in 2011 and it is not clear if the technology ever left the lab scale or pilot scale. As is common with many devulcanization methods, the inherent process and environmental risks associated with organic solvents and the high temperatures and pressures used combined with loss of 50% of the polymer molecular weight likely made commercializing the technology unappealing to Goodyear.

2.2.2.2.2 Mechanical Devulcanization

In contrast to chemical devulcanization where sulfur crosslinks are broken by chemical reactions, mechanical devulcanization uses shear force to physically pull apart sulfur bonds. The method relies on the difference in covalent bond strength between the C-C and C=C bonds versus C-S and S-S bonds. For reference, below is a table comparing the covalent bond energies:

Table 4 - Covalent Bond Energies of Carbon and Sulfur

BOND TYPE	BOND ENERGY (kJ/mol)
C-C	347
C=C	614
C-S	259
S-S	266

With the measurable difference in bond strength, theoretically this approach is possible, but it is difficult to impart consistent shear across the entire rubber matrix. Given the technical challenges, it would seem this technology is the most likely to cause undesired degradation of C-C and C=C bonds in the polymer backbone. However, this method of devulcanization has seen the most commercial success, likely due to its simplicity.

The most successful example of mechanical devulcanization is a technology developed by Dr. Costas Tzoganakis of Waterloo University and licensed by a Canadian company called Tyromer Inc. This technology takes pulverized tire rubber (170-500 microns) as the input and uses a combination of supercritical CO_2 and a twin-screw extruder to impart shear and promote the scission of sulfur crosslinks. At temperatures of 240-260 °C, the supercritical CO_2 caused the rubber to swell, placing tension on the sulfur crosslinks. The shear imparted by the twin screw extruder then breaks the tensioned sulfur cross links and devulcanizes the polymer. The outcome of this process is a rubber “dough” that can be re-formed and re-vulcanized. Unlike in the 2-butanol devulcanization process, the molecular weight change was not reported. However, the patent (Canadian patent CA2500372A1) shows a significant loss in physical properties of the rubber when re-vulcanized when compared with typical values expected in new tire rubber (27). For example, tensile strength for the re-vulcanized material was reported at 3.7 MPa versus the 15-20 MPa expected for tire rubber (28). Thus, as with other methods of devulcanization, the mechanical shear method appears to cause damage to the C-C and C=C in the polymer backbone.

Despite the loss of physical properties of the devulcanized rubber, Tyromer has been quite successful at commercializing their process. Tyromer reports that their material has been used in parts of passenger tires since 2016. Further, in a Rubber World magazine article published in 2019, Dr. Costas Tzoganakis states that “in a tire tread compound Tyromer’s devulcanized rubber can usually be added at 10-20% with excellent results”. More recently, Tyromer and Continental Tire announced a partnership where Tyromer devulcanized rubber would be used in Conti tires moving forward (29). This represents the first time that a major tire manufacturer has openly reported that devulcanized rubber will be used in tires which is a significant development for the rubber industry and an important step on the long road to sustainability.

2.2.2.2.3 Biological Devulcanization

Biological devulcanization is a relatively new concept to the field of devulcanization overall. Conceptually, it could potentially be superior to both physical and chemical devulcanization process. Rather than using an energy intensive mechanical process or an environmentally hazardous chemical process, biological devulcanization, or microbial desulfurization as it is also known, uses bacterial microorganisms such as *T. ferrooxidans*, *T. thiooxidans*, *T. thioparus*, and *Sulfolobus acidocaldarius* to selectively break sulfur bonds on the surface of ground rubber. Reports showed that up to 30% sulfur reduction was possible. Despite some of these positive results, the reality is that biological devulcanization research is in its infancy and has some significant technical challenges to overcome. The ground rubber must be cryogenically ground to increase interfacial area and then treated with ethanol to leach out tire additives that are toxic to the bacteria. Even after both a chemical and energy intensive mechanical step, the devulcanization only occurs on the surface of the rubber particle, thus limiting the interfacial area to re-vulcanize and making this devulcanized rubber more akin to carbon black in the way it is used as a powdered filler rather than rubber (25). Bredberg et al reported in a study looking at the effect of *P. Furiosus* on cryogenically ground rubber that the properties even at a 15% mix rate with virgin rubber had a significant reduction stress at break (30). Unfortunately, the data supports the conclusion that without significant development and technological breakthroughs, it is unlikely that biological devulcanization will play a significant role in solving the world's rubber problem.

2.2.2.2.4 Microwave Devulcanization

Microwave devulcanization uses microwave energy to heat powdered rubber in a very even manner and selectively break sulfur crosslinks, taking advantage of the lower bond energies shown in Table 4. The Goodyear Tire and Rubber Company first filed for a patent (US4104205A) for microwave devulcanization in 1976. This process fed a continuous stream of rubber particles 0.25 inch and smaller through a glass tube via a steel auger. Microwave radiation between 915 and 2450 MHz was dosed at a rate of 75-100 W-hours per pound of rubber heating the rubber to between 230- 430 °C. The material taken from this process was then re-vulcanized in various mixtures and compared with a virgin rubber control sample. The data reported in this patent showed that the devulcanized material when mixed with virgin material in the range of 15-25% had similar properties to the virgin control sample. While this atypical result for a devulcanized material could have been a positive sign for microwave devulcanization in general, the technology has not found widespread use in the nearly 50 years since its invention. In 2004, the State of California Integrated Waste Management Board produced a report entitled *Evaluation of Waste Tire Devulcanization Technologies* and discussed the challenges that have plagued microwave devulcanization. They found that the process requires that the that the rubber being devulcanized be polar enough to react to the microwave radiation and that the process was expensive to scale (31). Ground tire rubber is not polar enough by itself to facilitate the microwave process and a study published in 2012 showed that even with the addition of carbon black powder to the process to enhance polarity, the degree of devulcanization in tire rubber was considered low (32). Therefore, due to the lack of applications for this technology, it is unlikely to find widespread use in the future.

2.2.2.2.5 Ultrasonic Devulcanization

Ultrasonic devulcanization is similar to the microwave process in that energy is added to the powdered rubber sample in a way that the S-S and C-S bonds are broken but the C-C and C=C remain intact. First discussed by Okuda and Hatano in 1987, rubber is treated with ultrasonic waves (~50 kHz) for a period of 20 minutes. After this treatment the ultrasonically devulcanized rubber becomes soft and malleable thus enabling the material to be reformed into new rubber products. In practice, ultrasonic devulcanization is typically combined with a high-shear mechanical extrusion to process the material continuously, making it a combination ultrasonic and mechanical devulcanization process (31).

In a process developed and patented (US Pat US5258413A) by Avraam Isayev from the University of Akron, a mechanical extruder feeds rubber crumb under high pressure through a die and into a chamber containing an ultrasonic horn. The horn emits ultrasonic waves with a frequency between 15 and 50 kHz and an amplitude of 10 to 200 microns. The combination of mechanical shear and ultrasonic energy breaks the sulfur crosslinks and some of the polymer chain and per the patent “the longer residence time of the elastomer in the ultrasonic field, the greater the degree of depolymerization” (33).

In the early 2000s, the University of Akron licensed their devulcanization patent to Ultramer Inc of Massillon OH. Ultramer reportedly built a prototype unit for scaled ultrasonic devulcanization and went through testing of their material in truck tires (31). It is not clear whether that project was successful, but it does not appear Ultramer is operating in 2022. Further, an online search for recent patents in the field or companies that claim to be using ultrasonic devulcanization does not yield any positive results. It is likely that due to the extent of depolymerization reported, the molecular weight of the devulcanized rubber was not high enough to yield adequate physical properties in re-vulcanized.

Overall, devulcanization research and development has had a rich history but very little success. The challenge has been, and will continue to be, producing a malleable, formable material from waste rubber that when re-vulcanized has a high enough tensile strength and modulus for use in the majority of rubber applications. The following sections provide important background information on the chloramine devulcanization process. Chloramine formation and chemistry is introduced and then previous work to understand the effect of chloramine on rubber is discussed. Finally, the potential advantages and attributes of chloramine devulcanization are explored.

2.3 Chloramine Devulcanization

2.3.1 Chloramine Chemistry

Chloramines are a classification of haloamine produced from chemical reactions between ammonia and chlorine species. There are three subspecies of chloramines: (1) monochloramine (NH_2Cl, (2) dichloramine ($NHCl_2$), and (3) trichloramine (also known as nitrogen trichloride, NCl_3). All species of chloramine are reactive and thermodynamically unstable, preferring to degrade and form more stable chlorine and nitrogen species. Of the three chloramine subspecies, monochloramine is the most stable and the most widely used. We have presently found no industrial applications where dichloramine or nitrogen trichloride are used. The terms “monochloramine” and “chloramine” are often used interchangeably and all references to “chloramine” in this research refer to monochloramine (34).

2.3.2 Chloramine Synthesis

Chloramine is primarily used in the water distribution industry as a disinfectant, but also has applications as a precursor to hydrazine and other chemicals used in pharmaceuticals. There are multiple pathways for chloramine synthesis and the preferred pathway is usually dependent upon the application and the required ending chloramine concentration. In the water distribution industry, chloramine is formed from the following reaction of aqueous hypochlorite and aqueous ammonia:

$$\mathrm{NH_3}\ (aq) + \mathrm{OCl^-}(aq) \rightleftharpoons \mathrm{NH_2Cl}\ (\mathrm{aq}) + \mathrm{OH^-}$$

Chloramine is rarely produced in concentrations above 70 PPM (0.0014 M) for drinking water disinfection. Aqueous sodium hypochlorite is often used as the hypochlorite source, though it is possible to synthesize chloramine from calcium hypochlorite ($Ca(OCl)_2$) or hypochlorous acid (HOCl). In aqueous solutions, chloramine decomposes via hydrolysis and reacts readily with H^+ and OH^- ions, so pH plays an important role in chloramine stability and the preferred pH range for chloramine synthesis and stability is 8-10. At room temperature, chloramine can remain stable at low concentrations (<100 PPM, 0.0019 M), provided no other contaminants are present, for several weeks.

Chloramine used for hydrazine production must be produced in higher concentrations than chloramine used in water treatment. Until the mid-2000s, it was typically only produced from the following gas phase reaction of chlorine and ammonia:

$$2\ \mathrm{NH_3}\ (\mathrm{g}) + \mathrm{Cl_2}(\mathrm{g}) \rightleftharpoons \mathrm{NH_2Cl}\ (\mathrm{g}) + \mathrm{NH_4Cl}\ (\mathrm{s})$$

This reaction produces chloramine vapor but is challenging to implement practically due to the formation of ammonium chloride solids and the need for chlorine gas. In the early 2000s, Delalu et. al. produced a series of publications and patents related to the production of stable aqueous chloramine solutions at concentrations at 1-2 M. He discovered that high concentration chloramine could remain stable if the reactions were performed at temperatures below 0 °C and if a buffering agent was used to keep the pH of the solution at 10 during the chloramine formation reaction. In *Synthesis of enriched solutions of chloramine starting from hypochlorite at high chlorometric degree*, Delalu uses ammonium salts to buffer the pH because they produce ammonia as they are consumed leading to higher conversion (35).

Chloramine concentrations used in devulcanization research are typically closer to the water distribution industry than hydrazine production. Concentrations used in the past and throughout this research typically are between 30 ppm (0.0058 M) and 5000 ppm (0.097 M). Due to chloramine's auto-decomposition reaction, it is important to find a balance between increased devulcanization rate and chloramine stability, especially considering the low diffusivity of chloramine into the rubber matrix.

2.3.3 Chloramine-Rubber Research: AWWA Work – Pre 2012

For most of the 20th century, free chlorine, usually in the form of a hypochlorite ion was used in water distribution industries to disinfect water. In the 1970s, the EPA began to look at the effects of free chlorine on water quality and discovered that unexpected reactions produced carcinogenic trihalomethane compounds. Chloramine was identified and implemented as a safer alternative soon after and steadily became accepted as a new standard for water disinfection in the United States. After the implementation of chloramine as a disinfectant, rubber components in water distribution facilities and homes began to fail more quickly than was previously observed. As a result, the American Water Works Association commissioned a study in the early 2000s to investigate chloramine and test if it was the cause of the accelerated rubber degradation.

The degradation of rubber by chloramine was reported in a study published by the American Water Works Association (AWWA) in 2007. The study exposed samples of various types of rubber to chloramine solutions for 30 days. Researchers observed rubber degradation in virtually all samples of rubber that were exposed to chloramine, with significant degradation occurring at higher temperatures (70 °C) and concentrations (60 ppm chloramine) than would be found in drinking water. In fact, samples exposed to these highest temperatures and concentrations for 30 days were observed to lose their cross-linked properties. Anecdotally, researchers stated that the rubber coupon samples used in the research would become grease-like when squeezed between their hands. The AWWA study concluded that chloramine degrades rubber materials found in water distribution systems (6). However, before 2012, no research had been done to determine what became of the degraded material, what form it took, and if it had any potential use.

2.3.4 UofL Chloramine Devulcanization Research 2012-2013

The AWWA report showed that aqueous chloramine degraded rubber, but it did not focus on what happened to the polymer after degradation. So, the first phase of our research focused on chloramine devulcanization feasibility and asked the following two questions:

1. Could the rubber degradation process be accelerated by increasing temperature and chloramine concentration?
2. Is the product of chloramine-rubber degradation a high molecular weight devulcanized polymer?

These two questions were important to demonstrate feasibility. If the degradation process could not be accelerated, then the process may not be economical. Also, if the product(s) of the degradation are a low molecular weight oil, then chloramine degradation of waste rubber may not have been more effective than other methods of rubber reclamation that break carbon-carbon bonds in the polymer backbone.

Our initial experiments on feasibility lasted from 2012-2013. Although waste rubber can be made up of many different types of base polymer, we focused our initial feasibility study on styrene butadiene rubber, which was at the time (and still is today) the highest volume produced rubber in the world. We discovered that the degradation could be accelerated by increasing temperature and chloramine concentration, but that degradation rate was also dependent on the particle size of the waste rubber being reacted and amount of agitation in the reacting solution. During the experiments, we observed that the particle size of the reacting rubber particles decreased over time, indicating that they were losing mass to the aqueous solution. A liquid-liquid extraction was performed with hexane on the aqueous solution and FTIR of the dried residue from that extraction showed corresponding peaks to SBR. Visual observation of the extraction showed evidence that polymer was in solution.

With positive outcomes to our feasibility study, showing both that rubber degradation could be accelerated, and that polymer had been suspended in the aqueous solution, we concluded that chloramine devulcanization showed promise as a solution to waste rubber and that further research was needed to expand this new field.

2.3.5 Chloramine Devulcanization

The chloramine devulcanization shares a common feature with other devulcanization methods but there are some key differences that could enable the technology to have a more meaningful impact. All the devulcanization technologies covered, including chloramine, seek to preferentially sever the S-S and C-S bonds while maintaining the C-C and C=C bonds and they all achieve that to some degree. Any devulcanized rubber or recycled material will have a loss of molecular weight because the degradation of C-C and C=C bonds occurs during the rubber mixing process and in the rubber products useful life and a perfect devulcanization process cannot change that.

However, chloramine devulcanization shows promise in that the relatively mild reaction conditions increase the likelihood that C-C and C=C bonds are preserved. Further, multiple products can be recovered from chloramine devulcanization process and there is a lower risk of environmental impact of the process than some other chemical devulcanization processes that have been tried in the past. These three differences are discussed below.

2.3.5.1 Devulcanization Reaction Conditions

High temperature and shear exert forces on the polymer backbone as well as the sulfur crosslinks. The reported temperature range in some of the other devulcanization methods listed was 230-400°C. Shear forces reported by Tyromer in their twin screw extruder were 970-2170 psi. Contrastingly, the aqueous chloramine process has been shown to achieve devulcanization between 70 °C and 100 °C with only low shear agitation in a CSTR. Chloramine devulcanization may be able to produce a higher molecular weight polymer than other devulcanization processes. However, since both temperature and shear force appear to affect the rate of devulcanization in the chloramine system, it is likely that a balance must be achieved between the rate of production of devulcanized rubber and the rubber quality as the chloramine method is scaled.

2.3.5.2 Multiple Products Possible

The common feature of all the other devulcanization methods reviewed here is that they produced a single product: devulcanized rubber. This devulcanized rubber contains all the fillers, additives, and rubber polymer from the original rubber application. Rubber applications are very sensitive to the type of rubber and the specific mixture of fillers and additives. An EPDM hose application will have a completely different recipe of ingredients than tire tread. However, those devulcanization techniques do not separate out these individual components and therefore limit the applications where that the material can be used. The chloramine devulcanization method differs from these other methods by devulcanizing and then dispersing the devulcanized rubber, filler, and additives in a dilute aqueous solution. No longer closely mixed in the rubber matrix, those materials can be separated from each other using separation and mass transfer operations. The chloramine devulcanization process offers the possibility for multiple products at a higher grade than other methods of rubber waste disposal. Unfortunately, this method also comes with a price since the separation of the devulcanized rubber, filler, and additives from each other is as much of a technical hurdle as the devulcanization itself and adds additional processing cost with every step. If the chloramine process eventually is shown to be unscalable, it is likely due to the quantity of separation operations that must be utilized after the devulcanization reaction is complete.

2.3.5.3 Environmental Considerations

Although this does not apply to mechanical devulcanization methods, compared with other chemical methods of devulcanization, the aqueous chloramine has the potential to have less environmental risk and impact. The organic solvent in the chemical devulcanization process covered earlier, 2-butanol, can cause explosive vapors and has strict air and environmental emission limits. Further, another chemical devulcanization technology developed by B.C. Sekhar and Vitaly Kormer and licensed by Green Rubber Global Ltd uses what they call “delinking accelerators” to devulcanize rubber. The patent for this technology states that their DeLink material is “selected from the group of zinc salts of thiocarbamates and zinc salts of dialkyl dithiophosphates, 2-

mercaptobenzothiazole or derivatives thereof, thiurams, guanidines, 4,4'-dithiomorpholine and sulphenamides, and a zinc oxide activator in an amount sufficient to act as an activator for the accelerator(s) to delink the elastomeric material at a temperature below 70° C" (36). A 2008 study looking into one of those compounds, 2-mercaptobenzothiazole, found that 2-MBT may be a human carcinogen and recommended further study into its effects on humans. Contrastingly, chloramine is widely used in the water distribution industry as a disinfectant in drinking water and the risk to human population is well understood. Compared with other devulcanizing agents, chloramine is relatively benign.

Overall, when compared with other devulcanization methods, the chloramine process shows promise and is worth continuing to explore. With only 8-10 years of overall research, the technology is in its infancy compared with the other methods reviewed here. The goal for this work is to lay the initial groundwork for understanding the chloramine devulcanization process and the materials recovered from it.

CHAPTER 3 – CHLORAMINE DEVULCANIZATION EFFICACY

The work in Chapter 3 focuses on the efficacy of chloramine devulcanization. Our prior work, completed in 2012-2013 timeframe, built on the AWWA's research into chloramine's effects on sulfur vulcanized rubber. The results were not conclusive yet, through FTIR, NMR, and visual observations of the reacted chloramine-rubber solutions, we showed evidence that the aqueous solutions contained chloramine devulcanized rubber (CdR) (5). This important first step appeared to indicate that the chloramine solutions were preserving the polymer backbone rather than converting it to low molecular weight monomer compounds, but more analysis was needed. The work presented here in Chapter 3, conducted in 2014-2015, expands on those initial results and focuses on recovering and analyzing the CdR produced by the chloramine process, thus confirming the underlying efficacy of the process. This work focuses primarily on evaluating CdR to confirm that devulcanization is occurring and the chloramine recovered carbon black (CrCB) was not discussed or analyzed. CrCB is covered and discussed in depth in Chapters 4 and 5.

3.1 Research Objectives

The three objectives below were selected as parameters of this research:

1. Show repeatability of the original chloramine devulcanization work (5)

2. Extract and isolate CdR material from the aqueous solutions
3. Analyze molecular structure and assess physical characteristics of the extracted CdR

The extraction and isolation of the CdR polymer was the most technically challenging of the three goals presented. Chloramine solutions synthesized using sodium hypochlorite as the chlorine source have a significant amount of residual sodium content in the form of sodium chloride and sodium hydroxide. During our previous work, we found that salt crystallization occurred when the aqueous CdR solutions were concentrated via evaporation and that salt crystallization impeded recovery of the CdR in the extraction processes that were attempted (5). Thus, developing an effective extraction process was the critical step to being able to evaluate the CdR material and test our project hypothesis. The following section describes the materials and methods that have been used to devulcanize, extract, and characterize CdR.

3.2 Materials and Methods

3.2.1 Source of Waste Rubber

The waste rubber for these experiments was obtained from Lehigh Technologies Inc. Lehigh Technologies Inc processes spent tires cryogenically to form rubber powders that are used as filler products often in new rubber applications. Polydyne-140, a product derived from end-of-life truck tire tread and whole tire rubber, is a 140-mesh powder with a surface area to volume ratio of 0.751 m^2/g. As stated previously, tire formulations typically contain a mix of SBR and natural rubber, though the specific contents and ratios are proprietary to each tire manufacturer.

3.2.2 Synthesis of Monochloramine

Monochloramine was synthesized using the ASTM D 6284 method. Sodium hypochlorite was diluted with water and reacted with aqueous ammonia to form chloramine and the pH was adjusted with phosphoric acid to achieve the range that is preferable for monochloramine formation (8-9 pH). A boric acid pH 9 buffer was then added to stabilize the solution in the monochloramine pH range. The targeted starting concentration of each solution was 5000 ppm monochloramine.

3.2.3 Rubber Devulcanization

The monochloramine synthesized above was added to 50 grams of Polydyne-140 rubber powder in a stainless-steel container. The solution was reacted in the stainless-steel container immersed in a hot water bath for periods ranging from 8-24 hours at a temperature of 50 °C. After the period of reaction time, the devulcanized solution was removed from the stainless-steel reaction container via vacuum filtration and stored. Fresh monochloramine was then added to the stainless-steel container containing the rubber and the process was repeated. Solutions were changed on a quantitative, not qualitative, basis meaning that solutions were changed with as much frequency as could be by the research team. For the span of 30 days, solutions were charged with fresh chloramine solution between one and four times daily.

3.2.4 Devulcanized Rubber Extraction

Filtered solutions from the process above were stored with open lids in a hot water bath at 50 °C to promote evaporation of the water from the samples. Once 50-70% evaporation was achieved across single containers, multiple evaporated solutions were combined to form a solution of greater concentration. This more concentrated solution was then evaporated, and the overall process repeated until the evaporated solution had become viscous and yellow in appearance as seen in Figure 1 below.

Figure 12 - Aqueous CdR Solutions in Hot Water Bath

Due to the high sodium concentration in the solutions, the concentrated CdR solutions were added to acetone to “salt-out” the residual sodium content. Since water is miscible in acetone, a portion of the CdR solution was transferred into the acetone during each extraction attempt. Once extraction equilibrium had been reached, the solutions (water and acetone) formed two separate phases with the water on the bottom and acetone on the top. At this point, an emulsified layer of CdR was often observed at the interface between phases. While several methods were employed attempting to extract the CdR, the following was the most successful:

1. Add acetone to the CdR solution until extraction equilibrium is reached and no more CdR solution can be absorbed by the acetone.
2. Remove the top liquid phase containing acetone, water, and CdR from the container.
3. Boil the acetone/water/rubber solution in the fume hood beginning at approximately 60 °C until the measured boiling point reaches 80 °C. This step will remove most of the acetone.
4. Remove solution from heat at 80 °C and allow remaining solution to vent to fume hood until all acetone has evaporated.
5. Slowly and systematically remove CdR film that has formed on top of the remaining water solution and place in separate container.

The extracted CdR acetone solutions are shown in Figures 13-15 below.

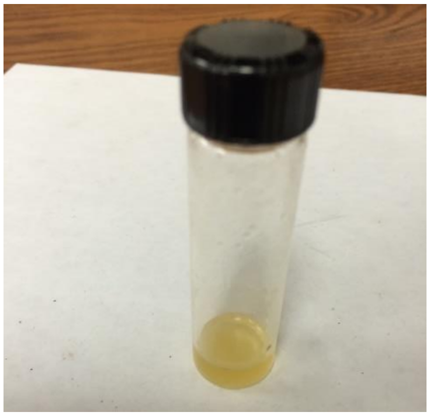


Figure 13 - "Pure" CdR Sample 1

Figure 14 - "Pure" CdR Sample 2

Figure 15 - CdR Precipitated in Acetone Solution

3.2.5 FTIR/NMR Spectroscopy

The extracted CdR that was recovered via the procedure above was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Nuclear Magnetic Resonance spectroscopy. The results and analysis of these characterizations are detailed in the following section.

3.3 Results and Discussion

The CdR sample presented above was characterized using Fourier Transform Infrared Spectroscopy (FTIR), Carbon NMR (C^{13}NMR), and Proton NMR (H^1NMR). The resulting spectra presented below are analyzed individually first, then collectively. However, before interpreting the spectra, it is important to understand the functional groups that are found in the rubber polymer chain. As mentioned previously, tire rubber is composed typically a mixture of styrene butadiene rubber (SBR) and natural rubber (NR). To simplify the analysis, the following section focuses on identifying major functional groups present in SBR, since most of the rubber found in tires is SBR and SBR contains the same functional groups as natural rubber plus the aromatic styrene group.

3.3.1 Identifiable Functional Groups

The chemical structure for SBR is presented below in Figure 16. One important note is that the Figure 16 arrangement while typical is not necessarily the exact repeat unit arrangement found in the tire rubber used in these experiments. The samples used in this test were taken from micronized rubber supplied by Lehigh Technologies Inc. As stated previously, this product was selected due to the high surface area-to-volume ratio for the degradation reaction and since most tire manufacturers have trade-secret SBR blends, the exact butadiene to styrene ratio is unknown. However, the functional groups (alkane, alkene, and aromatic) found in Figure 16 are also found in the tire rubber used in this application even though the specific repeat unit may not be exactly what is depicted below.

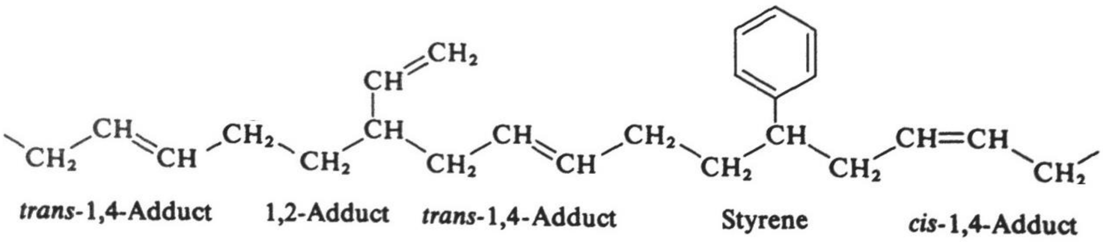


Figure 16 - Styrene Butadiene Rubber

The assumption of this research has been that the monochloramine attacks the sulfur crosslinks in the SBR crosslinked network. That hypothesis was based on a visual analysis of the CdR sample from previous research where the degraded sample appeared to have lost its vulcanized properties and exhibited polymer properties. Previous research also suggested that the polymer backbone and relevant functional groups were likely intact but did not provide overwhelming evidence to support that theory. Thus, it is important to characterize this extracted CdR sample to better determine if the assumptions stated above are supported.

Based on the chemical structure of SBR, a characterization of the CdR should present evidence of high concentrations of alkanes (C-H and C-C bonding), alkenes (cis, trans, and vinyl carbon-carbon double bonds) and an aromatic ring corresponding to styrene. The cis, trans, and vinyl double bond sites serve an important function in re-vulcanization as the sulfur atoms bond to form cross links at those sites. However, since only a fraction of the available double bond sites is used up in the initial vulcanization process, the CdR should have remaining carbon-carbon double bond sites available for re-vulcanization. If the characterizations of the CdR show evidence that those double bonds are still intact, then this evidence shows that the degraded sample can be re-vulcanized.

3.3.2 FTIR Spectra

The FTIR spectra for the CdR sample are presented below in Figure 17.

28

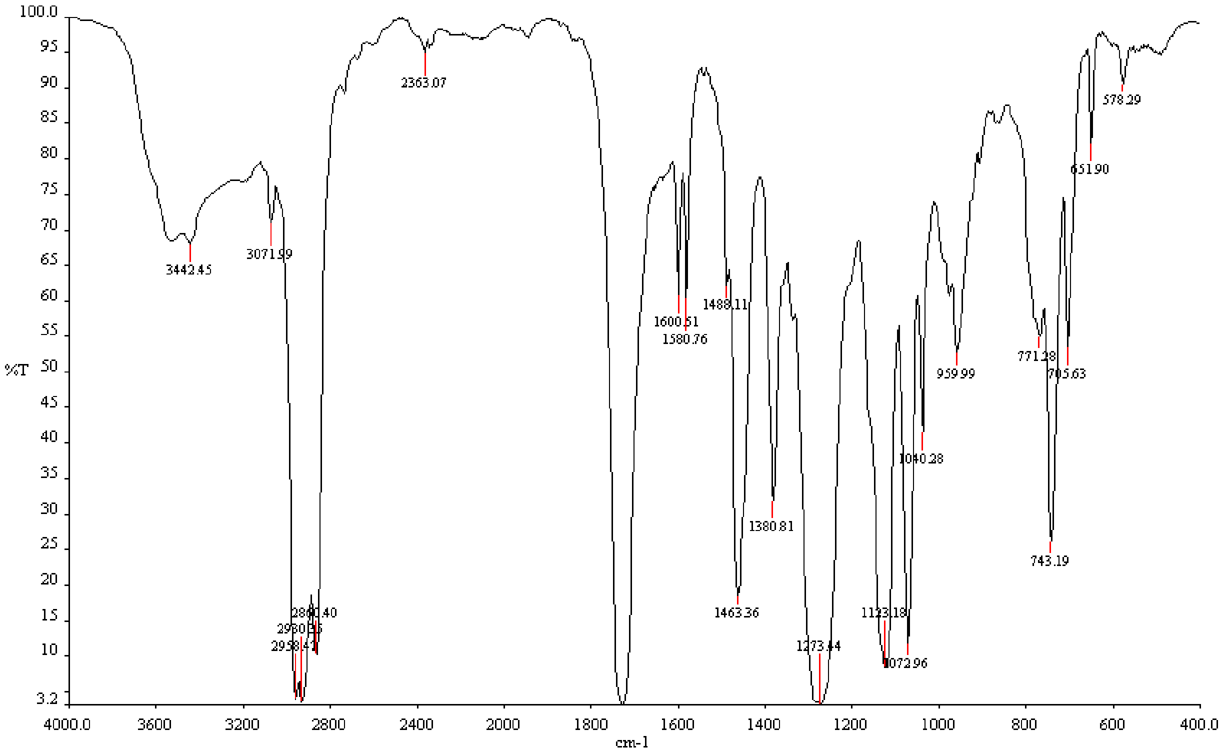


Figure 17 - FTIR Spectra for Devulcanized Rubber Sample

Spectral Data for Structure Determination of Organic Compounds by Pretsch et. al serves as a good tool for analyzing various types of spectral data including CNMR, HNMR, and FTIR. Much of the analysis in the following paragraphs is taken from the tables in this book.

Various texts including Pretsch state that a C=CH_2 stretch from a vinyl group occurs generally in the 3100-3000 cm^{-1} range and more typically in the 3095-3075 cm^{-1} range. This is depicted in Figure 17 as a peak 3071 cm^{-1}. The C=C stretch from the cis and trans double bonds are usually found in the 1635-1690 cm^{-1} range. However, Pretsch states that subsequent conjugation typically lowers the frequency (37). Roeges states that for a X-CH=CH-X conjugated arrangement (which is typical of the SBR shown in Figure 5), the C=C stretch occurs at approximately 1590 cm^{-1} for the cis arrangement and 1580 cm^{-1} for the trans arrangement which correspond to the 1600 cm^{-1} and 1580 cm^{-1} peaks found Figure 17 (38). Furthermore, Pretsch and Smith state that the cis and trans C-H bending can be found in the 990-960 cm^{-1} and 725-675 cm^{-1} ranges (37) (39). Smith states more specifically that the cis arrangement can be found at 690±50 cm^{-1} and the trans arrangement can be found at 965±5 cm^{-1} (39). These ranges correspond to peaks at 705 cm^{-1} (cis) and 965 cm^{-1} (trans) in Figure 17.

Aromatic group spectra (styrene) can be found in similar regions as the cis and trans groups and in many cases the exact location depends on the overall functional arrangement of the polymer. Various texts report styrene peaks at 1600, 1580, 1490, 727-761, and 695 cm^{-1} (38) (40) (41). In this case, three of the peaks have been already attributed to the butadiene double bonds. However, the occurrence of styrene and butadiene overlap is well supported. ISO standard ISO-21561-2 (*Styrene-butadiene rubber (SBR) — Determination of the microstructure of solution-polymerized SBR — Part 2: FTIR with ATR method*) indicates that when the styrene content is over 30 %, the peak of the cis bond is hidden between the two large styrene absorptions at around 758 cm^{-1}and around 698 cm^{-1} (40). In Figure 17, the presence of styrene can possibly be attributed to peaks at 1600 cm^{-1}, 1580 cm^{-1}, 1488 cm^{-1}, 743 cm^{-1}, and 705 cm^{-1}. Again, while these peaks overlap, such overlap is typical in a SBR sample and can be considered further evidence that the chemical structure of the CdR remains consistent with virgin samples.

Other peaks of note are the spectra found at 2958 cm^{-1}, 2930 cm^{-1}, 2958 cm^{-1} and at 3442 cm^{-1}. The first three peaks are attributed to the numerous alkane groups found in the butadiene backbone (37) (41). The peak at 3442 cm^{-1} and the subsequent higher untagged peak (~3530) are typical of an N-H bond in an amine group. While this is not part of the original SBR structure, it may be indicative of a by-product bond from the devulcanization process. Future investigations to determine the degradation mechanism may find this set of peaks useful.

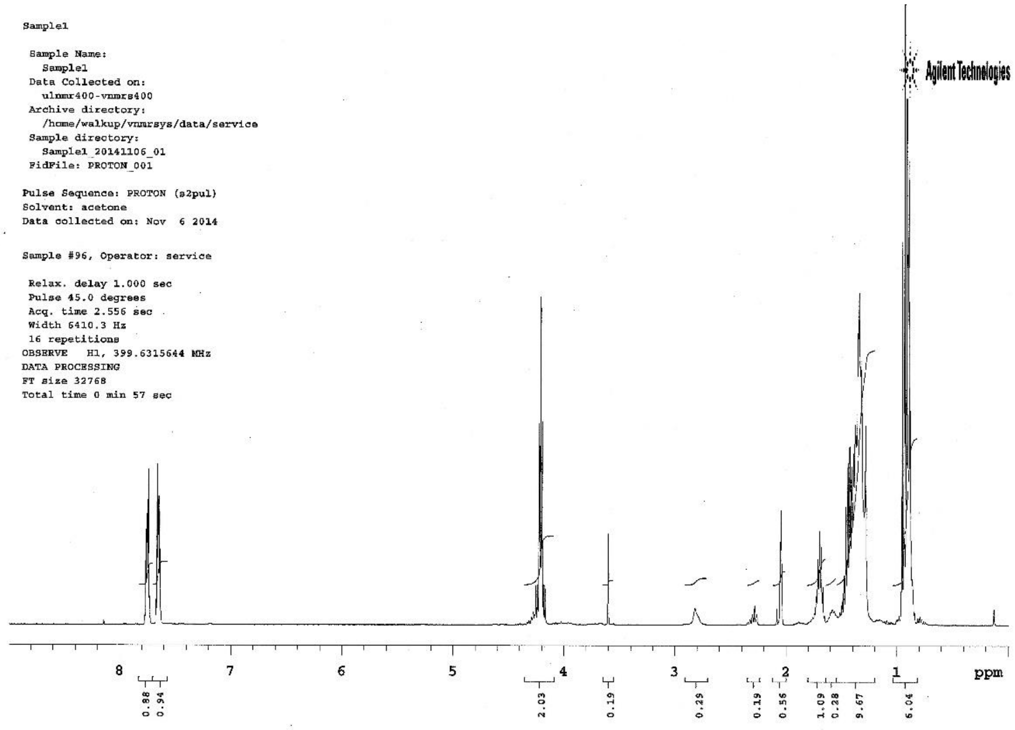
3.3.3 NMR

Nuclear Magnetic Resonance (NMR) is useful for characterizing functional groups and whole molecular structures by analyzing nuclear spin on atoms in a sample. NMR is accomplished by exposing the sample to a magnetic field and measuring the frequency at which the atoms respond to the stimulation. The frequency and, in turn, chemical shift is dependent upon the electron environment surrounding the characterized atoms (hydrogen atoms for proton or HNMR and carbon atoms for carbon or CNMR). The chemical shift of the sample is measured against the frequency of a reference compound, Tetramethylsilane, where the magnitude of the shift is determined by the electron affinity of the atoms surrounding the characterized atom. The specific chemical shift of functional groups is heavily dependent upon the overall electron environment of the molecule. However, as with FTIR, alkane, alkene, and aromatic functional groups are found at specific and unique chemical shift ranges. One other useful tool that HNMR

(CNMR does not) provides is that the areas under the peaks correspond to the relative concentration differences of the atoms within the overall molecule/molecules.

3.3.4 Proton NMR Analysis

The CdR sample was characterized by proton NMR in a deuterated acetone solvent. The resulting spectra are shown in Figure 18.



```
Sample1

 Sample Name:
   Sample1
 Data Collected on:
   ulnmr400-vnmrs400
 Archive directory:
   /home/walkup/vnmrsys/data/service
 Sample directory:
   Sample1_20141106_01
 FidFile: PROTON_001

Pulse Sequence: PROTON (s2pul)
Solvent: acetone
Data collected on: Nov  6 2014

Sample #96, Operator: service

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.556 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 399.6315644 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 57 sec
```

Figure 18 - Proton NMR of Devulcanized Rubber Sample

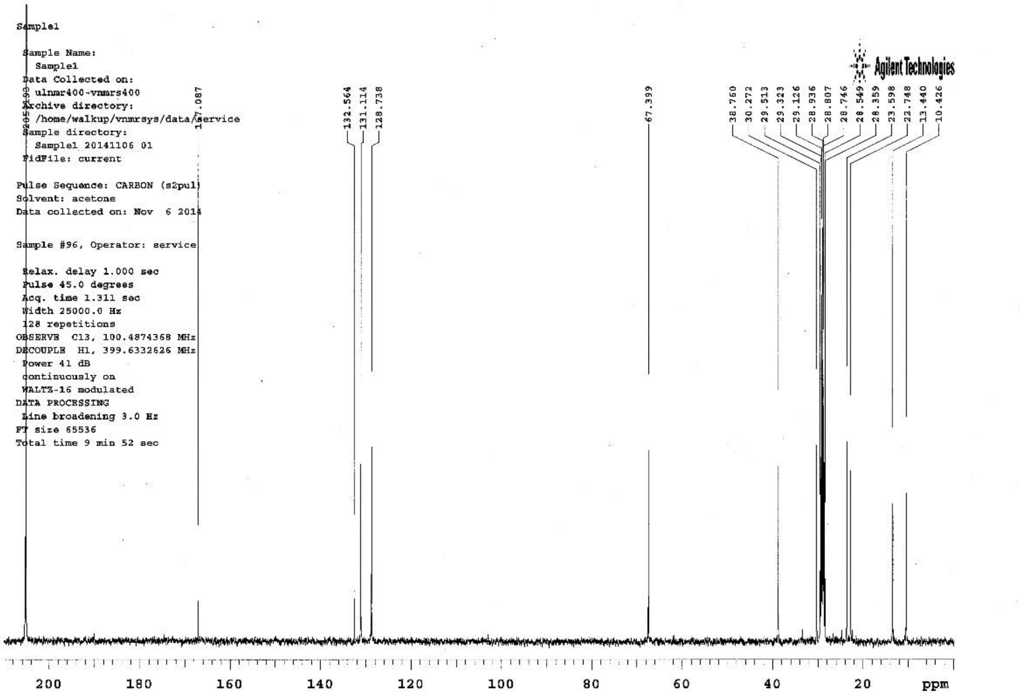
Multiple texts including Abraham, Nelson, and Pretsch list typical chemical shifts for HNMR and all generally agree on the ranges where alkanes, alkenes, and aromatics can be found. Alkanes can be found over a range from ≈0.8 ppm to ≈2.1 ppm. More specifically, alkanes with the structure R-CH_2-R (R being alkyl groups) are found from 1.1-1.8 ppm. This corresponds to the large peaks in Figure 18 at 0.8-1.0 ppm (beginning of peak to end of peak), 1.25-1.5 ppm, and 1.6-1.8 ppm. These high area-under-curve values for these peaks (6.04, 9.67, and 1.09 respectively) represent the high number of alkane bonds in the backbone of the polymer repeat unit as seen in Figure 16 (42) (43) (37).

Alkene groups can be found in different ranges depending on the specific functional groups surrounding the carbon-carbon double bond. A hydrogen atom bound to one of the carbons in the double bond can be found in the 3.8-7.8 ppm range (Pretsch lists a tighter 4.5-6 ppm range). This range corresponds to the peak from ≈4.15-4.35 ppm in Figure 7 (42) (43) (37). Additionally, hydrogen atoms bonded to a carbon atom adjacent to a double bond (CH_2-(C=C)) are found at ≈2ppm (37). This may correspond to both the peak at 2.0 ppm and also to the peak at 1.6-1.8ppm, which was previously attributed to the alkane groups.

Aromatic groups can be found in the 6.5-9 ppm range per Abraham and Nelson whereas Pretsch lists a tighter range of 6.8-7.5 (42) (43) (37). This corresponds to the peaks at 7.6 and 7.8 ppm in Figure 18. Prestch also indicates that an alkyl group bonded to an aromatic (CH-(ArC)), which is typical of the styrene bond, may be found at ≈2.9 ppm (37). This may correspond to the centered around 2.8 ppm, however, this also may be a water impurity in the sample as H_2O in the deuterated acetone solvent shows up as a peak at 2.83 ppm. Nevertheless, the Figure 18 shows strong evidence that aromatic groups are present within the CdR compound.

3.3.5 Carbon NMR Analysis

As with Proton NMR, the CdR sample was diluted in deuterated acetone and characterized using carbon NMR. The results are presented in Figure 19.



```
Sample1

 Sample Name:
  Sample1
 Data Collected on:
  ulnmr400-vnmrs400
 Archive directory:
  /home/walkup/vnmrsys/data/service
 Sample directory:
  Sample1 20141106 01
 FidFile: current

Pulse Sequence: CARBON (s2pul)
Solvent: acetone
Data collected on: Nov  6 2014

Sample #96, Operator: service

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.311 sec
 Width 25000.0 Hz
 128 repetitions
OBSERVE  C13, 100.4874368 MHz
DECOUPLE  H1, 399.6332626 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 3.0 Hz
FT size 65536
Total time 9 min 52 sec
```

Figure 19 - Carbon NMR of Devulcanized Rubber Sample

Multiple authors list functional groups within specific chemical shift ranges (Pretsch, Nelson, Abraham) and the authors are in agreement with where these functional groups are found. Alkanes are found from 5-60 ppm. Alkene groups are found between 100-150 ppm while carbon atoms bonded directly to alkene carbons can be found from 10-40 ppm. Aromatics are also found in the 100-150 ppm range with carbons bonded directly to the aromatic group being found from 10-60 ppm (42) (43) (37). Figure 8 shows multiple peaks in those ranges corresponding to alkane, alkene, and aromatic groups. One point worth noting is that there are only three peaks found in the alkene and aromatic double bond region when, depending on the exact structure of the original SBR, there should be up to 6 peaks, representing all non-symmetric carbons on the aromatic styrene group and on the cis, trans, and vinyl carbons. There are peaks found in unaccounted for regions (67 ppm, 167 ppm, and 205 ppm). These peaks could be other rubber types, impurities in the sample, or possibly carbons that have been shielded/deshielded based on the specific electron environment of the sample. Despite this observation, the carbon NMR provides evidence that alkane, alkene, and aromatic functional groups exist within the sample.

3.3.6 Overall Discussion of Characterization Results

It is important that the carbon backbone of the CdR stays intact with all functional groups, especially C=C bonds, for re-vulcanization. The prevailing theory is that monochloramine attacks the sulfur crosslinks in the vulcanized SBR matrix but is unable to effectively attack and degrade the stronger carbon backbone. The FTIR, H-NMR and C-NMR characterizations support this analysis as all three methods provide strong evidence that the degraded rubber has left alkane, alkene (cis, trans, and vinyl), and aromatic functional groups intact. Combine this with the visual observation of high viscosity in the CdR, a marker of high molecular weight, we can conclude that devulcanization has occurred and that the CdR is relatively intact and capable of being re-vulcanized.

While the evidence that has been presented strongly indicates that the devulcanized rubber is capable of being re-vulcanized, one missing piece of information is the molecular weight and overall chain length of the sample. To date, not enough pure

CdR has been recovered to run through a viscosity test or GPC to determine the molecular weight. Determination of polymer molecular weight through HNMR has been done effectively and accurately, however, this method requires knowledge of end groups. In this case, the end groups are not known, hence this method cannot be used. Despite lacking molecular weight, the characterizations and visual observation provide enough evidence to indicate that the SBR is capable of being re-vulcanized and recycled.

3.3.7 Conclusions and Future Work

The overall goal of this portion of research was to show chloramine devulcanization efficacy. This was accomplished by exposing micronized tire rubber to solutions of chloramine, extracting material from those reacted solutions, and analyzing the recovered CdR with FTIR, H-NMR, and C-NMR. From this work, we observed that after extraction via acetone, a viscous material typical of a high molecular weight elastomer was present. FTIR, H-NMR, and C-NMR spectroscopy showed that alkane, alkene (cis, trans, and vinyl), and aromatic functional groups were present. This spectroscopy indicates that the polymer backbone has not been significantly changed by the reaction with chloramine and that there are many carbon-carbon double bonds present that could enable re-vulcanization. This work confirms that devulcanization of tire rubber, which is the transformation of a vulcanized elastomer to its pre-vulcanized state, has taken place via aqueous chloramine and that this process could be further developed into a sustainable method of tire recycling.

Significant work remains to show that the chloramine devulcanization process can be a sustainable method of tire recycling. The rubber, carbon black and other materials recovered from this process should be studied to determine how their properties affect new rubber compounds. Further the rate of devulcanization and consumption of chloramine should be analyzed to determine if the process could be economical and what factors play into chloramine devulcanization efficiency. Finally, more work should be done to determine both the chemical and physical mechanism of devulcanization as understanding this mechanism could contribute significantly to the development of this technology as a whole. A significant portion of this work is completed in Chapters 4 and 5.

CHAPTER 4 – CHLORAMINE DEVULCANIZATION PHYSICAL MECHANISM AND RATE

As discussed in Chapter 2, the chloramine devulcanization process has been shown to disperse the products of the devulcanization reaction and fillers and additives from the rubber compound into the aqueous solution. This process appears to be unique when compared with other methods of devulcanization and the phenomena for the breakup of particles of powdered rubber up to this point was not well understood. This work was completed between 2016-2022 and from 2019 on was part of a partnership with Arduro Sustainable Rubber to commercialize chloramine devulcanization technology. Following the efficacy phase of work described in Chapter 3, our team, in 2016, sought to develop a pilot scale process to produce more devulcanized rubber and set the technology up to be commercialized. After Arduro Sustainable Rubber licensed technology from ULRF, the work focused on defining the manufacturing process that would combine a pilot scaled chloramine devulcanization reactor with a set of separation operations to isolate and recover the carbon black (CrCB) and devulcanized rubber (CdR) as products of chloramine devulcanization. From this effort to build a functioning manufacturing process, our team developed a working theory of the physical mechanism for the devulcanization and breakup of the vulcanized rubber particle and then used that mechanism to understand the factors that impact and limit overall devulcanization rate.

4.1 Research Objectives

The objectives presented below were selected as the desired outcomes for this phase of development:

1. Develop the chloramine devulcanization manufacturing process including the devulcanization reactor and separation operations processes.
2. Analyze the composition and morphology of the carbon black and devulcanized rubber recovered from the process and propose a physical mechanism for the diffusion of chloramine into the rubber matrix, breakup of the vulcanized rubber particle, and condition of the product carbon black and devulcanized rubber.
3. Analyze the factors associated with the rate of chloramine auto-decomposition, rate of chloramine reaction with sulfur, and rate of diffusion of chloramine into the rubber matrix to evaluate whether the chloramine-rubber system is rate limited or diffusion limited.

The three goals above are an important next step for progressing the chloramine devulcanization technology from lab scale to commercial scale.

4.2 Materials and Methods

The work in Chapter 4 was completed in partnership with Arduro Sustainable Rubber using their pilot plant located in Louisville, KY. Certain details of the Arduro manufacturing process are kept as trade secret, however, the following sections on materials and methods show some details about the process flow of the chloramine devulcanization.

4.2.1 Source of Waste Rubber

The waste rubber for this portion of research was the Polydyne-40 micronized rubber powder sourced from Lehigh Technologies. Polydyne-40 is a micronized rubber with 40 mesh / 400 micron rated particle size. Though not disclosed on their website or product technical datasheet, Lehigh technologies stated that their Polydyne-40 product is sourced from used passenger tires and truck tires.

Figure 20 - Polydyne-40 taken from Lehigh Technologies’ Website

4.2.2 Chloramine Production Process

Chloramine for this work was produced continuously. Aqueous sodium hypochlorite (bleach) and ammonia diluted from bulk concentrations and stored in IBC totes as seen Figure 21.

Figure 21 - Bleach and Ammonia Storage at Arduro Pilot Plant

The bleach and ammonia were then fed continuously at a stoichiometric ratio to a plug flow reactor (PFR) using centrifugal pumps. The reaction was performed at ambient conditions and reactor conversions to chloramine were typically 60%.

Figure 22- Bleach pump

Figure 23 - Chloramine Plug Flow Reactor

4.2.3 Devulcanization

Chloramine devulcanization was performed in a continuous stir tank reactor. The reactor was loaded with approximately 50 kg of Polydyne-40 micronized rubber and mixed with water until wetted properly. Aqueous chloramine was then fed continuously to this CSTR and separation of unreacted micronized rubber solids from the smaller recovered CrCB particles and aqueous suspension of CdR was done using a decanter centrifuge.

Figure 24 - Chloramine Devulcanization CSTR

4.2.4 Products Separation

The particles of CrCB were separated from the CdR aqueous suspension using a closed loop ultrafiltration and centrifugation process. The pore size of the ultrafiltration membrane was selected to capture the CrCB and allow the aqueous CdR suspension to pass through. The CrCB was then accumulated in the centrifuge while the aqueous CdR suspension was captured in a separate tank.

4.2.5 Thermogravimetric Analysis

TGA was performed using a TA instruments Q50 TGA unit. The samples of CrCB and CdR were measured using an auto-stepwise dual gas method. The first stage of the process is heating the sample from ambient conditions to 700 C in a nitrogen atmosphere. The heating process is adjusted from a steady ramp rate to isothermal conditions if the controller detects that a significant weight loss event occurs. Weight loss in this first stage nitrogen gas process is typically water, volatile organic compounds, extending oils, and polymers like SBR and NR. After the sample reaches 700 C in nitrogen, the gas is automatically switched to air and heated at a constant rate from 700 °C to 900 °C. Any carbon black in the sample combusts in this region and any remaining material is classified as ash. Ash from tire derived materials is typically silica, zinc oxide, and iron/steel compounds from tire steel belts. Sodium and calcium are also present due to the aqueous chloramine process.

Figure 25 - TA Instruments Q50 TGA

4.3 Results and Discussion

This section covers the results of the work completed in Chapter 4. The characteristics and composition of the CrCB and CdR are analyzed first and then this information is used to propose a mechanism for this physical breakup of the rubber particle. Then the rubber-chloramine reaction is analyzed to evaluate whether the reaction is rate limited or diffusion limited and what factors affect those conditions.

4.3.1 Analysis of Carbon Black from Chloramine Devulcanization

The waste rubber used to determine chloramine efficacy in Chapter 3 was PolyDyne-140 sourced from Lehigh Technologies. However, Polydyne-40, a 40-mesh rubber (400 micron), was used in this work in Chapter 4. The Polydyne-140 micronized rubber product is produced by cryogenically freezing crumb tire rubber and milling it repeatedly until the material passes through a 140-mesh screen. While working with Arduro, our team discovered that cryogenically pulverized rubber consumes up to 10 kg of liquid nitrogen per kg of micronized rubber powder produced. If using this energy intensive and costly pulverization process is required as a precursor to chloramine devulcanization, there could be significant economic hurdles to commercialization of the technology. Size reduction of bulk rubber continues to be an important part of devulcanization technologies because the dense rubber matrix resists diffusion and thus restricts access to the sulfur crosslinks. This effect is mitigated by reducing the particle size and increasing the surface area of the rubber exposed to the devulcanization chemicals. Fortunately, rubber powder can be produced in high volumes without cryogenic pulverization down to a size of about 40 mesh (400 micron). Although smaller sized rubber would promote greater devulcanization efficiency, this efficiency is lost due to the liquid nitrogen consumption. Thus, 40 mesh rubber is used in this Chapter 4 work as the input to the chloramine devulcanization process. Figure 26 shows an SEM image of the Polydyne-40 micronized rubber. This image serves as a useful starting point to analyze the breakdown of these rubber particles in the devulcanization process.

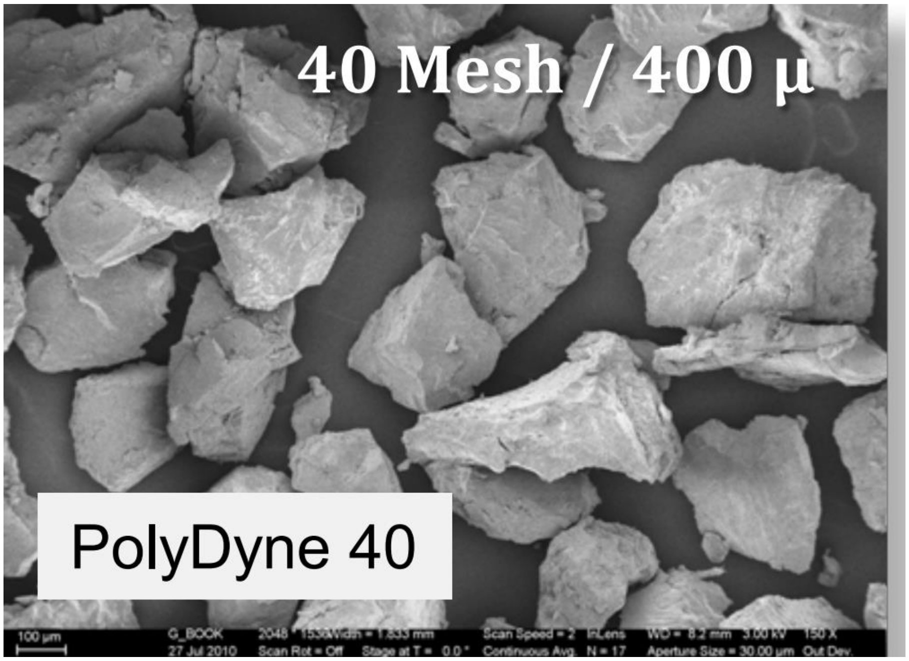


Figure 26 - SEM Image of Polydyne-40 Micronized Rubber Powder (150X Zoom)

The chloramine devulcanization process was performed continuously in a CSTR at concentrations of 1000-2500 ppm and approximately 80 °C. Separation of products from unreacted micronized rubber was completed via centrifuge, with solids fraction composed of larger MR particles sent back to the CSTR system for additional chloramine treatment and liquid fraction being the smaller CrCB and the aqueous CdR sent to the products separation and collection systems. The combination ultrafiltration and centrifugation process then separated and recovered the CrCB from the aqueous CdR stream. The operation of the reactor system was intermittent with 4-6 hours of continuous operation and then 18-20 hours of down time before operation the next day. It took approximately 2 operating day cycles to begin visually observing the blackening of the liquid fraction of the reactor centrifuge outlet and the recovery of CrCB in the via the CrCB centrifuge. The CrCB analyzed in the following sections was taken from operation day 10. The wet CrCB material removed from the centrifuge had the consistency of a dense paste as seen in Figure 27.

Figure 27 - Wet Carbon Black Paste

The CrCB was oven dried at 120 °C for 24 hours and then milled in a kitchen blender to convert it to a powder (Figure 28).

Figure 28 - Dried Carbon Black Powder

The dried CrCB was analyzed via SEM to determine particle size and surface morphology and TGA to determine overall composition. The SEM images are presented in Figure 29 and Figure 30.

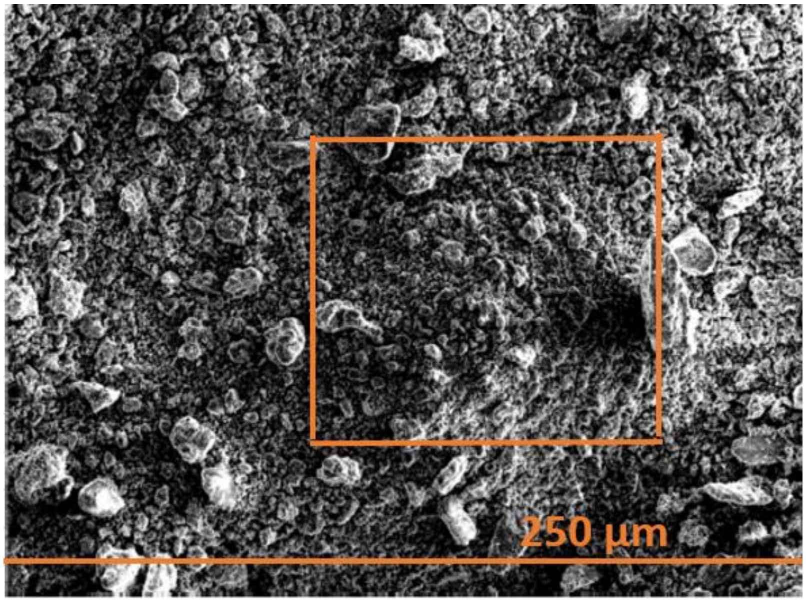


Figure 29 – SEM (500X) of CrCB

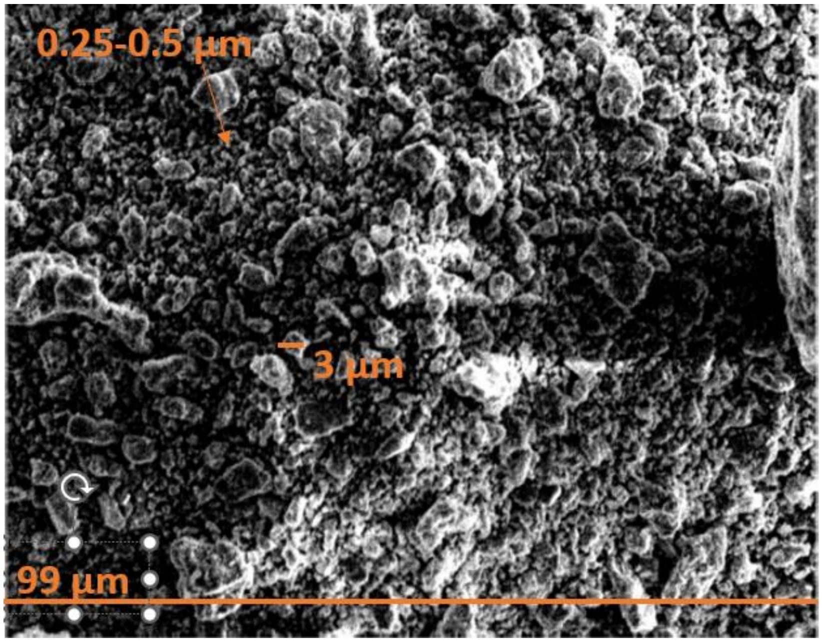


Figure 30 - SEM (1000X) of CrCB

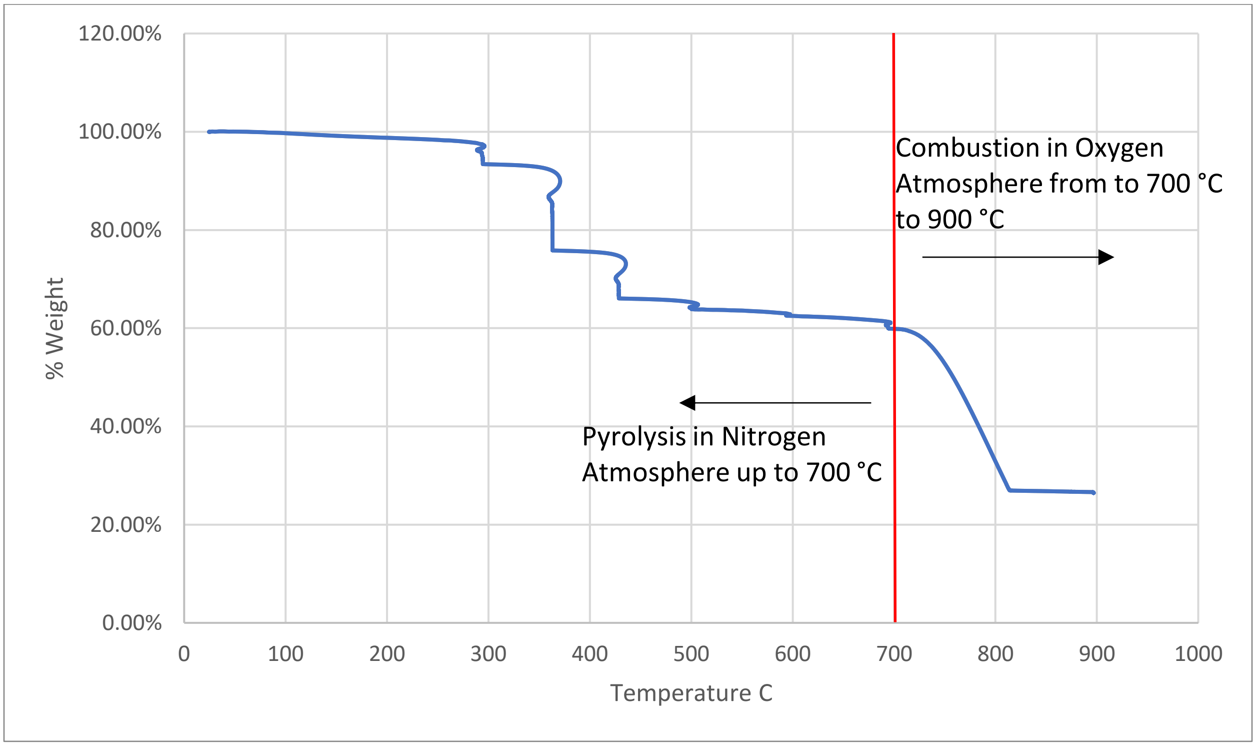


Figure 31 - Thermogravimetric Analysis of CrCB Recovered from Chloramine Process

Thermogravimetric Analysis (TGA) of the CrCB is shown in Figure 31. The TGA was run in a two-stage auto-stepwise fashion where the instrument ramps the temperature at a rate of 20 °C/min unless the derivative weight change measured above a defined threshold, usually 2 to 4 weight percent per minute. In areas of higher weight loss, the instrument switches an isothermal hold at the temperature the switch occurred and holds until the weight loss has slowed or ended. Combining this technique with a two-stage gas process where nitrogen is used as the sample gas up to 700 °C and oxygen is used between 700 °C and 900 °C allows the user to clearly see oils, polymers, carbon black, and remaining ash content in each sample.

4.3.2 Discussion of Carbon Black Composition and Characteristics

Figure 32 is used as a starting point to analyze the TGA of CrCB in Figure 31. The Polydyne-40 micronized rubber used as the process input was analyzed via TGA using the same auto stepwise procedure as the carbon black. In this method, evaporation and pyrolysis occurs in a nitrogen atmosphere up to 700 C. Within the pyrolysis regime, multiple weight loss events can be observed at 260 C, 320 C, 395C and at 460C. Identification of individual polymer types within a TGA of waste rubber can be difficult as many rubber types could be present. From our analysis of typical tire formulations, styrene butadiene rubber, natural rubber, butyl rubber, and chloroprene rubber are known to be used in tires.

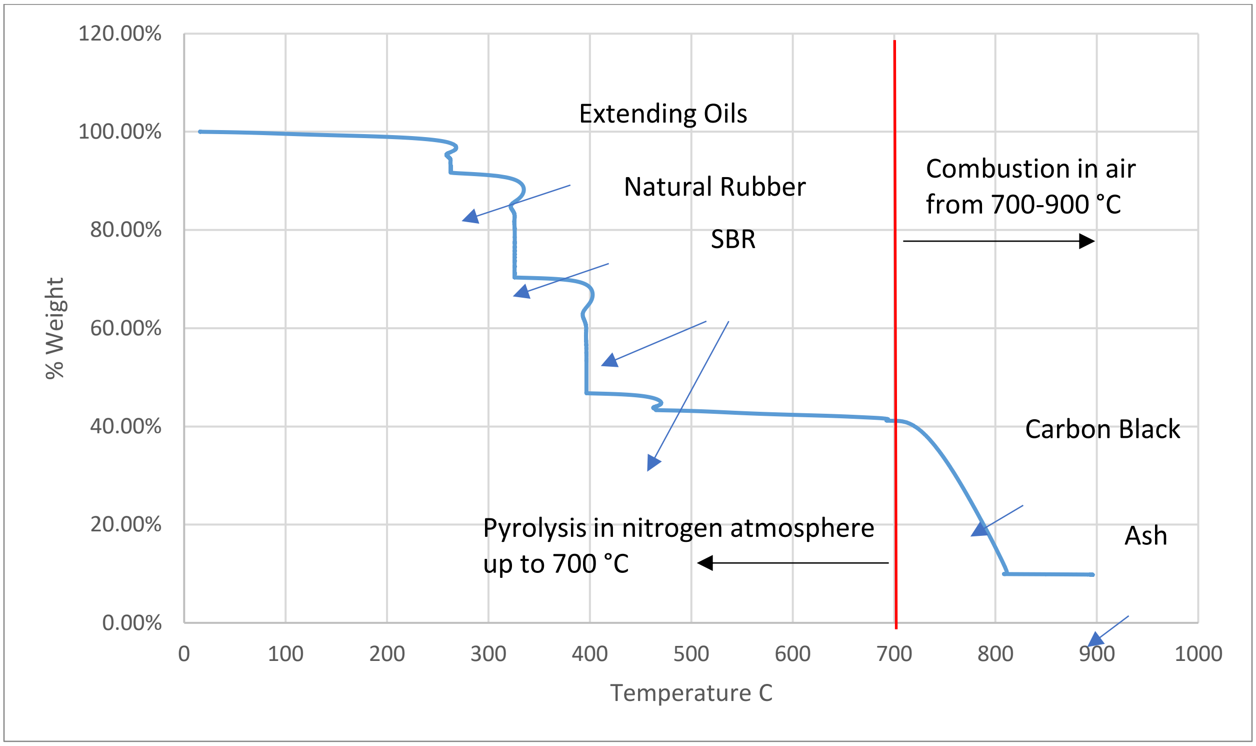


Figure 32 - TGA of Polydyne-40 Micronized Rubber Input Material

Table 5 - Pyrolysis Temperature Ranges for Rubber

Polymer Type	Typical Onset Pyrolysis Temperatures
Styrene Butadiene Rubber	384 °C – 434 °C (44)
Polyisoprene Rubber (Natural Rubber)	310 – 456 °C (44)
Chloroprene Rubber	350 °C – 375 °C (45)
Butyl Rubber	300-400 °C (46)

Polymer pyrolysis temperatures can vary significantly and numerous factors such as molecular weight and crosslink density contribute to that variance. Further, blends of rubber polymers will have different thermal degradation properties than pure components (44). Varkey et. al reports that natural rubber degradation can be seen as one clear event often starting around 310 °C. SBR typically has more heat resistance and is known to have two peaks present: a large initial peak starting between 350 °C and 400 °C and a second peak starting below 500 °C. Despite all the uncertainty around specific polymer types in tire rubber, the Polydyne-40 material analyzed shows clear signs of a natural rubber peak starting around 320 °C and the characteristic dual SBR peaks between 400 °C and 490 °C. The other peak seen at 260 °C in the evaporation/pyrolysis regime represents the extending oils in rubber. Other rubber types, though assumed to be present, are likely hidden within the curves for NR and SBR due to their lower concentrations and temperature overlap. The remaining components of the micronized rubber, carbon black and incombustible ash, can be seen after the TGA transitions to air in the combustion regime.

Compositions from TGA data in Figure 31 and Figure 32 are summarized in Table 6.

Table 6 - Composition Comparison of MR and CrCB

Component	Polydyne-40 MR (%wt)	CrCB
Volatiles (<250 C)	1.7%	1.7%
Extending Oils	6.8%	5.0%
Polymer (NR + SBR)	48.2%	29.6%
Unidentified Components (600-700 C)	2.1%	3.9%
Carbon Black	31.2%	33.0%
Ash	9.9%	26.9%
Polymer : Carbon Black Ratio	1.54	0.89

As we can see from the from the Figure 31 and Figure 32, describing the powder seen in Figure 28-Figure 30 powder as carbon black is a bit of a misnomer. Though from a macroscopic perspective it looks like carbon black, the composition retains many of the characteristics of the input micronized rubber though the particle size is significantly lower.

One important observation is the reduction in polymer content of the CrCB particles. The polymer-carbon black ratio of the Polydyne-40 versus the CrCB seen in Table 6 is reduced to 0.89 from 1.54. To further investigate the maximum amount of unbound polymer within the CrCB, a solvent extraction experiment was performed on the CrCB powder in xylene. Three total extractions were performed at 130 C for 3 hours each. Between each extraction the spent solvent was replaced with fresh xylene. The data for those experiments are presented in Figure 33 and summarized in Figure 34.

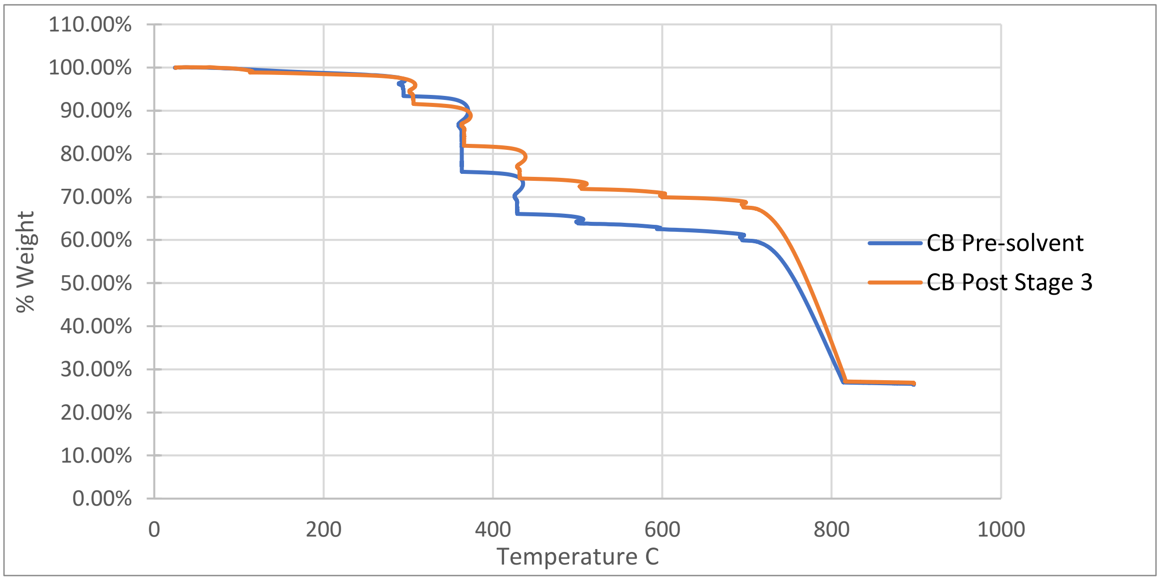


Figure 33 - TGA Analysis of Unbound Rubber Content in Chloramine CB

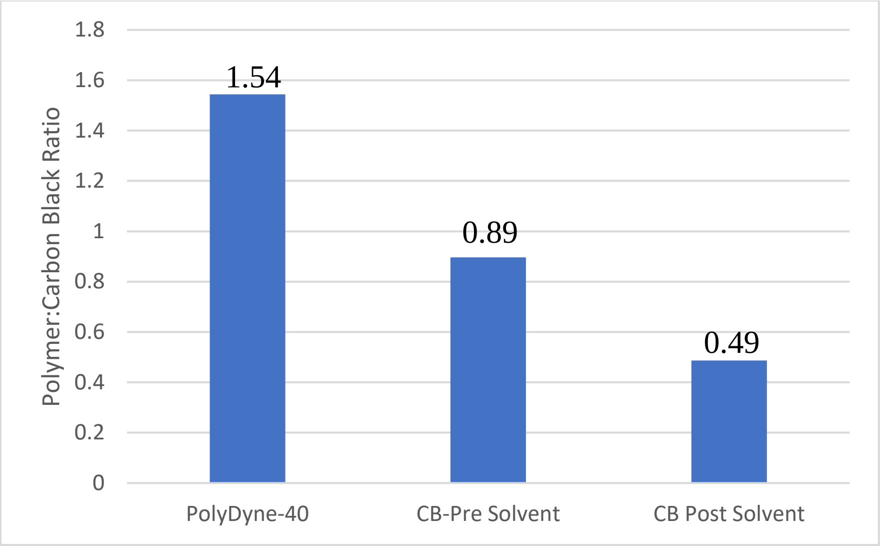


Figure 34 - Polymer to Carbon Black Ratio

TGA showed that there was approximately 19.6% polymer remaining in the post-solvent extracted sample. Overall, the polymer to carbon black ratio in the CrCB sample decreased to 0.48 from 0.89 prior to the solvent extraction and 1.54 in the Polydyne-40 input material.

4.3.3 Analysis of CdR from Chloramine Devulcanization

As described in the previous section, the aqueous solution containing devulcanized rubber was separated from the CrCB by an ultrafiltration process. That aqueous solution was concentrated using a nanofiltration membrane. A xylene liquid-liquid extraction (LLE) was performed on the concentrated aqueous solution by homogenizing the solutions with a high shear mixer. The xylene was then separated from the aqueous solution, dried and then analyzed via TGA in the same manner as the CrCB in the previous section. In addition, xylene from the solid-liquid solvent extraction on the CrCB in the previous section was dried and analyzed via TGA to determine CdR content.

The data is presented in Figure 35 and Figure 36.

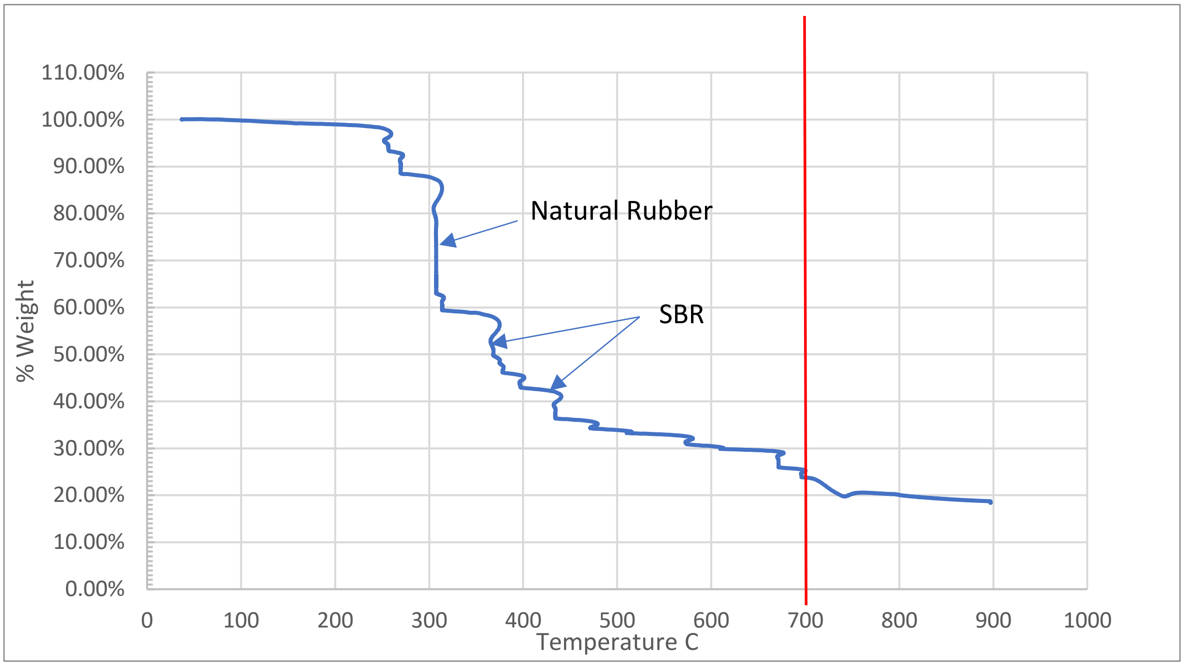


Figure 35 - TGA of CdR Recovered from Xylene-Aqueous Liquid-Liquid Extraction (LLE)

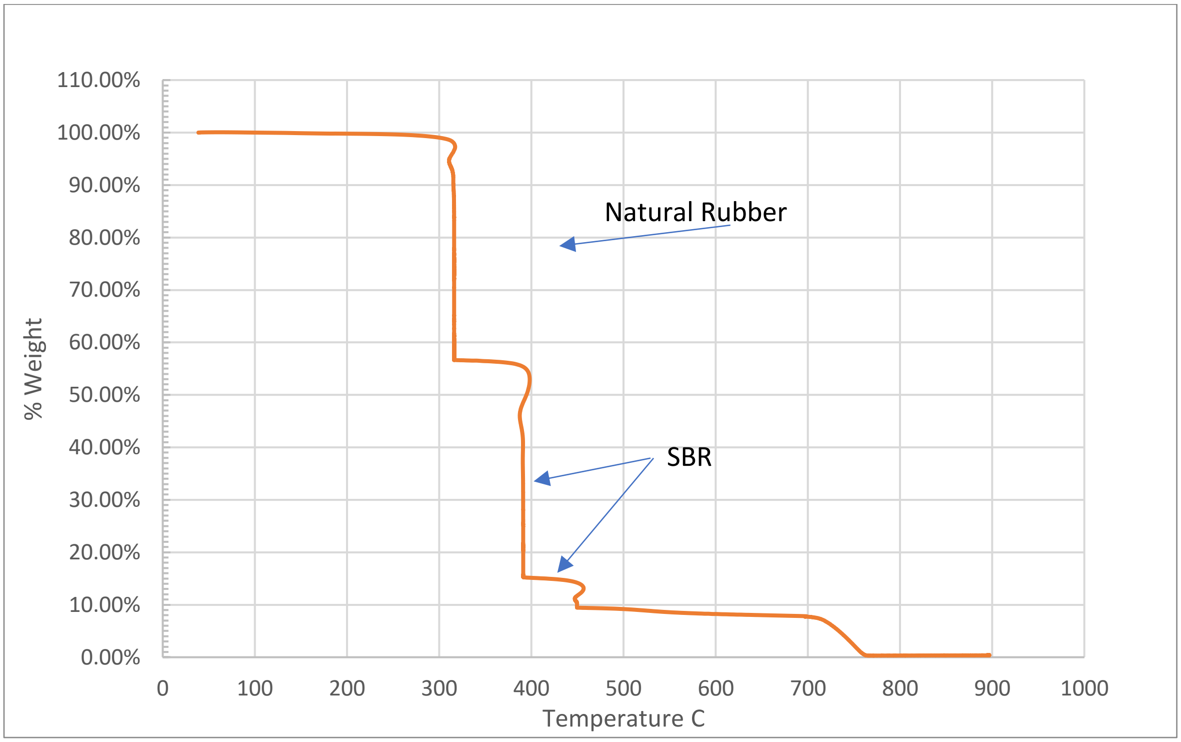


Figure 36 - TGA of CdR Recovered from Carbon Black Solid-Liquid Extraction (SLE)

Though Figure 35 shows a significant amount of signal noise, both spectra show weight loss that corresponds to NR at (300-320 °C) and SBR (dual peaks at ≈400 °C and 450 °C). The spectra in both appear slightly shifted to the left in their onset temperatures and isothermal regions. Table 7 presents the isothermal weight loss points for the NR and SBR regions in Figure 31, Figure 32, Figure 35, and Figure 36.

Table 7 - Isothermal Weight Loss Temperatures for Rubber in Analyzed Samples

	PolyDyne-40 (Figure 32)	CrCB (Figure 31)	LLE CdR (Figure 35)	SLE CdR (Figure 36)
Natural Rubber	325 °C	363 °C	307 °C	316 °C
SBR Peak 1	396 °C	428 °C	368 °C	391 °C
SBR Peak 2	466 °C	506 °C	434 °C	462 °C

Varkey et. al showed that sulfur crosslinking adds to thermal stability of polymers and shifts the observed TGA weight loss temperature of NR and SBR to the right on the TGA curve (44). Upon reviewing literature on carbon black reinforcement, Robertson and Hardman noted that sulfur crosslink density was likely higher at the polymer filler interface and that both physisorption and chemisorption was responsible for the reinforcement observed when carbon black is added to rubber (11). These combined effects may be responsible for the behavior seen in Table 7. The Polydyne-40 input material is crosslinked but has regions of higher and lower crosslink density depending on relative distance from the polymer-filler interface. The CrCB has been through the devulcanization process and has less residual polymer and what polymer is remaining, since it is in closer proximity to the carbon aggregate interface, has higher average crosslink density. Contrastingly, the lower onset temperatures seen in the extracted polymers in Figure 31 and Figure 32 are due to the lack of sulfur crosslinks in those materials. Finally, the relative difference between the weight loss temperatures in the CdR in Figure 31 and Figure 32 and reported values for virgin material characterized by Varkey et. al could be due to a reduction in molecular weight (44). It is well known that there is carbon-carbon chain scission during the high shear rubber mixing process in tire manufacturing (11). Further, the stress and degradation that occurs during the life cycle of a tire also contributes to molecular weight reduction. Hence, it is expected that there is molecular weight loss from the original virgin material. Whether the chloramine devulcanization process adds to these initial losses in molecular weight is unknown. Further investigation is needed into this mechanism and is not within the scope of this work.

The results in the previous two sections are used to propose a mechanism for the physical breakup of the micronized rubber particle.

4.3.4 Discussion of Physical Mechanism

The products derived from chloramine treatment of waste tires have been shown to consist of two major components. The first component is CrCB particles averaging between 0.5-20 µm that are composed of oil, polymer, carbon black, and ash. These CrCB particles have a relative composition that is slightly altered from the input micronized rubber where the polymer to carbon black ratio has been reduced to 0.89 from 1.54. Additionally, the CrCB particles contain unbound polymer where further extraction reduces the polymer-carbon black ratio to 0.48. The second component of the products is an aqueous suspension of polymer where the polymer is primarily a mix of NR and SBR.

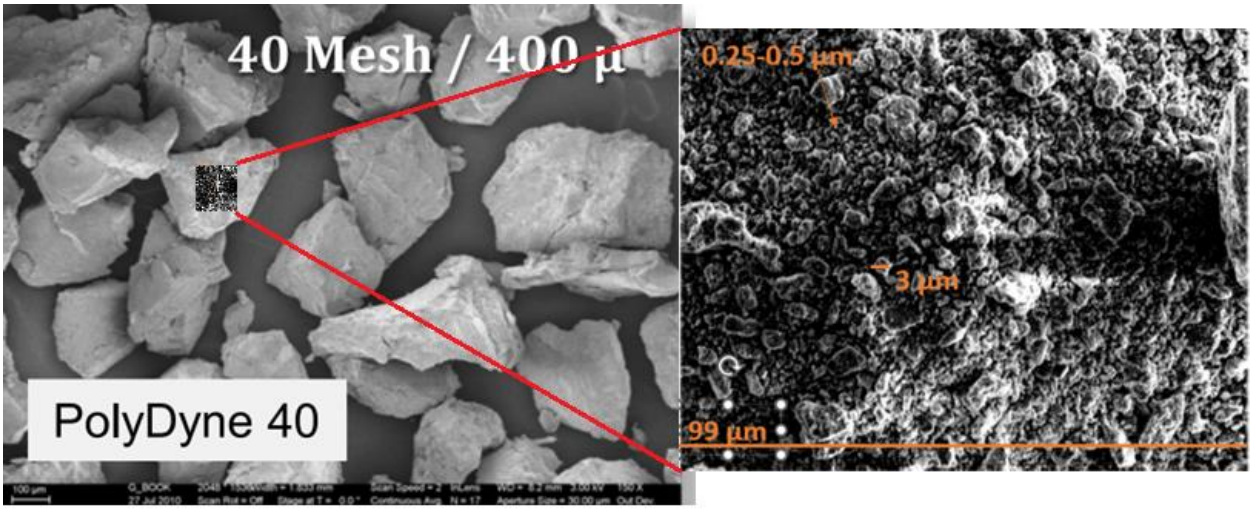


Figure 37 - Particle Size Comparison of Input Polydyne-40 Material to Recovered Carbon Black Particles

From an analysis of this material, we propose the following mechanism to explain the chloramine devulcanization phenomenon.

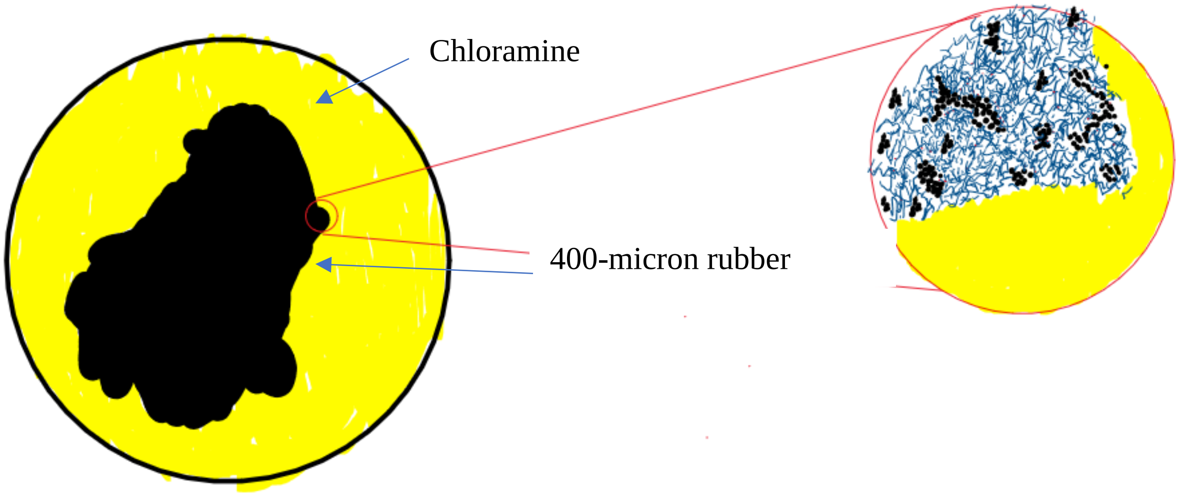


Figure 38 - 400-micron Rubber Particle in Chloramine Solution

Consider a particle of 400-micron rubber introduced to a solution of aqueous chloramine. At the rubber-chloramine boundary, there is initially a clear interface where empty space in the rubber matrix is filled with air and aqueous chloramine is only present on the surface and in the bulk phase. This is visually represented in Figure 39 where the yellow region is aqueous chloramine, the black dots/structures are carbon black, the blue lines are polymer, and the smaller red dots are sulfur crosslinks.

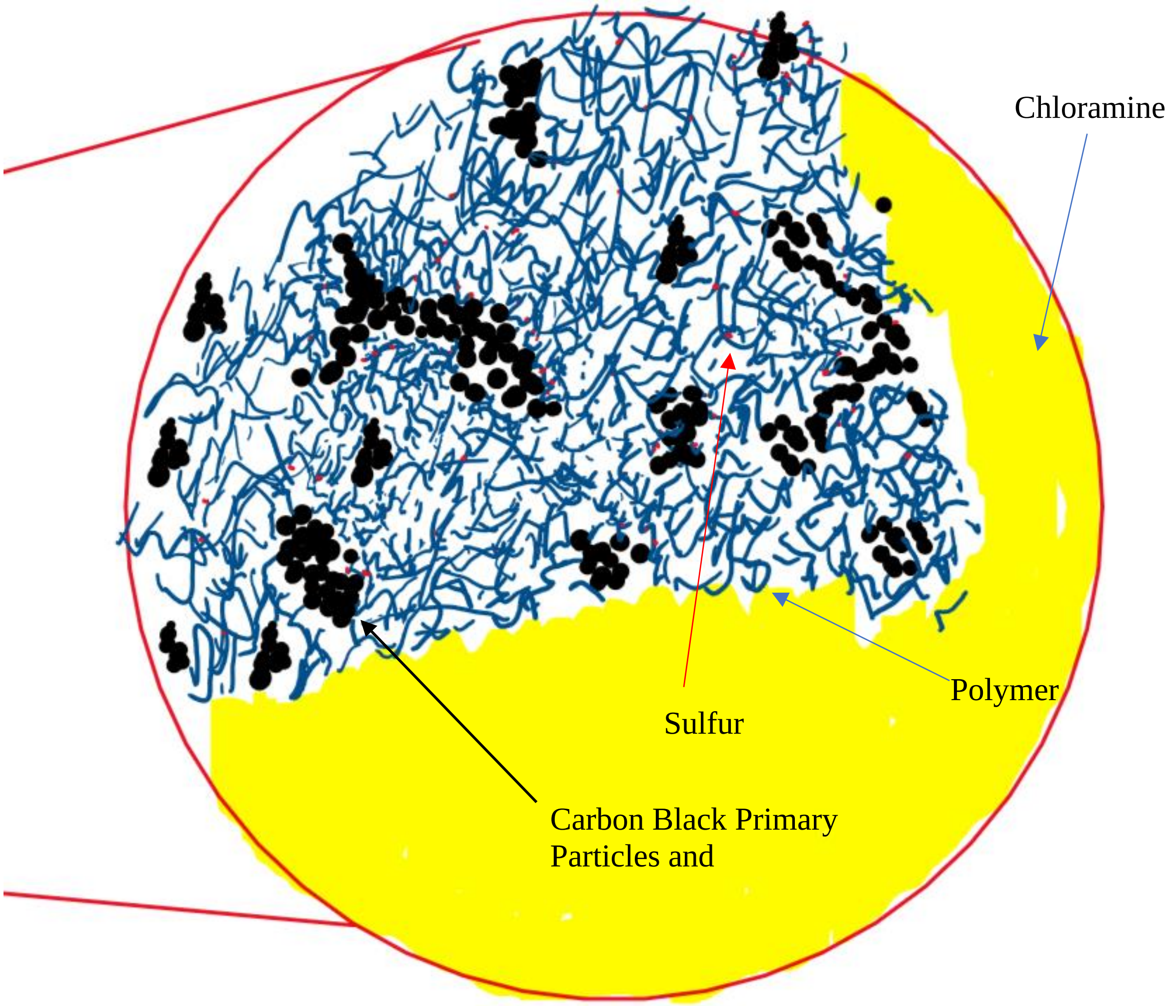


Figure 39 - Rubber-Chloramine Interface at Initial Chloramine Contact

At initial conditions, there is a significant concentration gradient between the boundary and the center of the particle both in the concentration of chloramine and water. This concentration gradient creates a diffusive flow that is represented in Figure 40. The flow of aqueous chloramine takes the path of least resistance as it passes between carbon black aggregates that are dispersed within the rubber matrix.

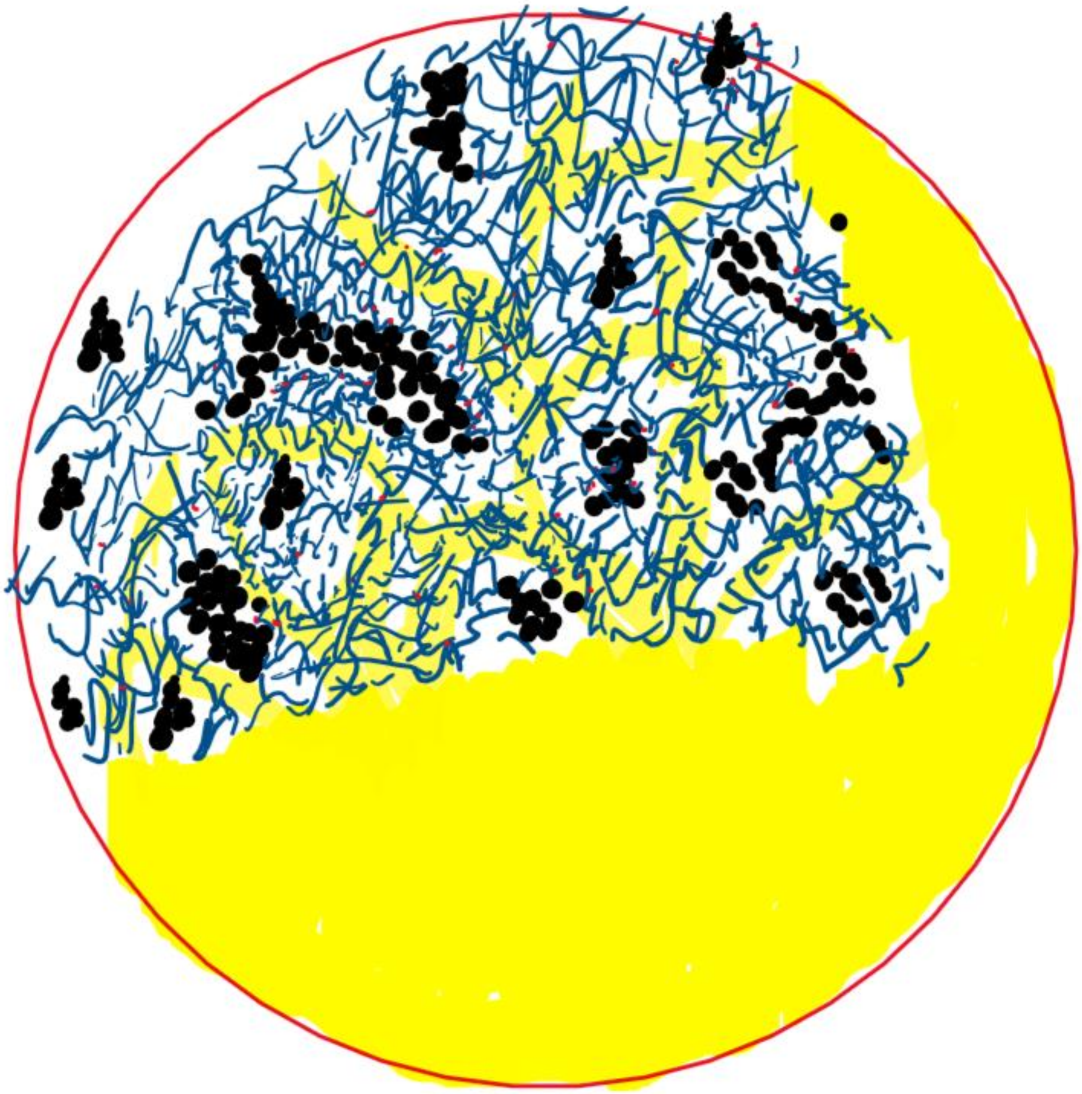


Figure 40 - Diffusive Flow of Aqueous Chloramine into the Rubber Matrix

Due to these flow paths, the concentration of chloramine is greater at the center of channel between carbon black aggregates than near the polymer-carbon black interface. Further, since the crosslink density has been shown to be higher near the polymer carbon black interface, cracks begin to form in the rubber matrix where the concentration of chloramine is highest and crosslinking is lowest (11). Figure 41 shows a visual representation of the crack formation and particle breakup.

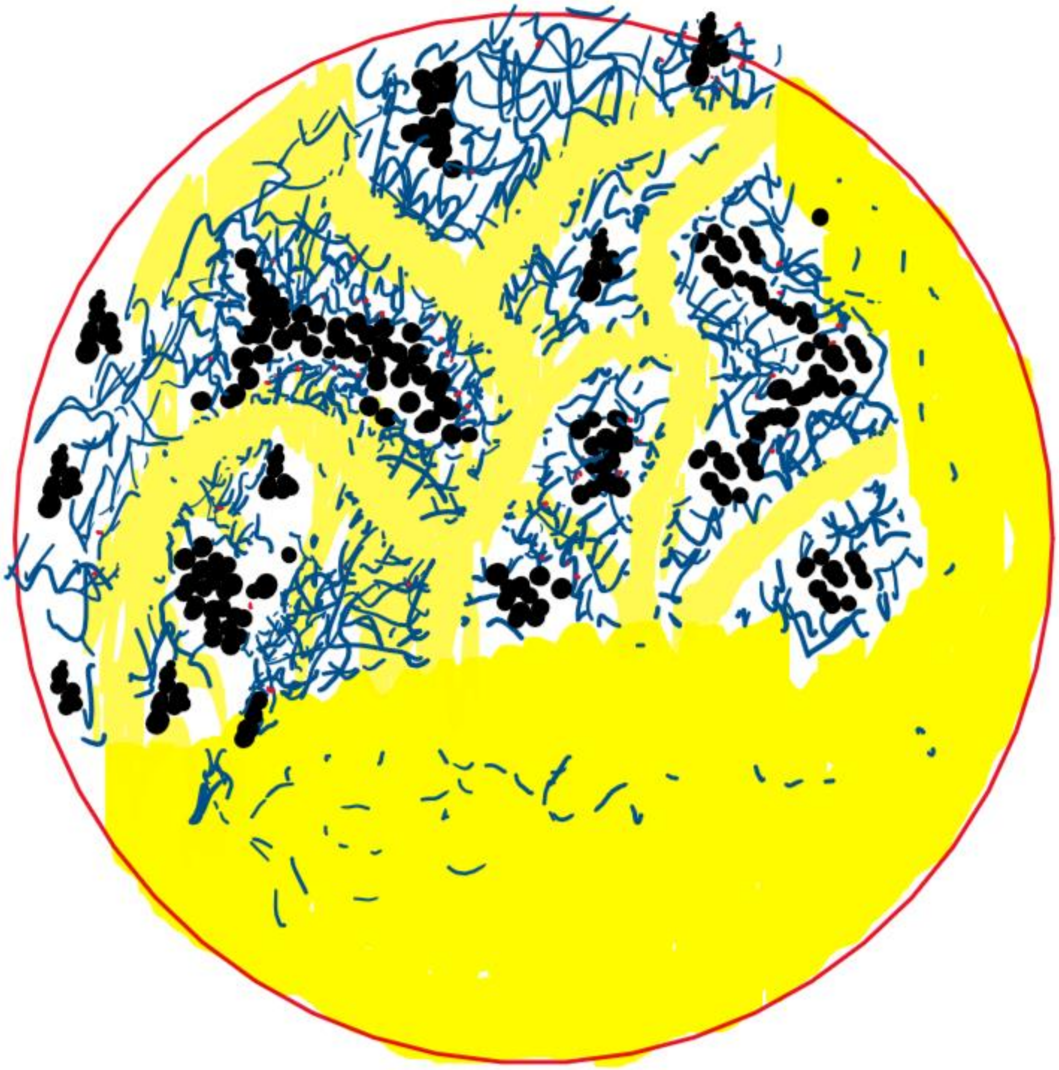


Figure 41 - Crack formation and Rubber Particle Breakup

The crack formation, assisted by the agitation of the solution, creates wider flow channels for additional chloramine solution to permeate, causing the cracks to grow wider and the rubber matrix to break apart. The CrCB particles also undergo devulcanization within their matrix but are more resistant to breakup since they are reinforced by the carbon black aggregate structure, higher crosslink density, and the chemical and physical adsorption at the polymer-carbon black interface. Evidence of this small particle devulcanization is seen in the further reduction of the polymer-carbon black ratio after xylene solvent extraction. At the crack interfaces, individual polymer molecules, freed from the sulfur crosslinks, are released into the aqueous solution. On a macro scale, this mechanism is occurring at the surface of the micronized rubber particle. The leaving CrCB particles allow further crack formation into the bulk rubber particle and the process repeats itself until complete breakup of the rubber particle occurs.

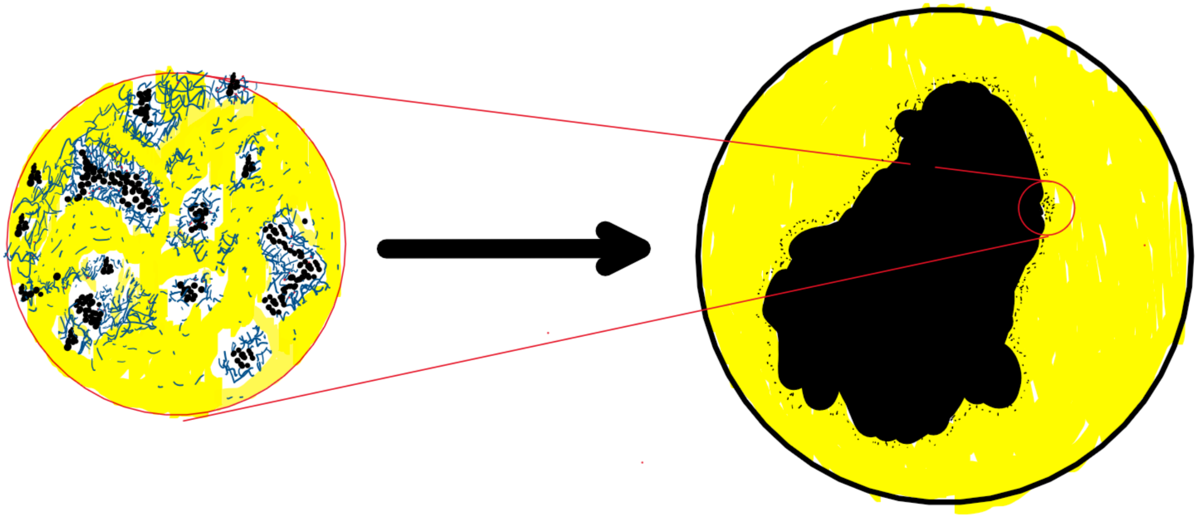


Figure 42 - Rubber Particle Breakup from the Macro Scale View

From this proposed mechanism, it stands to reason that devulcanization on the CrCB particle is somewhat incomplete and further treatment of the CrCB could reduce the polymer-carbon black ratio further and lead to a reduction of CrCB particle size and possibly an improvement in surface morphology through exposure of the carbon black primary particles and aggregates. This particle size reduction and improvement in surface morphology should lead to better overall reinforcement when re-compounded in rubber. Further, additional treatment of CrCB with chloramine would produce additional CdR and further separate and purify the two products. Additional research is needed to determine the extent of polymer removal from CrCB.

The following section discusses the reaction rate of the chloramine-rubber system. A model of chloramine auto decomposition is selected from literature and then used to evaluate whether the chloramine-rubber reaction is rate limited or diffusion limited.

4.3.5 Chloramine Devulcanization Reaction Rate

The density of rubber limits the diffusion of gas and liquid media through its matrix. At first glance without analysis, the devulcanization reaction rate appears to be diffusion limited. Although that may be the case, it is important to understand the factors that influence the rate of devulcanization. Aqueous chloramine is reactive and undergoes auto-decomposition via hydrolysis and reactions with other compounds typically found in water. In preferred reaction conditions, the decomposition of chloramine and diffusion limiting effects are minimized and devulcanization reaction is promoted. Thus, the factors that impact stable diffusion of chloramine into the rubber matrix are discussed in the following subsections.

4.3.5.1 Chloramine Auto-Decomposition

The set of reactions that make up chloramine formation and decomposition are complex. Because of chloramine’s use in water disinfection, research over the last 30-40 years has provided a nearly complete picture of the chloramine decomposition pathway. Figure 43 lists the reactions that lead to chloramine ultimately decomposing into N_2, NH_3, and HCl.

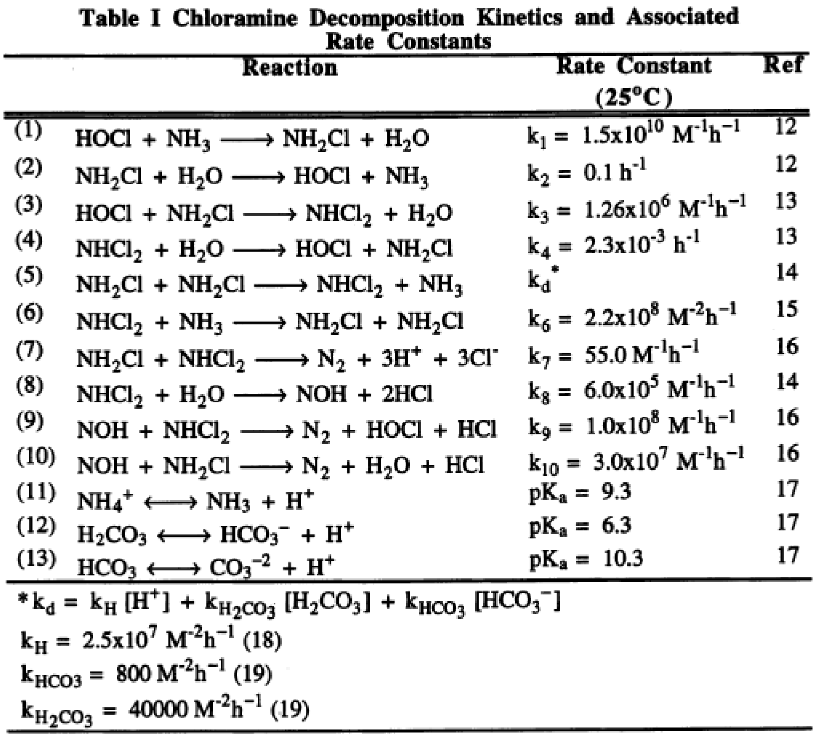


Table I Chloramine Decomposition Kinetics and Associated Rate Constants

	Reaction	Rate Constant (25°C)	Ref
(1)	$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O$	$k_1 = 1.5x10^{10}\ M^{-1}h^{-1}$	12
(2)	$NH_2Cl + H_2O \longrightarrow HOCl + NH_3$	$k_2 = 0.1\ h^{-1}$	12
(3)	$HOCl + NH_2Cl \longrightarrow NHCl_2 + H_2O$	$k_3 = 1.26x10^{6}\ M^{-1}h^{-1}$	13
(4)	$NHCl_2 + H_2O \longrightarrow HOCl + NH_2Cl$	$k_4 = 2.3x10^{-3}\ h^{-1}$	13
(5)	$NH_2Cl + NH_2Cl \longrightarrow NHCl_2 + NH_3$	k_d^*	14
(6)	$NHCl_2 + NH_3 \longrightarrow NH_2Cl + NH_2Cl$	$k_6 = 2.2x10^{8}\ M^{-2}h^{-1}$	15
(7)	$NH_2Cl + NHCl_2 \longrightarrow N_2 + 3H^+ + 3Cl^-$	$k_7 = 55.0\ M^{-1}h^{-1}$	16
(8)	$NHCl_2 + H_2O \longrightarrow NOH + 2HCl$	$k_8 = 6.0x10^{5}\ M^{-1}h^{-1}$	14
(9)	$NOH + NHCl_2 \longrightarrow N_2 + HOCl + HCl$	$k_9 = 1.0x10^{8}\ M^{-1}h^{-1}$	16
(10)	$NOH + NH_2Cl \longrightarrow N_2 + H_2O + HCl$	$k_{10} = 3.0x10^{7}\ M^{-1}h^{-1}$	16
(11)	$NH_4^+ \longleftrightarrow NH_3 + H^+$	$pK_a = 9.3$	17
(12)	$H_2CO_3 \longleftrightarrow HCO_3^- + H^+$	$pK_a = 6.3$	17
(13)	$HCO_3 \longleftrightarrow CO_3^{-2} + H^+$	$pK_a = 10.3$	17

$*k_d = k_H [H^+] + k_{H_2CO_3} [H_2CO_3] + k_{HCO_3} [HCO_3^-]$

$k_H = 2.5x10^7\ M^{-2}h^{-1}$ (18)

$k_{HCO3} = 800\ M^{-2}h^{-1}$ (19)

$k_{H_2CO_3} = 40000\ M^{-2}h^{-1}$ (19)

Figure 43 - Chloramine Decomposition Reactions Taken from Ozekin et. al (47)

Due to the large rate constants and number of rate equations, these reaction rates are difficult to model but researchers have sought to simplify the degradation model through empirical correlations. Ozekin et. al propose that the monochloramine loss is caused primarily by dichloramine formation where the mechanism from Figure 43 can be simplified to include only reactions 1, 2, 3, 5, and 7. The model is a second order rate law where the change in concentration of chloramine and rate constant are described by the following equations (47):

$$\frac{d[NH_2Cl]}{dt} = -k_{VSC}[NH_2Cl]^2 \qquad (1)$$

$$\frac{1}{[NH_2Cl](t)} = \frac{1}{[NH_2Cl]_0} + k_{VSC}t \qquad (2)$$

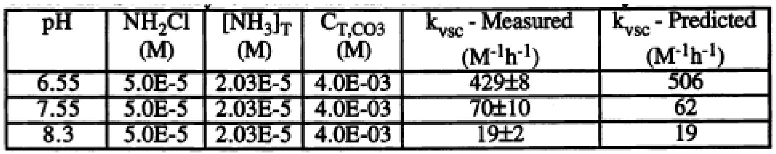
where the temperature dependence of rate constant k_{VSC}, also called the Valentine Stability Coefficient can also be described by the Arrhenius equation

$$k_{VSC}(T) = k_{298} exp\left\{-\frac{E}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right\} \tag{3}$$

and where the activation energy and ideal gas constant ratio, E/R, is 3551 ± 705 K (48). The Valentine Stability Coefficient, k_{VSC} was shown to be dependent on several known rate and equilibrium constants, pH, alkalinity, and residual ammonia concentration per the following relationship:

$$k_{VSC} = 3\left\{k_{H^+}[H^+] + \alpha_0 k_{H_2CO_3} C_{T,CO_3} + \alpha_1 k_{HCO_3} C_{T,CO_3}\right\} + \frac{2\, k_3 K_e}{\alpha_{0,N}[NH_3]_T} \tag{4}$$

This model was developed and tested against water quality conditions with temperatures up to 50 °C and pH ranges from 6.55 to 8.3. Ozekin et. al reported generally good agreement with their model and measured data as shown below in



pH	NH_2Cl (M)	$[NH_3]_T$ (M)	$C_{T,CO3}$ (M)	k_{vsc} - Measured ($M^{-1}h^{-1}$)	k_{vsc} - Predicted ($M^{-1}h^{-1}$)
6.55	5.0E-5	2.03E-5	4.0E-03	429±8	506
7.55	5.0E-5	2.03E-5	4.0E-03	70±10	62
8.3	5.0E-5	2.03E-5	4.0E-03	19±2	19

Figure 44 - Valentine Stability Constant model reported values

To corroborate the data from this model at higher temperatures and chloramine concentrations, we took data from the 2007 AWWA report titled *Performance of Elastomeric Components in Contact with Potable Water*, where the decomposition of a 120 ppm (1.94×10^{-3} M), 70 °C, pH 8.3 chloramine solution was measured over a 24 hour period, and plotted it in the form of Equation 2 (49).

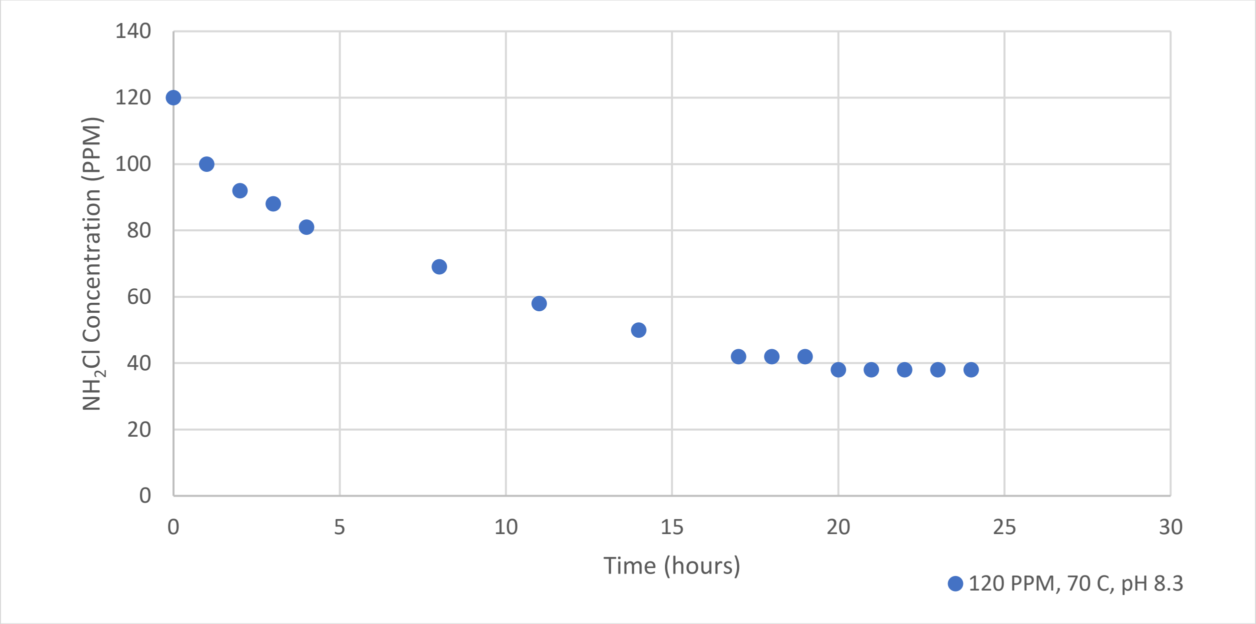


Figure 45 - AWWA Chloramine Decomposition Data for 120 ppm, 70 °C, pH 8.3 Solution

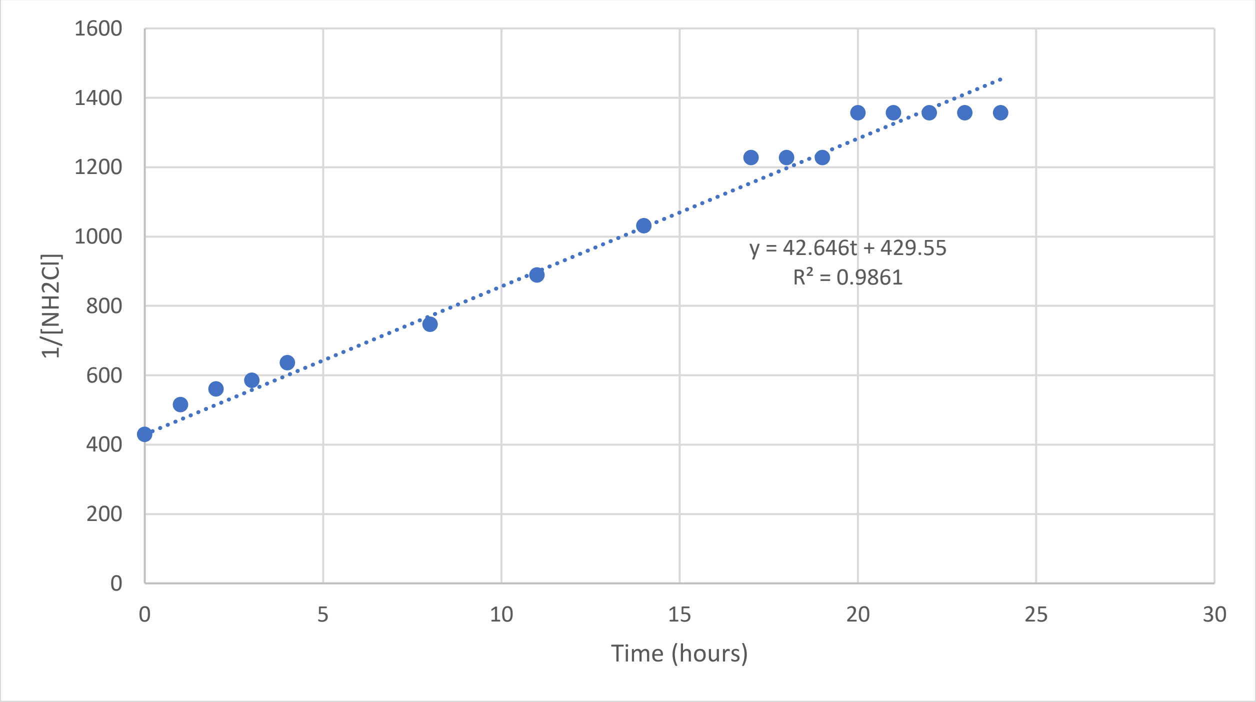


Figure 46 - Chloramine Decomposition Data Plotted in the Form of Equation 2

The linear regression in Figure 46 shows that the rate constant of the second order decomposition reaction is 42 M^{-1} h^{-1} for the chloramine solution at 70 °C and pH 8.3.

Figure 44 value for chloramine decomposition at pH 8.3 and 25 C is then transformed using Equation 3 and the activation energy to ideal gas constant ratio, E/R, is 3551 ± 705 K. The output of the Arrhenius transformation is shown in Table 8, which also accounts for the error in the E/R ratio.

Table 8 - Arrhenius Transformation of Second Order Rate Constant

k_{VSC} @ 25 °C, 8.3 pH (M^{-1} h^{-1})	T (°C)	E/R (K)	k_{VSC} Calculated (M^{-1} h^{-1})	k_{VSC} Measured (M^{-1} h^{-1})
19	70	2846	67	42
		3551	91	
		4256	124	

Despite that the k_{VSC} data reported by Ozekin et. al was produced at concentrations of only ~3-5 ppm (5×10^{-5} M), we can see from Table 8 that their second order model and rate constant data are acceptable (42 M^{-1} h^{-1} vs 67 M^{-1} h^{-1}) for this analysis even at concentrations up to 120 PPM. It is important to note that we are using the Valentine Stability Coefficient model outside of the tested model parameters for chloramine concentration. It is expected that the model may not hold its confidence level for extrapolated ranges, but we believe that the modeled values vs the measured values presented in Table 8 are acceptable for this analysis.

4.3.5.2 Chloramine-Sulfur Reaction Rate

Limited information exists on the rate of reaction between chloramine and sulfur/disulfide bonds. Work by Scully and White in a study published by the EPA entitled *Reactions of Potential Organic Water Contaminants with Aqueous Chlorine and Monochloramine* states that

> *Work of Jacangelo and Oliveri suggests that a 5 fold excess of the sulfur-containing amino acids cysteine, cystine, or methionine completely reduced monochloramine within 2 min. They determined that each monochloramine oxidized two cysteine resides to one cystine which*

> *contains the -S-S- bond. In the presence of excess oxidant cystine can be oxidized further to thiolsulfinates, sulfinyl sulfones, sulfinic and sulfonic acids*

Further they state that the reaction between chloramine-T and dimethylsulfide is second order with a rate constant equal to 2.7 x 10^4 M^{-1} s^{-1}. Overall, they describe monochloramine as “very reactive” (i.e. 50% reacted within <5 minutes) with alkyl sulfides (50). Not enough information is available to determine whether these reaction rate constants apply to the types of disulfide bonds found in rubber. Further research into this is needed.

4.3.5.3 Diffusivity of Monochloramine Through Rubber

As with chloramine-sulfur reactivity, there is limited information on the diffusivity of chloramine through rubber. Two studies conducted at the University of Louisville by Schoenbaechler and Nagisetty et. al present values for the diffusion of monochloramine through rubber. Nagisetty specifically reports diffusivity of chloramine through NR and SBR to be 1.89 x 10^{-9} cm^2/s and 1.38x10^{-9} cm^2/s, respectively, for 30 ppm chloramine solutions at 45 °C (51). This information, along with reaction rates constants, is used going forward to determine whether the reaction is rate or diffusion limited.

4.3.5.4 Rate of Reaction vs Rate of Diffusion: Thiele Modulus

It is important to select the proper method to determine whether the chloramine rubber reaction is rate limited or diffusion limited. In chemical reactor engineering design, the Thiele modulus is used to describe the relationship between surface reaction rate and diffusion through a catalyst pellet as follows (52):

$$\varphi_n^2 = \frac{reaction\,rate\,of\,species\,A\,on\,surface\,of\,pellet}{diffusion\,rate\,of\,species\,A\,through\,pellet} \quad (5)$$

$$\varphi_n^2 = \frac{k_n R^2 C_{As}^{n-1}}{D_e} \quad (6)$$

Where

$\varphi_n = Thiele\ modulus\ for\ nth\ order\ reaction$

$k_n = reaction\ rate\ constant\ for\ nth\ order\ reaction$

$R = radius\ of\ pellet\ or\ particle$

$C_{As} = concentration\ on\ particle\ surface$

$D_e = Effective\ diffusivity\ of\ substance\ A\ through\ particle$

$n = reaction\ order$

For a second order reaction with diffusion through a spherical catalyst pellet, the Thiele modulus is simplified to:

$$\varphi_2 = R\sqrt{\frac{k_2 C_{A0}}{D_e}} \quad (7)$$

4.3.5.5 Selection of Reaction Rate Constant for Thiele Modulus Analysis

The Thiele modulus is typically used to analyze diffusion into and reactions on the surface of a catalyst pellet. In these catalytic reactions, the reactants are converted to products without reacting with and consuming the catalyst. The chloramine rubber reaction is interesting because although the flow of chloramine through the rubber matrix on its tortuous path between carbon black aggregates is analogous to the flow of reactants through a catalyst pellet, the chloramine in this case is reacting with a portion of the rubber, unlike in the catalyst system. Because of this reaction with the rubber, the chloramine-sulfur reaction rate constant is likely not appropriate for use in the Thiele modulus analysis. The next section discusses the Thiele modulus for the chloramine-sulfur reaction in greater detail.

4.3.5.5.1 Discussion of Chloramine-Sulfur Reaction in Thiele Modulus Context

The Thiele modulus for a second order reaction of chloramine with sulfur using the diffusivity of chloramine through a 400-micron sphere of SBR and the reported second order reaction rate from the previous section returns a value of 4268. Catalytic Kinetics page 369, shows the curves for Thiele modulus plotted on a c/c^s (concentration-surface concentration ratio) vs (radius vs outside radius ratio) r/R. A Thiele modulus of 4268 is well off the curve which classifies the chloramine rubber reaction as extremely diffusion limited.

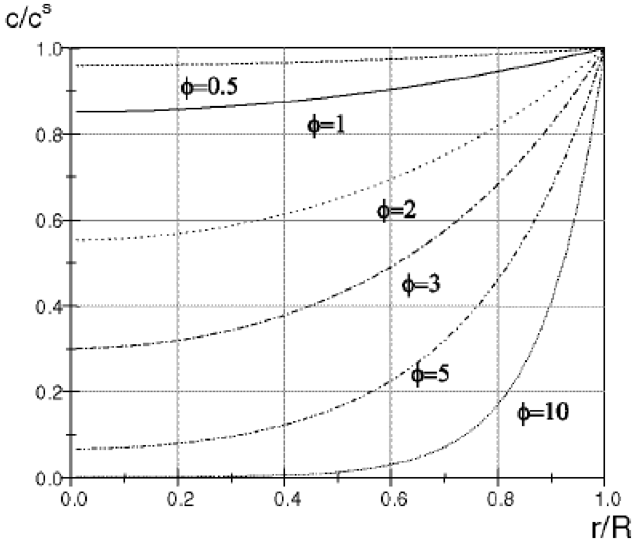


Figure 47 – Concentration vs Radius of a Spherical Particle at different Thiele Modulus

However, since the chloramine is reacting with sulfur as it is diffusing into the rubber matrix, this Thiele modulus does not adequately describe the ability of the chloramine to penetrate the SBR. If the only chloramine losses occurred via sulfur reactions and the sulfur content was depleted as the chloramine moved from the exterior of the particle to the center of the particle, the steady state concentration profile seen in Figure 47 would not exist. Instead, as the sulfur is depleted, the concentration at that radius would then become equal to the surface concentration. Once the sulfur in the rubber matrix had been completely depleted, the concentration at all points within the sphere would equal the concentration at the surface. This behavior is not observed, however, due to chloramine auto-decomposition. In fact, Nagisetty et. al showed concentration profiles similar to Figure 47 in their work to determine diffusion rates into elastomers as seen in Figure 48.

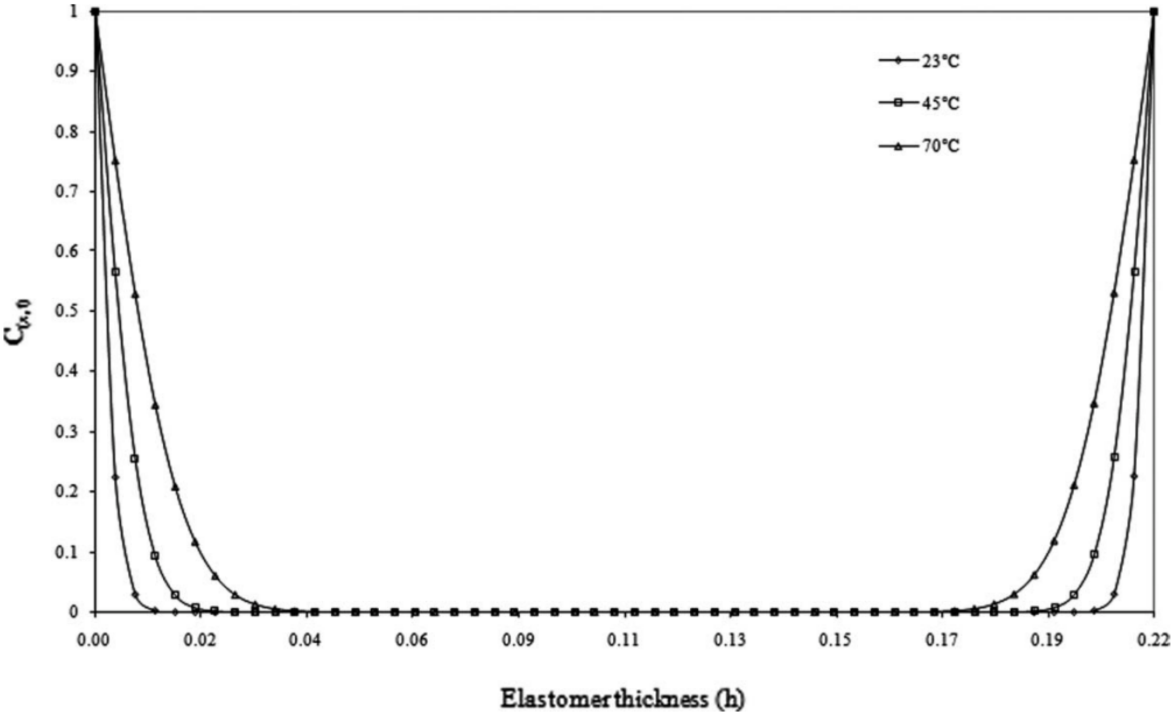


Figure 48 – Nagisetty et. al Concentration profiles of Monochloramine in Rubber Coupons over 30 days at 23 °C, 45 °C, and 70 °C (51)

Thus, the chloramine-sulfur reaction is not appropriate for this Thiele modulus analysis and the auto-decomposition reaction should be used instead. It is ultimately the auto decomposition reaction rate that governs the ability of chloramine to penetrate the rubber matrix and should be used to determine whether the chloramine devulcanization is rate limited or diffusion limited.

4.3.5.6 Calculation of Thiele Modulus for Second Order Chloramine Decomposition

The second order Thiele modulus, φ_2, is plotted in Figure 49 versus temperature at 100 ppm chloramine concentration at 3 different pH measurements for a 400-micron spherical particle. The Valentine Stability Coefficients from Figure 44 and the Arrhenius equation are used to create this plot. The diffusivity is estimated at different temperatures using the data on diffusivity and activation energy from Nagisetty et. al and the relationship below:

$$ln\, D = ln\, D_0 - \frac{E_D}{RT} \tag{8}$$

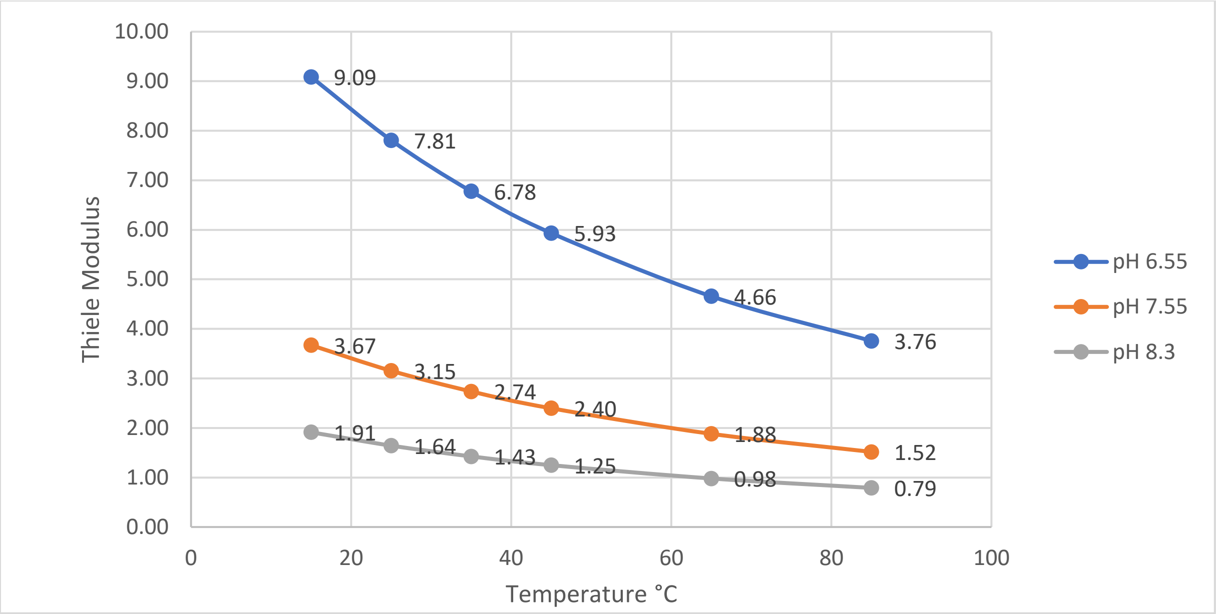


Figure 49 - Thiele Modulus φ Plotted vs Temperature at pH 6.55, 7.55, and 8.3

As mentioned before, this data has been produced with an incomplete dataset for diffusivity and the concentration used is out of the range of the chloramine loss model, however, it provides a picture of what factors cause the reaction to transition from extreme diffusion limiting to rate limiting. The pH of solution has a significant impact on chloramine stability and Thiele modulus. Rejecting the pH 6.55 and 7.55 operating conditions as non-viable, the pH 8.3 operating condition shows decreasing φ_2 with increasing temperature indicating that the diffusivity is increasing at a faster rate than the chloramine loss rate.

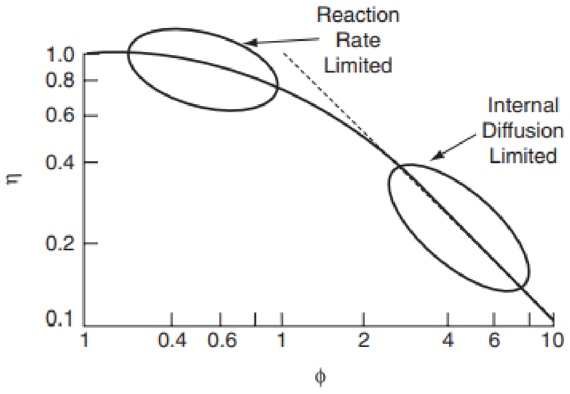


Figure 50 - Thiele Modulus versus Effectiveness Factor

Using Figure 50 as a reference, φ_1 at pH 8.3, 100 ppm, and above 60 °C lies within the reaction rate limited window. It is preferred that the reaction is rate limited rather than diffusion limited as a rate limited condition allows chloramine to penetrate deeper into the rubber matrix to break sulfur crosslinks.

Further research is needed to determine if 100 ppm is a chloramine concentration that allows the chloramine-sulfur reaction to occur at a sufficient rate. Plotting φ_2 against chloramine concentration out over an extrapolated range shows a transition back to a diffusion limiting state. It is unlikely that the steady state concentration in a chloramine-rubber devulcanization CSTR would be above 500 ppm, based on observed operating data using the Arduro Sustainable Rubber pilot plant.

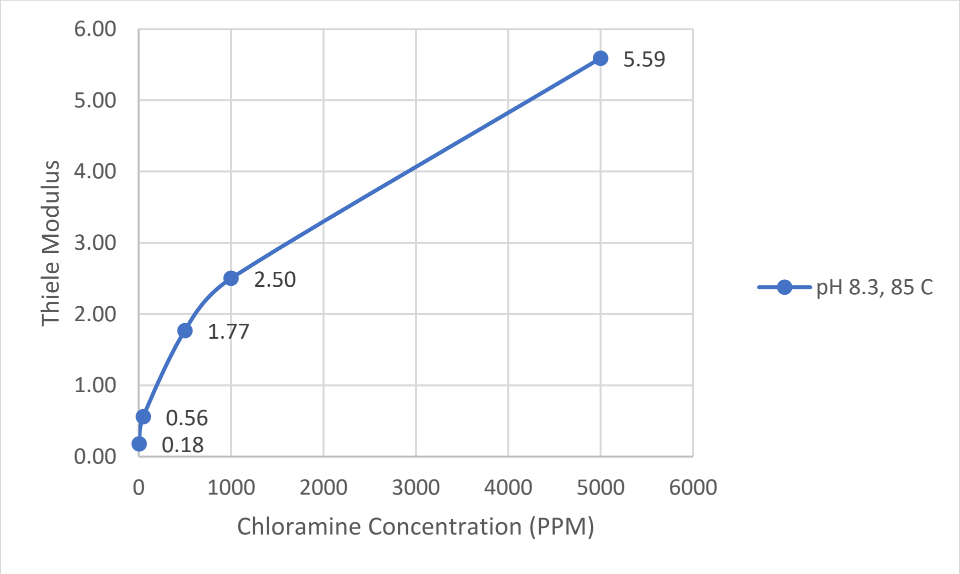


Figure 51 - Thiele Modulus vs Increasing Chloramine Concentration

Thus, this reaction appears to be rate limited in practical operation at pH 8, 85 °C, 100 ppm or less chloramine, and the 400-micron particle size.

4.3.6 Conclusions and Future Work

The work in Chapter 4 first evaluated the condition of both the CdR and CrCB recovered from the chloramine devulcanization reaction. Analysis conducted on the CrCB via SEM and TGA showed particles between 0.5-20 µm containing residual polymer but at a reduced polymer-carbon black ratio than found in the input micronized rubber (0.89 vs 1.54). An additional solvent extraction step showed that polymer-carbon black ratio was reduced to 0.46. Analysis of both CdR recovered from the solvent extraction step and aqueous solutions showed that it contained SBR and NR at possibly a lower molecular weight, seen through reduced TGA onset temperature, than virgin material.

A physical mechanism for breakup of the rubber particle was proposed from analysis of the CdR and CrCB material. This mechanism proposed that chloramine diffuses through the rubber matrix between carbon black aggregates. Diffusive flow was proposed to be zero at the carbon black aggregate interface and highest in the channels between those aggregates. This flow gradient then produces a concentration gradient where more crosslink breaking reactions occur in the channels. This leads to crack formation in those channels and subsequently to rubber particle breakup along those initial cracks. The smaller (0.5-20 micron) particles are then allowed to leave the system based on the current separation methodology and are recovered as CrCB. Based on this information, the CrCB may be introduced to more chloramine and the polymer-carbon black ratio may be reduced further.

Future work is needed to verify this model and the assumption that the polymer-carbon black ratio can be further reduced with additional chloramine treatment. Though further reduction of that ratio is likely possible, reduction to zero is unlikely due to covalent bonding between the polymer and carbon black during initial vulcanization.

Reaction rate was also analyzed to determine whether the chloramine rubber reaction system is rate limited or diffusion limited. A model was selected for chloramine auto-decomposition loss based on several factors including pH, temperature, and chloramine concentration. The Thiele modulus φ_2, a dimensionless ratio of reaction rate versus diffusion rate, was applied and the reaction was found to be excessively sensitive to pH and minorly sensitive to temperature and chloramine concentration. In the ideal condition of pH 8.3, 85 °C, and 100 ppm chloramine concentration, the Thiele modulus was 0.79 which indicates the reaction is rate limited.

Further work is needed to verify these assumptions as the selected model was extrapolated beyond the author's original data collection. There is also a lack of available information on reaction rate of chloramine with sulfur compounds. A reported rate of $2.7 \times 10^4\ M^{-1}\ s^{-1}$ for a reaction of chloramine with dimethylsulfide was the only data point available and it is not known whether this reaction data of this order of magnitude is applicable to vulcanized rubber. Future work should focus on expanding the chloramine loss model into the operational conditions used by chloramine devulcanization and defining the reaction rate of chloramine with sulfur compounds. A study showing the difference between chloramine loss due to auto-decomposition and additional loss due to sulfur crosslink reactions is also necessary.

CHAPTER 5 –TESTING OF MATERIALS RECOVERED FROM CHLORAMINE DEVULCANIZATION

As mentioned previously, it is important for products derived from devulcanization process to have value in the market. A manufacturing process that produces products without value will not contribute to the reduction of the world's tire problem. Therefore, it is important to understand the characteristics of the materials recovered from chloramine devulcanization. Chapter 5 covers the analytical and physical testing of these recovered materials. Development on chloramine recovered carbon black (CrCB) material has progressed faster and further than for chloramine devulcanized rubber (CdR). This is due to CrCB being the easier product to recover and evaluate against ASTM testing standards. Thus, CrCB testing is the focus of this chapter. The work-to-date on testing of CdR is discussed briefly but significant work remains to properly characterize the value of CdR as a product in the rubber industry.

5.1 Research Objectives

Chapter 5 research objectives for CrCB are listed below:

1. Test CrCB in ASTM industry standard carbon black tests and compare against both virgin carbon black and pyrolytic recovered carbon blacks.

2. Mix CrCB with rubber and curing additives in new rubber compounds and evaluate the vulcanized compounds against virgin carbon black control samples in ASTM standard rubber physical tests.

In addition to the specific research objectives related to testing carbon black, a portion of the discussion section is devoted to chloramine devulcanized rubber (CdR). Testing for that material has not been completed to the same extent as CrCB due to the low yield of CdR current pilot scale extraction methods. Rather this section briefly covers the development work that has been done to increase that yield as well as the tests that should be run on future versions of CdR.

5.2 Materials and Methods

The work completed in Chapter 5 was done in partnership with Arduro Sustainable Rubber Inc and Ace Laboratories in Ravenna, OH. Arduro supplied 2 kg of CrCB of material and all ASTM standards testing was completed by Ace.

5.2.1 CrCB Material

The CrCB material for these tests was produced in Arduro Sustainable Rubber's pilot plant located in Louisville KY. The pilot plant is a continuous process that as of 2022 produces chloramine derived CrCB from waste tire rubber. The CrCB product composition is shown in Table 9 and an SEM image from this material is shown in Figure 52

Table 9 - Composition of Arduro CrCB used in analytical and physical testing

Component	Arduro CrCB
Volatiles (<250 C)	3%
Extending Oils	1%
Polymer (NR + SBR)	31.4%
Unidentified Components (600-700 C)	7.6%
Carbon Black	47.4%
Ash	10.3%
[redacted]	[redacted]
Polymer : Carbon Black Ratio	0.66

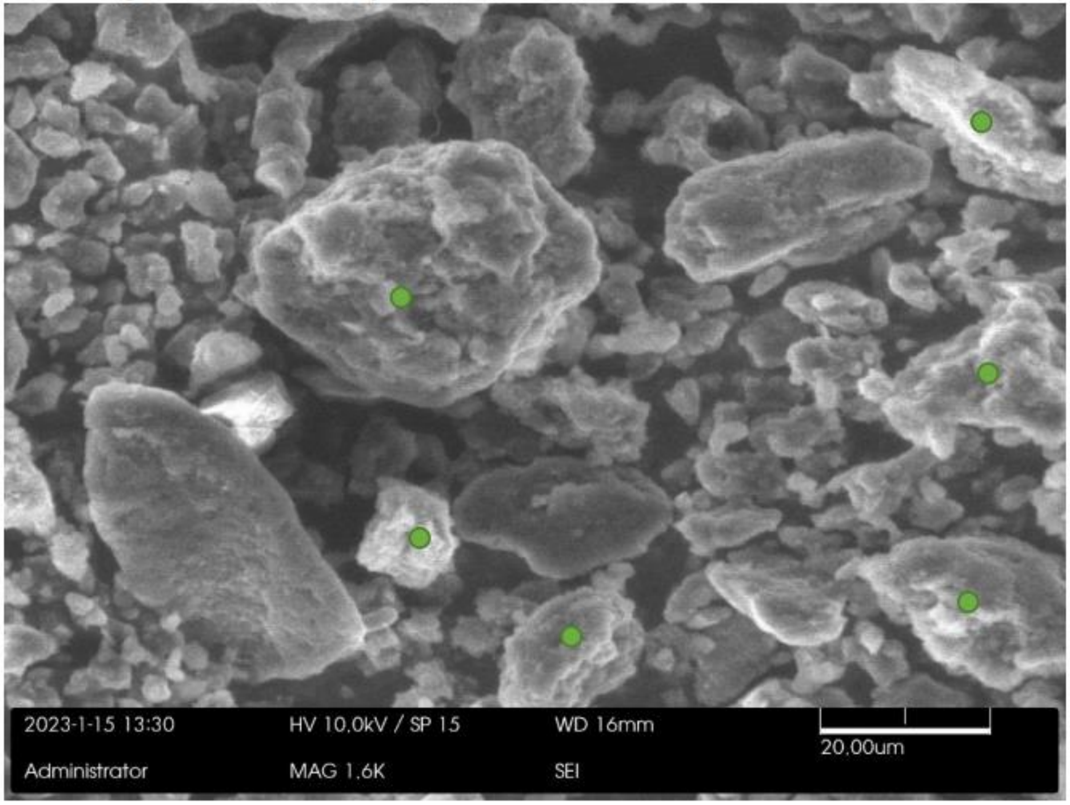


Figure 52 - SEM of Arduro CrCB used in analytical and physical testing

Both the composition data and SEM image are used in the results and discussion section to put context on the analytical results of testing.

5.2.2 Carbon Black Analytical Testing Standards

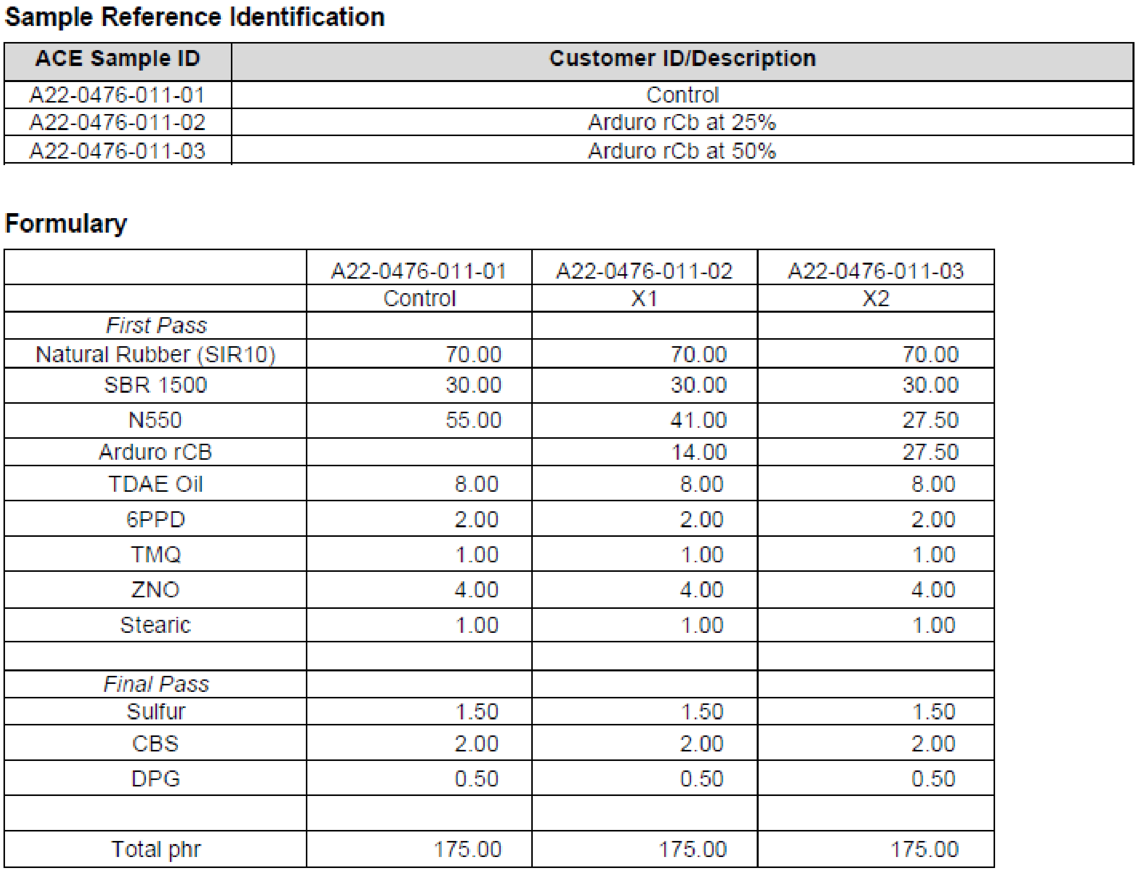
Ace Laboratories recommended the following tests for CrCB analytical testing:

1. ASTM D2414-21 Oil Absorption Number
2. ASTM D3493-21 Compressed Oil Absorption Number
3. ASTM D6556-21 Total and Statistical Surface Area by Nitrogen Adsorption

These tests are industry standard methodologies for determining estimating the particle size and aggregate structure of virgin carbon black and predicting the performance of carbon blacks in rubber.

5.2.3 Rubber Compound Recipe

The CrCB provided by Arduro Sustainable Rubber was mixed by Ace Laboratories with a lab mixer in accordance with industry standard practices. For the first test, three batches were made with the following characteristics: (1) a control sample with 100% virgin N550 carbon black, (2) a sample with 25% CrCB and 75% N550 carbon black, and (3) a sample with 50% CrCB and 50% N550 carbon black. The complete compound recipe is shown below in Figure 53.



Sample Reference Identification

ACE Sample ID	Customer ID/Description
A22-0476-011-01	Control
A22-0476-011-02	Arduro rCb at 25%
A22-0476-011-03	Arduro rCb at 50%

Formulary

	A22-0476-011-01	A22-0476-011-02	A22-0476-011-03
	Control	X1	X2
First Pass			
Natural Rubber (SIR10)	70.00	70.00	70.00
SBR 1500	30.00	30.00	30.00
N550	55.00	41.00	27.50
Arduro rCB		14.00	27.50
TDAE Oil	8.00	8.00	8.00
6PPD	2.00	2.00	2.00
TMQ	1.00	1.00	1.00
ZNO	4.00	4.00	4.00
Stearic	1.00	1.00	1.00
Final Pass			
Sulfur	1.50	1.50	1.50
CBS	2.00	2.00	2.00
DPG	0.50	0.50	0.50
Total phr	175.00	175.00	175.00

Figure 53 - Rubber Compound Recipes for Physical Testing

In addition to the baseline testing done with the compound recipe above, product specific testing was done in three different applications: (1) dock fenders, (2) dock bumpers, and (3) tarp straps. The rubber compound recipes for those tests are shown in the results and discussion section.

5.2.4 Rubber Compound Physical Testing

The compound recipes were vulcanized by Ace Laboratories and cut into sample coupons as outlined by the ASTM standards requirements. The following tests were conducted on those samples:

1. ASTM D2240 Shore A Durometer
2. ASTM D412 Elongation %
3. ASTM D412 Tensile Strength
4. ASTM D624 Tear Strength Die B

5.3 Results and Discussion

5.3.1 CrCB Analytical Testing Results

The chloramine derived CrCB was analytically tested to determine NSA, STSA, OAN and COAN in accordance with the ASTM standards in the previous section. The results are displayed in Table 10.

Table 10 - CrCB Analytical Testing Results

Test	ASTM Standard	Result
Nitrogen Surface Area	ASTM D6556-21	8.2 m^2/g
Statistical Thickness Surface Area	ASTM D6556-21	7.6 m^2/g
Oil Absorption Number	ASTM D2414-21	No result
Compressed Oil Absorption Number	ASTM D3493-21	No result

Although the test was successfully completed for NSA and STSA, the OAN and COAN test failed due to the material condition. Ace Laboratories reported that the material did not appear to absorb the oil and that the torque increased significantly and risked damage to the testing unit. Despite this apparent non-result, the feedback on this specific test can be understood through the lens of the other analytical testing and the rubber compounded physical test. These results are discussed further below.

5.3.2 Results of CrCB Compounded Rubber Physical Testing

The chloramine derived CrCB, compounded and vulcanized as described in the previous section, was tested per the previously mentioned ASTM standard tests. The results of the baseline test are shown in Table 11.

Table 11 - CrCB Physical Testing Data

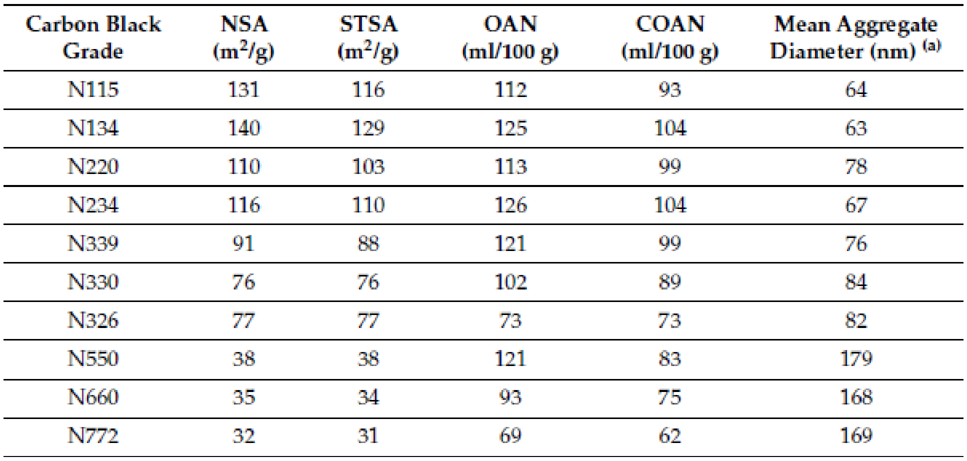
	Control 100% N550 0% CrCB	Sample 1 75% N550 25% CrCB	Sample 1 50% N550 50% CrCB
Shore A Durometer (Hardness)	63	60	57.5
Elongation %	455.92	475.29	508.81
Tensile Strength (Mpa)	20.26	17.35	15.37
Tear Strength Die B (kN/m)	77.89	60.31	50.72

5.3.3 Discussion of Analytical and Physical Testing

It is important to understand the purpose and mechanism of each of the analytical and physical tests to properly analyze the results. The following sections discuss the purpose of each test and the result for CrCB. Then finally the results are discussed together in the context of a new product in the rubber industry.

5.3.3.1 Carbon Black Analytical Testing Standards

The virgin carbon black analytical standards selected for these tests are used by the carbon black and rubber industry to estimate the reinforcement a given carbon black should have when compounded in rubber. These tests are also used to assign a grade to the virgin carbon black. Figure 54, seen first in Chapter 2 and revisited now, shows how the nitrogen surface area (NSA), statistical surface area (STSA), oil absorption number (OAN), and compressed oil absorption (COAN) are correlated to the mean aggregate diameter and used to assign grades to carbon black.



Carbon Black Grade	NSA (m^2/g)	STSA (m^2/g)	OAN (ml/100 g)	COAN (ml/100 g)	Mean Aggregate Diameter (nm) (a)
N115	131	116	112	93	64
N134	140	129	125	104	63
N220	110	103	113	99	78
N234	116	110	126	104	67
N339	91	88	121	99	76
N330	76	76	102	89	84
N326	77	77	73	73	82
N550	38	38	121	83	179
N660	35	34	93	75	168
N772	32	31	69	62	169

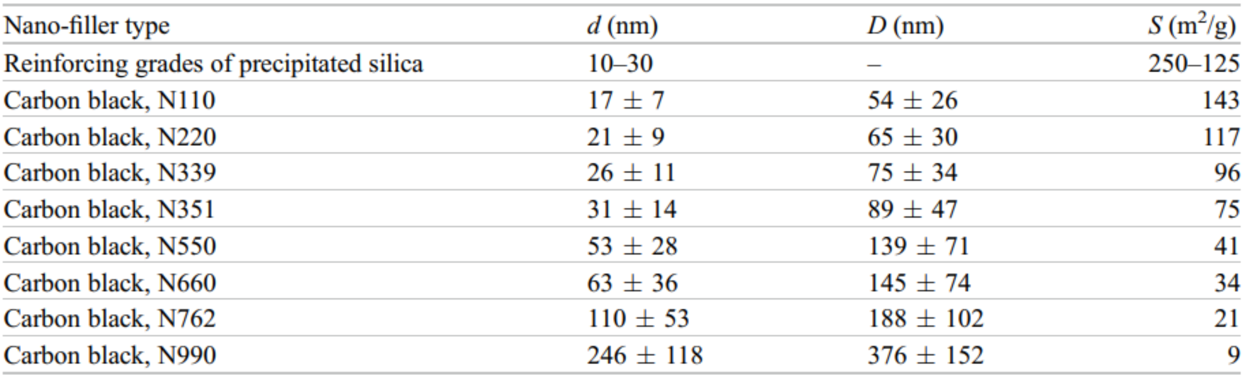
Figure 54 - Carbon Black Grades vs Analytical testing values

Generally, higher values for NSA, STSA, OAN, and COAN, are directly related to the reinforcement capability of the carbon black. When compounded and vulcanized with rubber, these carbon blacks with high surface areas and oil adsorption numbers have increased performance in many of the important physical tests such as tensile strength and tear strength.

5.3.3.2 Nitrogen Surface Area and Statistical Thickness Surface Area

Nitrogen surface area and statistical thickness surface area values are determined from a single test. The total surface area (NSA) is determined using the BET theory of multilayer gas adsorption while the external surface area (STSA) is determined by the statistical thickness surface area method using data from the total surface area test. The total surface area (NSA) returns a value for all surface area, both external surface and internal pores of the carbon black. The internal pores are not accessible by rubber during the compounding and vulcanization process, so they do not participate in the reinforcement of rubber. Since these internal sites are not available, the STSA method was developed to estimate the amount of surface area that is useable by the rubber.

CrCB shows low surface area when compared with virgin carbon blacks. The reported values of 8.2 m^2/g for NSA and 7.6 m^2/g for STSA put it into the N900 grades of non-reinforcing carbon black as seen in Figure 55.



Nano-filler type	*d* (nm)	*D* (nm)	*S* (m^2/g)
Reinforcing grades of precipitated silica	10–30	–	250–125
Carbon black, N110	17 ± 7	54 ± 26	143
Carbon black, N220	21 ± 9	65 ± 30	117
Carbon black, N339	26 ± 11	75 ± 34	96
Carbon black, N351	31 ± 14	89 ± 47	75
Carbon black, N550	53 ± 28	139 ± 71	41
Carbon black, N660	63 ± 36	145 ± 74	34
Carbon black, N762	110 ± 53	188 ± 102	21
Carbon black, N990	246 ± 118	376 ± 152	9

Figure 55 - Carbon Black Grades and Surface Area including N900 grades (53)

When looking at SEM imaging of the CrCB, it is evident that this low surface area is directly related to particle size and relative lack of surface morphology. Figure 56 compares the relative particle size of virgin N660 material, which is typically found in tires, to the CrCB taken from tires.

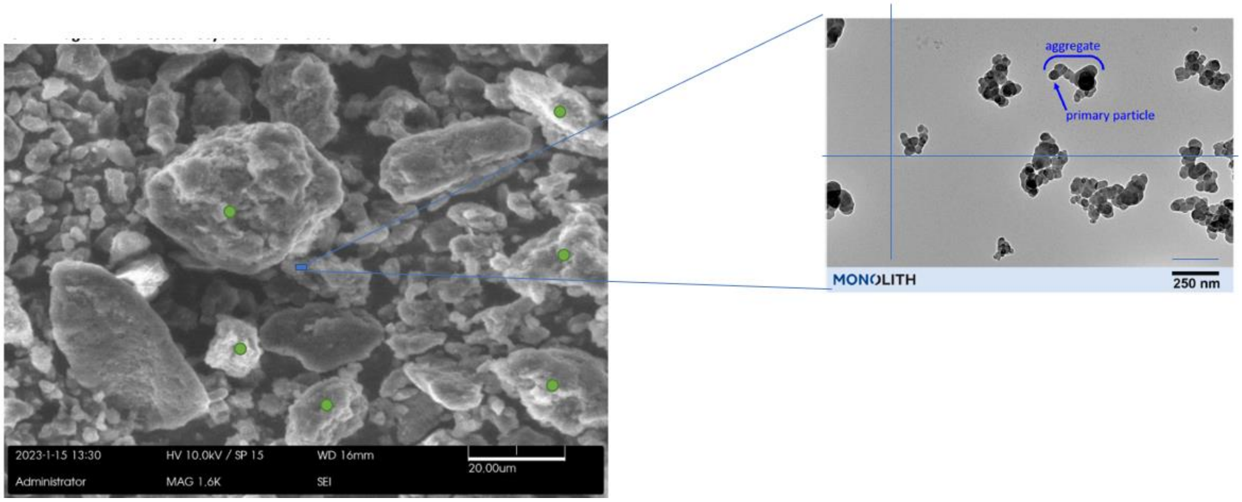


Figure 56 - Size comparison of N660 carbon black with CrCB

This analysis shows that the significant amount of polymer remaining on and around carbon black aggregates is covering up the surface morphology of the carbon black aggregates. If additional chloramine treatment was provided, the CrCB particles could likely be broken apart further reducing particle size and, if sufficient polymer has been removed, exposing the carbon black aggregates. This size reduction and exposure of aggregates would result in an increase of surface area measured by the NSA/STSA and also could contribute to increased performance in rubber. Further research is needed to validate this hypothesis.

5.3.3.3 Oil Absorption Number and Compressed Oil Absorption Number

The oil absorption number measures the ability of the carbon black to absorb liquids. This absorption capacity is a function of the structure of the carbon black (54). The structure of carbon black is a function of the number of primary particles and branching in the carbon black aggregates. The greater the branching the greater absorption of the oil into the carbon black. Hence, it is possible for two carbon blacks with the same size primary particles to have differing structures based on the degree of branching that occurs within the aggregate (55). The compressed oil absorption number is a slight variation on the oil adsorption number where the carbon black being tested is compressed four times in a compression cylinder at a pressure of 165 MPa (56). This pressure is sufficient to break down carbon black aggregate branching structure. Thus, high structured carbon blacks should have a large difference in OAN and COAN where low structured carbon blacks have a similar reported values for OAN and COAN.

The CrCB was not able to report a value for OAN and COAN. This is likely due to the surface morphology lacking any meaningful aggregate or branching structure. The structure as seen in Figure 56 of the CrCB shows relatively amorphous shapes with smooth surfaces that are not as effective for oil adsorption. Further, the CrCB with large particles containing residual vulcanized polymer would impart significantly higher torque to the absorption testing machine making it unable to run the sample properly. Overall, as with the NSA/STSA testing, further treatment to remove polymer and reduce particle size could lead to this test being performed properly. It is debatable whether this test, designed specifically for virgin carbon black, is applicable or relevant to a recovered material with a different composition and morphology and whether such results can be directly correlated to performance in a rubber compound, which is a more meaningful test of the effectiveness of the CrCB material.

5.3.3.4 Physical Testing of Rubber Compounded with CrCB

The physical tests run on CrCB are Shore A hardness, elongation %, tensile strength, and tear strength. Overall, a material that performs better across multiple tests has higher value in the rubber industry since it can be used in multiple different applications.

As with the carbon black analytical test, each physical test is discussed to provide context to why the test is important and what impact how inclusion of CrCB, with its known composition and characteristics, departs from the performance of the virgin carbon black material. However, due to the complexity of rubber compounding and the number of variables that impact it, it is usually only useful to compare a set of physical tests against a control that was mixed and compounded at the same time with the same procedure. Comparing the control against different loadings of the test material, as is done here, allows the researcher to see how performance changes from that control.

5.3.3.5 Shore A Hardness Tests

The Shore hardness scale, specifically the Shore A scale, measures the hardness of flexible materials like molded rubbers. This scale measures the resistance of a material to indentation by a needle pressed against the test material. Hardness of a material affects both performance and manufacturing. Rubber compounds fall widely across this scale between 20 and 95 shore hardness (57).

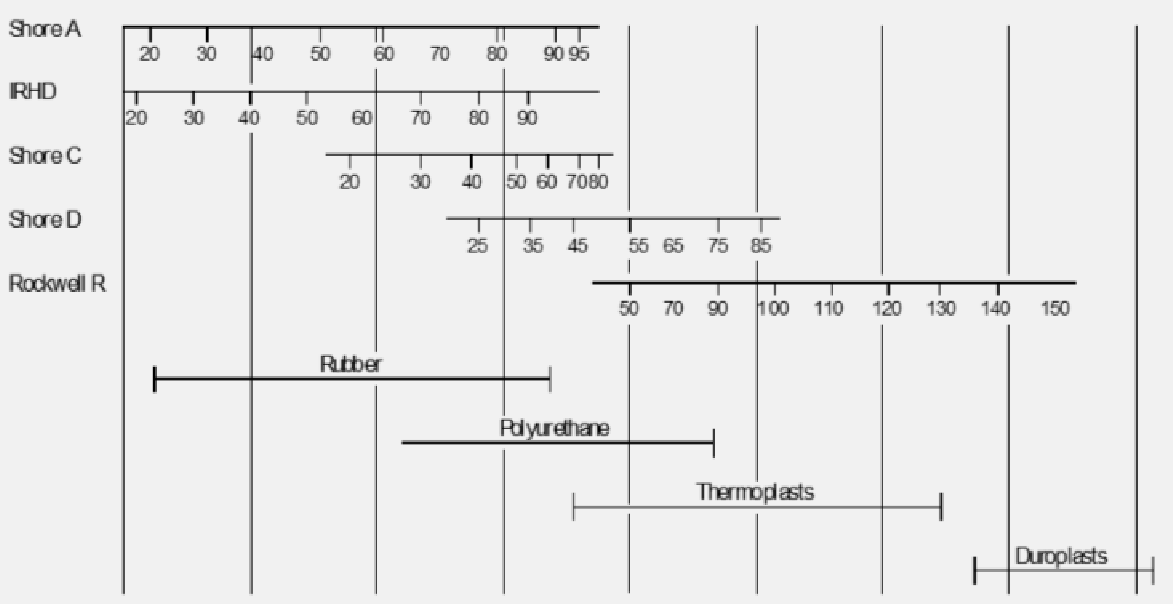


Figure 57 - Shore Hardness Scales vs Rubber (57)

Overall, the reported values for Shore A hardness do not depart significantly from the control value of 63 and are well within the acceptable hardness range.

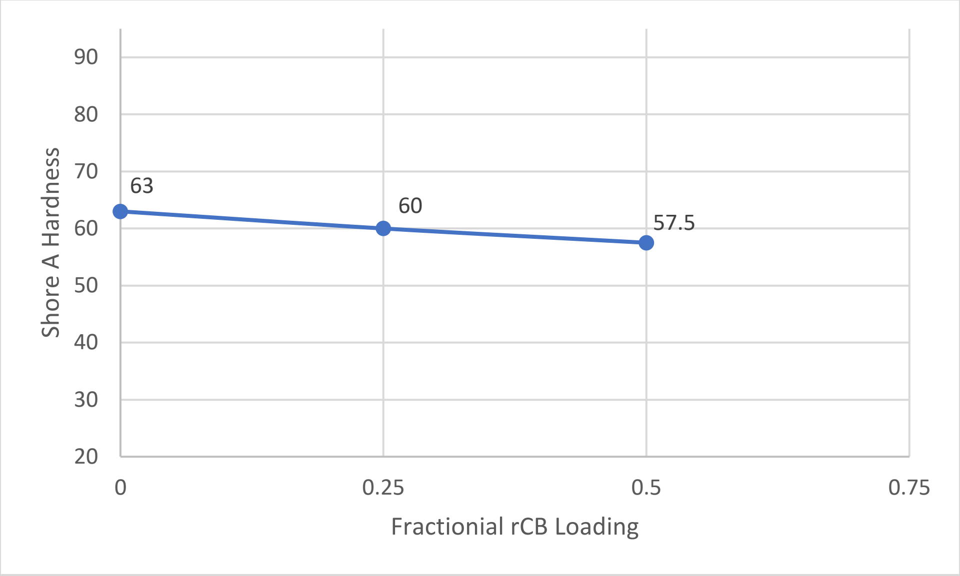


Figure 58 - Shore Hardness Change vs CrCB Loading

The reduction in hardness can be attributed to the presence of polymer within the CrCB and likely less reinforcement overall. This polymer, surrounding the carbon black aggregates, provides additional compressive capacity and thus reduces the hardness. While this decline in hardness is likely within spec for many applications, a further reduction of polymer content in the CrCB could lead to more consistency versus the control.

5.3.3.6 Tensile Strength and Elongation %

Tensile strength and Elongation are two related tests that are performed simultaneously on a universal test machine (UTM). Coupons of vulcanized rubber are pulled in tension as shown in Figure 59 until mechanical failure. The percent elongation from the coupon's original length at the moment of failure and the stress measured when that failure occurs are the values for % elongation and tensile strength, respectively (58). Both tests are an indication of the reinforcement capability of the carbon black/filler compound. Tensile strength increases with the higher surface area and surface activity of higher-grade carbon blacks. Contrastingly, elongation % decreases with increasing reinforcement as the carbon black limits the polymer's ability to stretch and elongate under a stress.

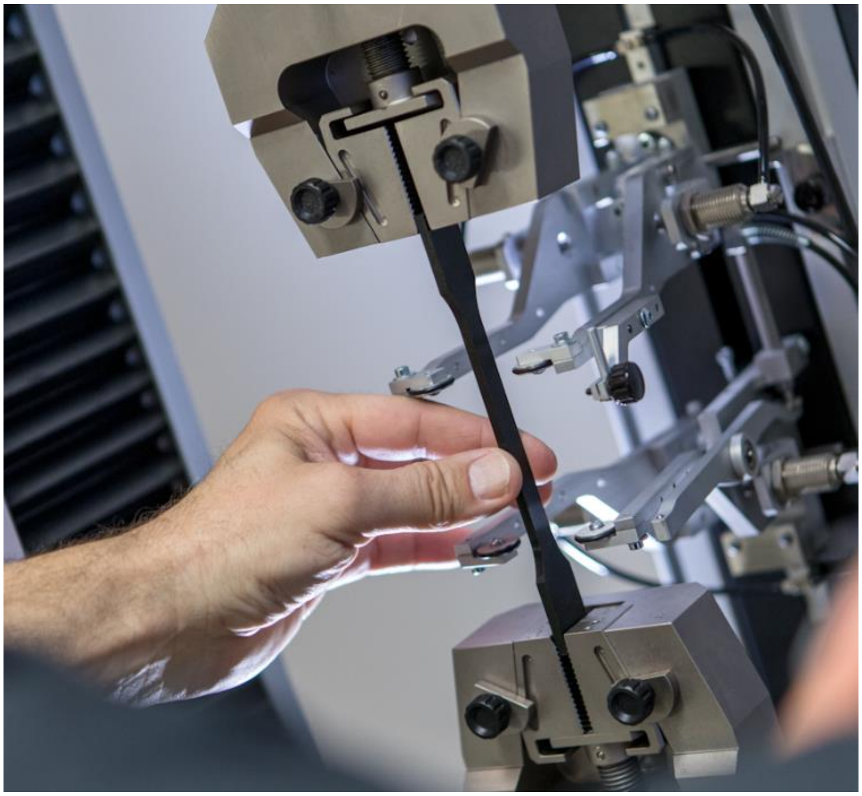


Figure 59 – UTM Testing a Rubber Coupon (59)

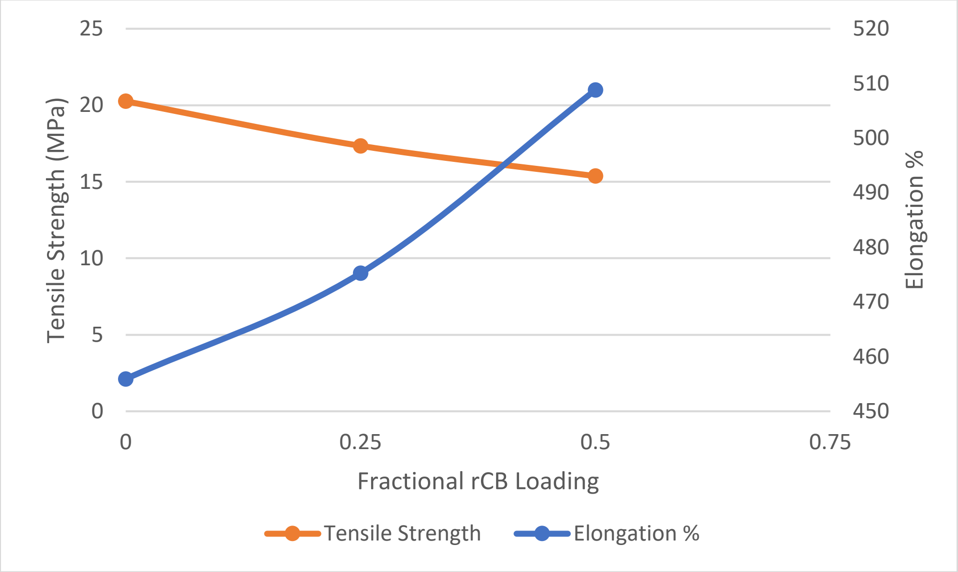


Figure 60 – Tensile Strength and Elongation % vs CrCB Loading

The data in Figure 60 shows that the tensile strength of the rubber compound decreases with CrCB loading while the elongation % increases. Our understanding of the reinforcement principles of carbon black indicates that reinforcement of rubber is proportional to the interfacial area (i.e. particle size and structure) of the carbon black. Thus, it is likely that the tensile strength falloff in this test is related to the lower CrCB interfacial area and surface morphology. The elongation % increasing can also be correlated to less reinforcement brought on by the larger particle size of the CrCB.

5.3.3.7 Tear Strength Die B

The tear strength of rubber is related to tensile strength and elongation and is also completed on the UTM. Unlike the previous tests which use an intact rubber coupon, the Tear Die B coupon has an “opposing ‘v’ shape which is nicked by a razor. The force acts along the major axis, perpendicular to the nick and measures tear propagation” (60).

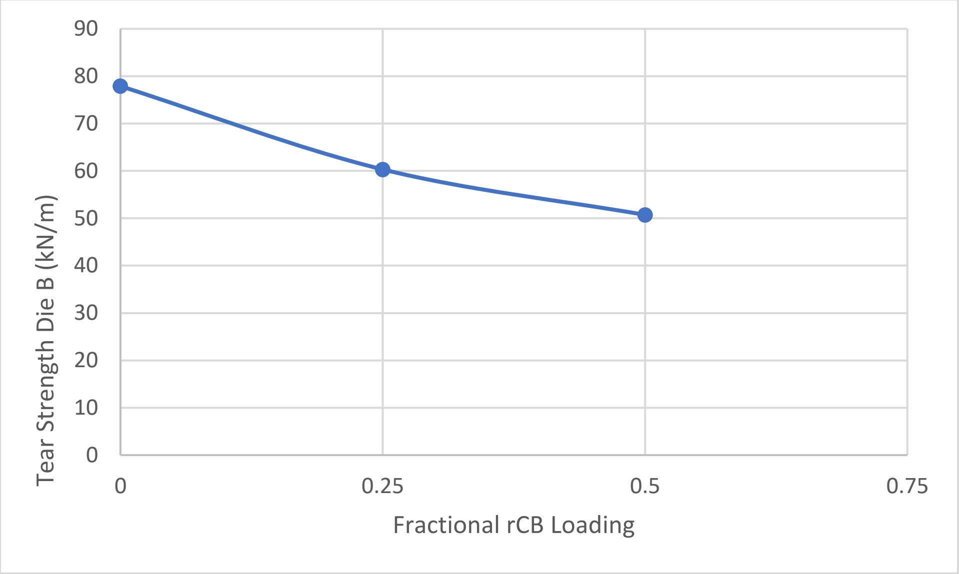


Figure 61 - Tear Strength Die B vs CrCB Loading

Figure 61, like the other tensile properties, shows a drop off in performance with increased CrCB loading. Although the mechanism for tear propagation and break is different from the tensile strength failure mechanism, the lower interfacial area and surface morphology of CrCB likely contribute the drop off in performance in this test as well.

5.3.3.8 Product Applications Testing of CrCB

In addition to the general rubber testing completed above, CrCB was compounded in formulations for three different molded good products: (1) dock bumpers, (2) dock fenders, and (3) tarp straps. These three products were selected as potential initial market entrant applications for CrCB. Ace provided the compound recipes for the three applications based on historical customer data and compounded the samples. The recipes are shown in Table 12-Table 14

Table 12 - Dock Bumper Compound Recipe

Dock Bumper				
FORMULARY	Control	X1 (100% CrCB)	X2 (50% CrCB)	X3 (25% CrCB)
First Pass				
SBR 1502	100.00	100.00	100.00	100.00
Whole Tire Reclaim	30.00	30.00	30.00	30.00
Sundex 790	43.00	43.00	43.00	43.00
N650	115.00	-	57.50	86.25
CrCB	-	115.00	57.50	28.75
Snowwhite (Omya)	45.00	45.00	45.00	45.00
AO67	3.00	3.00	3.00	3.00
Resin D	2.00	2.00	2.00	2.00
Akrowax 5031	2.00	2.00	2.00	2.00
Zinc Oxide	5.00	5.00	5.00	5.00
Stearic Acid	1.00	1.00	1.00	1.00
Carbowax 3350	1.00	1.00	1.00	1.00
Alphatac 95	2.50	2.50	2.50	2.50
TBBS	1.75	1.75	1.75	1.75
Sulfur	1.75	1.75	1.75	1.75

Table 13 - Dock Fender Compound Recipe

Dock Fender				
FORMULARY	Control	X1 (100% CrCB)	X2 (50% CrCB)	X3 (25% CrCB)
First Pass				
Royalene 512 EPDM	100.00	100.00	100.00	100.00
Napthentic Oil	160.00	160.00	160.00	160.00
N650	250.00	0.00	125.00	187.50
CrCB	0.00	250.00	125.00	62.50
Talc	8.00	8.00	8.00	8.00
Zinc Oxide	5.00	5.00	5.00	5.00
Stearic Acid	1.00	1.00	1.00	1.00
Alphatac 95	5.00	5.00	5.00	5.00
Calcium Stearate	5.00	5.00	5.00	5.00
TMTD	0.30	0.30	0.30	0.30
TBBS	1.50	1.50	1.50	1.50
ZDBC	0.50	0.50	0.50	0.50
ADMC	0.50	0.50	0.50	0.50
DPTT	0.50	0.50	0.50	0.50
Sulfur	1.25	1.25	1.25	1.25
Sulfasan R	0.25	0.25	0.25	0.25

Table 14 - Tarp Strap Compound Recipe

Tarp Strap				
FORMULARY	Control	X1 (100% CrCB)	X2 (50% CrCB)	X3 (25% CrCB)
First Pass				
Royalene 509 EPDM	100.00	100.00	100.00	100.00
N650	115.00	0.00	57.50	86.25
CrCB	0.00	115.00	57.50	28.75
Sunpar 2280	108.00	108.00	108.00	108.00
Snowwhite (Omya)	60.00	60.00	60.00	60.00
Zinc	5.00	5.00	5.00	5.00
Stearic Acid	1.00	1.00	1.00	1.00
PEH 100	2.00	2.00	2.00	2.00
MBTS	3.00	3.00	3.00	3.00
ZDBC	1.60	1.60	1.60	1.60
TMTD	0.50	0.50	0.50	0.50
Sulfur	1.75	1.75	1.75	1.75

The data table showing the individual results for dock bumper, dock fender, and tarp strap testing is shown in the Appendix. In this study, applications were selected that typically used N650 carbon black. As with the initial study, the control compound contains 100% N650 carbon black. Three variants in each application were selected with 25%, 50%, and 100% CrCB loading. All other ingredients, including rubber type, were selected based on application need. Figure 62 through Figure 65 shows the results for Shore A hardness, tensile strength, elongation %, and tear strength for the three product applications.

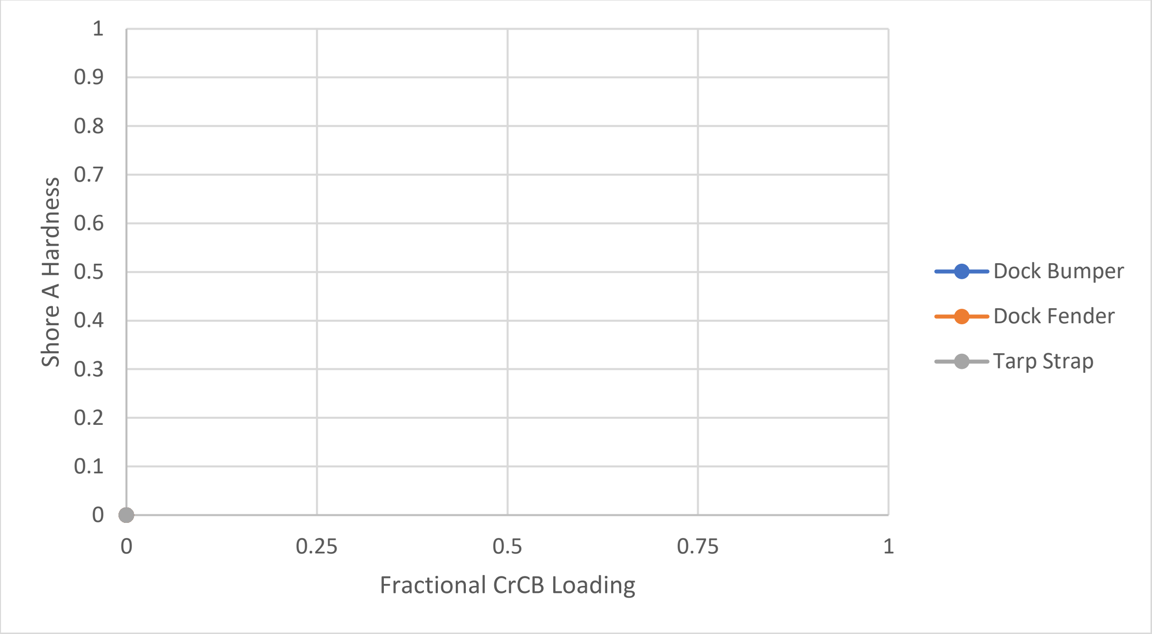


Figure 62 – Shore A Hardness for Dock Bumper, Dock Fender, and Tarp Strap Compounds

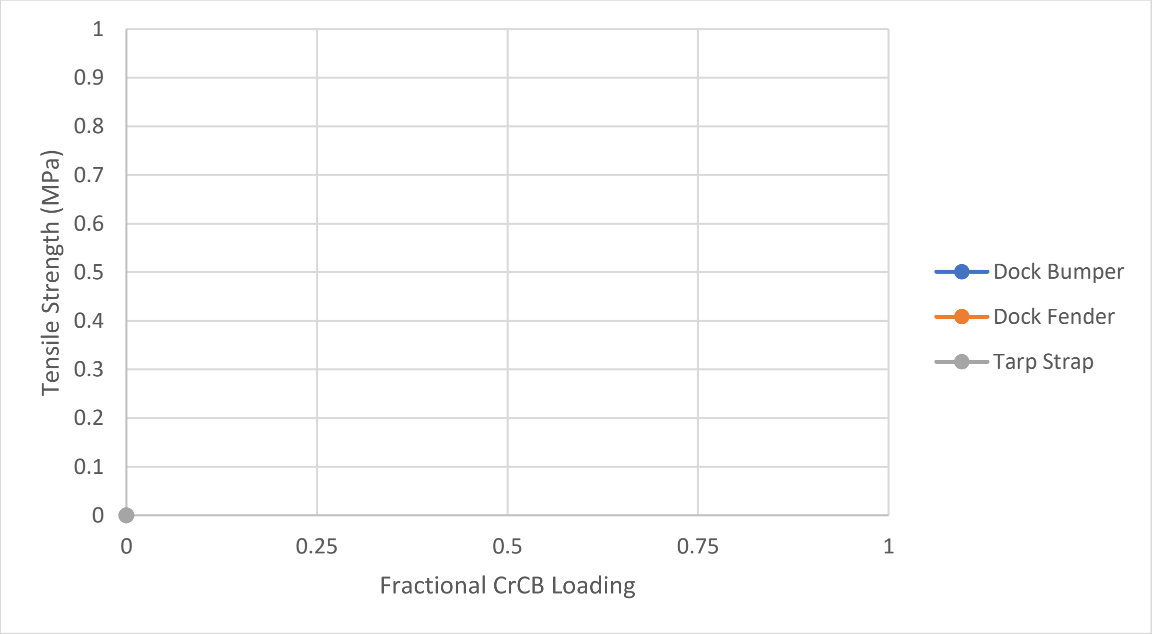


Figure 63 – Tensile Strength for Dock Bumper, Dock Fender, and Tarp Strap Compounds

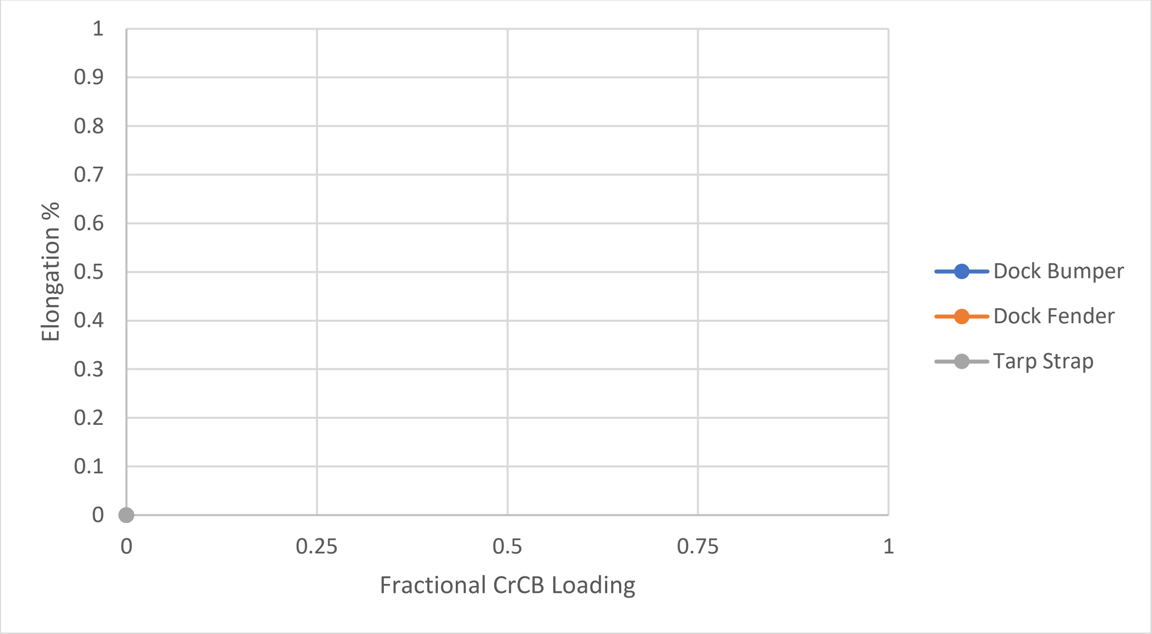


Figure 64 – Elongation % at Break for Dock Bumper, Dock Fender, and Tarp Strap Compounds

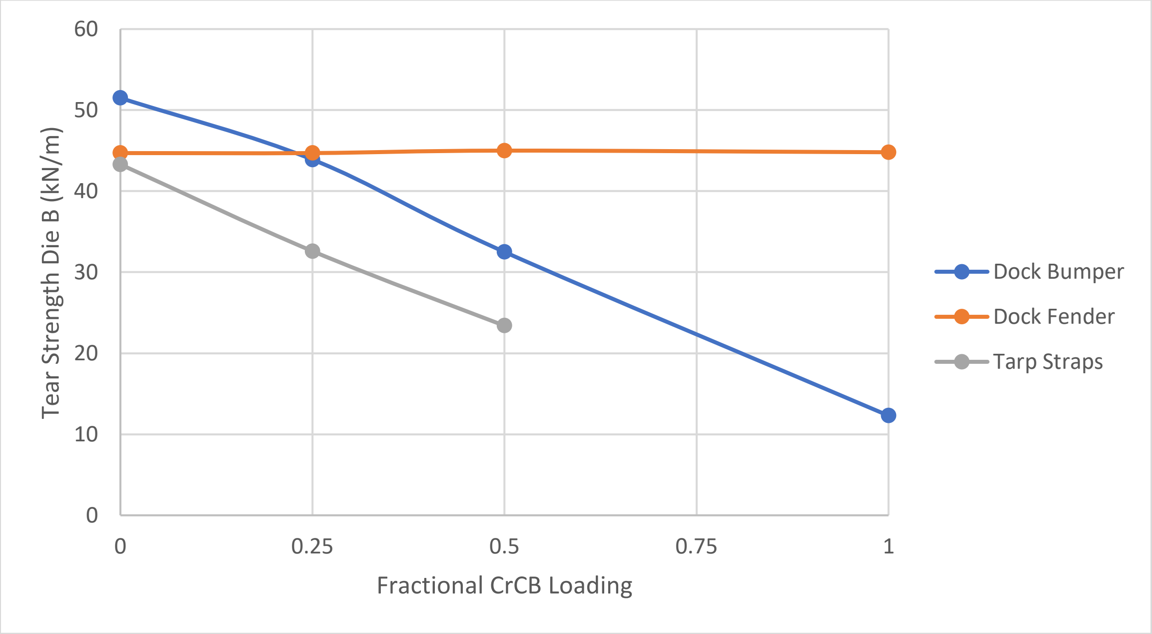


Figure 65 – Die B Tear Strength for Dock Bumper, Dock Fender, and Tarp Strap Compounds

Although the initial CrCB testing appeared to provide a rather straightforward view of the product characteristics and reinforcement capability, the product testing adds some additional nuance. In the dock bumper and tarp strap application, all measured proprieties drop significantly in performance with CrCB loading. In fact, the drop is more significant than in the initial study compared against N550. However, the Dock Fender application contrasts these views showing nearly equal or in some cases slightly better reinforcement against the control. When all four tests are compared against the control at 50% loading in, the Dock Fender test shows 7.6% improvement in tensile strength performance versus the control at only 12.9% additional elongation %.

Table 15 - Performance against Control at 50% CrCB Loading

Performance Against Control at 50% CrCB Loading				
	SBR/NR Test	Dock Bumper	Dock Fender	Tarp Strap
Shore A Hardness	-4.2%	-16.4%	-1.2%	-17.5%
Tensile Strength	-23.2%	-59.3%	7.6%	-66.1%
Elongation %	11.6%	23.6%	12.9%	0.5%
Tear Strength Die B	-34.9%	-36.9%	0.7%	-46.0%

When viewing the results of the CrCB in these tests, it is important to realize that this is a different material than virgin carbon black. Surface morphology and interfacial area play a significant role, but clearly there is more at play than just those two factors. Since the CrCB contains residual polymer, this residual polymer may be available to crosslink with the new rubber being added. The interactions between ingredients in the rubber compound recipe are so complex that seemingly insignificant components such as oil type, polymer type, sulfur loading, vulcanizing agent type may facilitate more or less reinforcement when CrCB is added. Despite this, it can be argued that if the CrCB particle size decreased and more of the original surface morphology was exposed, then performance across the rubber compounds would be more stable and approach the performance of virgin carbon black more closely.

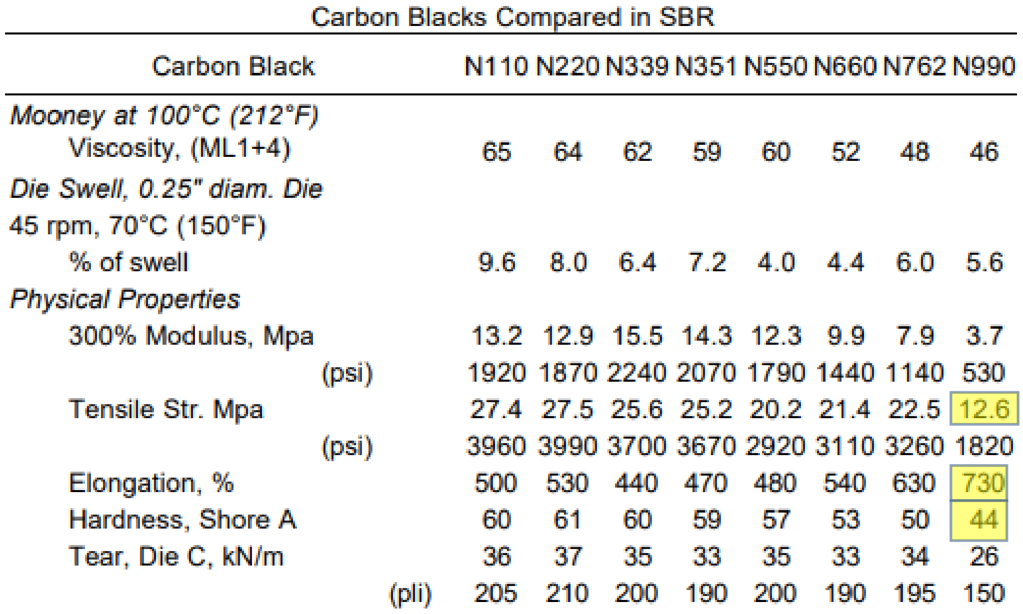
5.3.3.9 Assignment of Virgin Carbon Black Grade to CrCB

To predict product value in the rubber industry and defining potential applications, it is important to assign a grade to the CrCB material. As we have seen from the previous section, however, this may not be straight forward since it performs better some applications (i.e. Dock Fenders) versus others.

To begin the evaluation, we first look at our initial NR/SBR compound results and compare them with other carbon black grades. A study by Continental Carbon assessed performance of different grades of carbon black when compounded in NR and SBR. As mentioned in previous sections, it is difficult to compare one batch of test results directly to another because of the total number of variables in the rubber compounding process. However, the data produced by the study allows us to view grades that CrCB can be correlated with. First, Table 16 extrapolates on the data from NR/SBR physical testing to predict performance for CrCB at 100% loading.

Table 16 - Extrapolated Physical Testing Data for CrCB at 100% Loading

Test	Fractional CrCB Loading	Value
Hardness	1	51.9
Elongation %	1	617.4
Tensile (MPa)	1	11.6
Tear Strength Die B (kN/m)	1	32.6



Carbon Blacks Compared in SBR

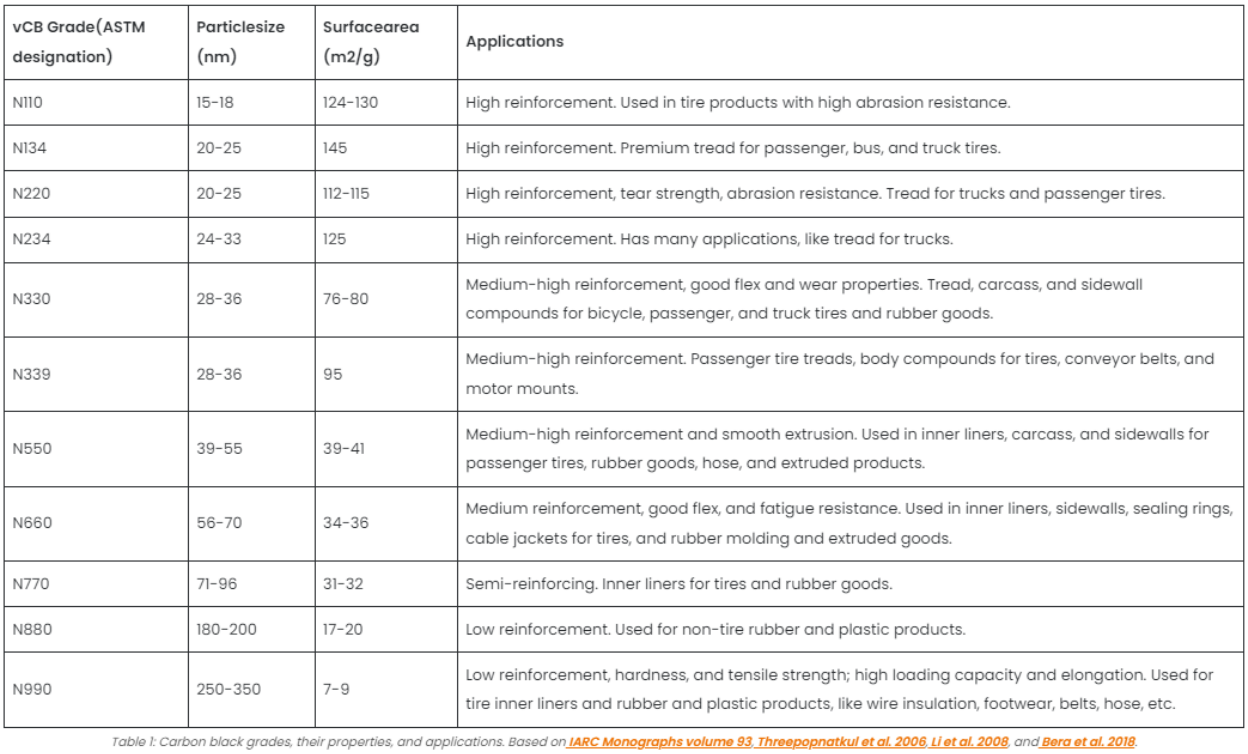
Carbon Black	N110	N220	N339	N351	N550	N660	N762	N990
Mooney at 100°C (212°F)								
Viscosity, (ML1+4)	65	64	62	59	60	52	48	46
Die Swell, 0.25" diam. Die								
45 rpm, 70°C (150°F)								
% of swell	9.6	8.0	6.4	7.2	4.0	4.4	6.0	5.6
Physical Properties								
300% Modulus, Mpa	13.2	12.9	15.5	14.3	12.3	9.9	7.9	3.7
(psi)	1920	1870	2240	2070	1790	1440	1140	530
Tensile Str. Mpa	27.4	27.5	25.6	25.2	20.2	21.4	22.5	12.6
(psi)	3960	3990	3700	3670	2920	3110	3260	1820
Elongation, %	500	530	440	470	480	540	630	730
Hardness, Shore A	60	61	60	59	57	53	50	44
Tear, Die C, kN/m	36	37	35	33	35	33	34	26
(pli)	205	210	200	190	200	190	195	150

Figure 66 - Study of Rubber Properties Based on Carbon Black Grade (61)

Figure 66 shows reported values for a compound with 100 PHR rubber and 50 PHR carbon black. Due to the nature of the CrCB and its composition, it does not appear to fit cleanly into one category but based on tensile strength and elongation % the CrCB submitted for testing would fall between an N762 and N990 carbon black. Contrastingly, the performance in the EPDM dock fender application shows that CrCB performance did not decrease from the performance of N650 virgin carbon black at 100% loading. Thus, CrCB may not fit cleanly into one virgin carbon black grade. Further, CrCB's performance in untested applications is less predictable than for virgin carbon black, as seen in the inconsistency of results across the dock bumper, dock fender, and tarp strap applications. What can be said is that the CrCB tested in this chapter is capable of replacing virgin carbon black in applications ranging from N650 to N990. More work is needed to understand the overall reinforcement mechanism of CrCB and to determine its sensitivity to ingredients in the rubber compound.

5.3.3.10 Potential CrCB Applications

Figure 67 lists applications used for various grades of carbon black including the N660-N990 range. There are a significant number of applications within these grades that include tire inner liners rubber molded goods (e.g. dock fenders), wire insulation, and footwear.



vCB Grade(ASTM designation)	Particlesize (nm)	Surfacearea (m2/g)	Applications
N110	15-18	124-130	High reinforcement. Used in tire products with high abrasion resistance.
N134	20-25	145	High reinforcement. Premium tread for passenger, bus, and truck tires.
N220	20-25	112-115	High reinforcement, tear strength, abrasion resistance. Tread for trucks and passenger tires.
N234	24-33	125	High reinforcement. Has many applications, like tread for trucks.
N330	28-36	76-80	Medium-high reinforcement, good flex and wear properties. Tread, carcass, and sidewall compounds for bicycle, passenger, and truck tires and rubber goods.
N339	28-36	95	Medium-high reinforcement. Passenger tire treads, body compounds for tires, conveyor belts, and motor mounts.
N550	39-55	39-41	Medium-high reinforcement and smooth extrusion. Used in inner liners, carcass, and sidewalls for passenger tires, rubber goods, hose, and extruded products.
N660	56-70	34-36	Medium reinforcement, good flex, and fatigue resistance. Used in inner liners, sidewalls, sealing rings, cable jackets for tires, and rubber molding and extruded goods.
N770	71-96	31-32	Semi-reinforcing. Inner liners for tires and rubber goods.
N880	180-200	17-20	Low reinforcement. Used for non-tire rubber and plastic products.
N990	250-350	7-9	Low reinforcement, hardness, and tensile strength; high loading capacity and elongation. Used for tire inner liners and rubber and plastic products, like wire insulation, footwear, belts, hose, etc.

Table 1: Carbon black grades, their properties, and applications. Based on ***IARC Monographs volume 93***, ***Threepopnatkul et al. 2006***, ***Li et al. 2008***, *and* ***Bera et al. 2018***.

Figure 67 - Carbon Black Applications within Carbon Black Grades (62)

Molded goods have particularly large usage in N600 and N700 series grades in items such as O-rings, gaskets, antivibration dampeners, diaphragms, bellows, and many others. See the Appendix for a detailed breakdown of applications and usage based on carbon black grade (63).

CrCB in its current form potentially has a significant number of N600-N900 applications where it can be used. In certain applications like dock fenders, it could be a like-for-like replacement for N660 carbon black and lead to the incorporation of more sustainable materials in rubber products. It is important to note that chloramine devulcanization research has only recently emerged and significant work remains to understand the mechanism of reinforcement and compatibility with various rubber compounds and applications. Further, if additional chloramine reaction stages are applied to the CrCB material used in these tests, based on our current understanding of the mechanism, this would likely result in a further reduction in particle size, polymer content, and an increase in physical performance in a rubber compound. This increase in interfacial area and surface morphology would likely lead to greater and more consistent performance in applications testing. Whether complete removal of the polymer (i.e. reduction of the polymer-carbon black ratio to 0) is possible via chloramine is not known. However, due to the known covalent reinforcement of carbon black with polymer, it is unlikely. The chloramine chemistry appears to not break covalent C-C and C=C bonds. If these are present at the carbon black rubber interface as literature suggests, the reduction of the polymer content in CrCB to zero would be not possible. Further research is required to determine the full extent of polymer-carbon black separation.

5.3.4 CrCB vs Pyrolytic Recovered Carbon Black (PrCB)

Pyrolysis derived recovered carbon black (PrCB) is currently the most widely used product recovered from waste rubber. The pyrolytic process removes polymer and oil exposing the carbon black primary particles and aggregates as seen in Figure 68.

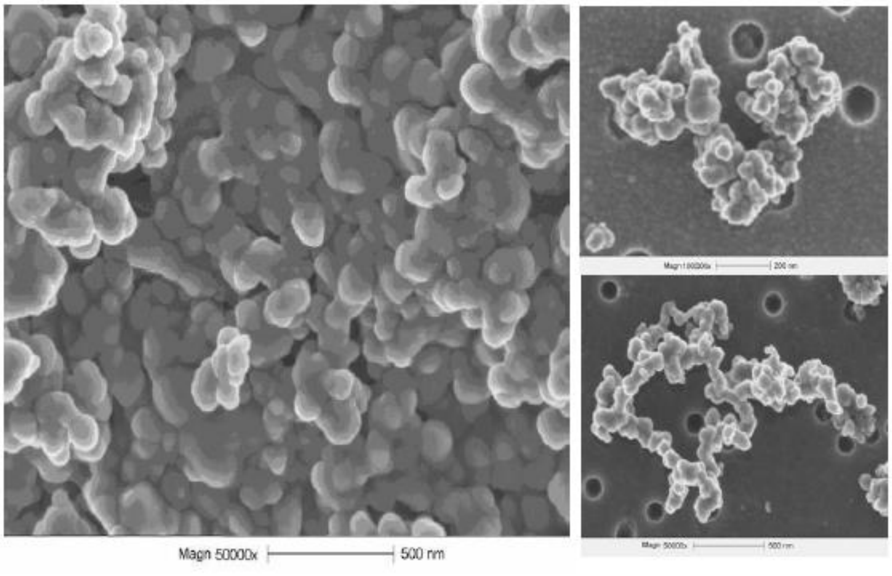


Figure 68 - PrCB Surface Morphology

Due to this relatively high structure, PrCB has relatively high performance in rubber compounds for recycled materials. A 2022 study compared a PrCB against N330, N550, N660, and N700 virgin carbon blacks. The PrCB had a recorded NSA of 44.0 m^2/g and STSA of 43 m^2/g, which places it in the N550 range when compared to the surface area values reported for virgin carbon blacks (64). PrCB cannot be directly compared to virgin carbon black based on surface area alone since the thermal degradation process eliminates reinforcing functional groups from the PrCB surface, which directly leads to less reinforcement. The 50 PHR PrCB was compounded with 100 PHR SBR and a standard curing package. Figure 69 and Figure 70 show the tensile strength and elongation % for PrCB versus N550 carbon black at 100% loading.

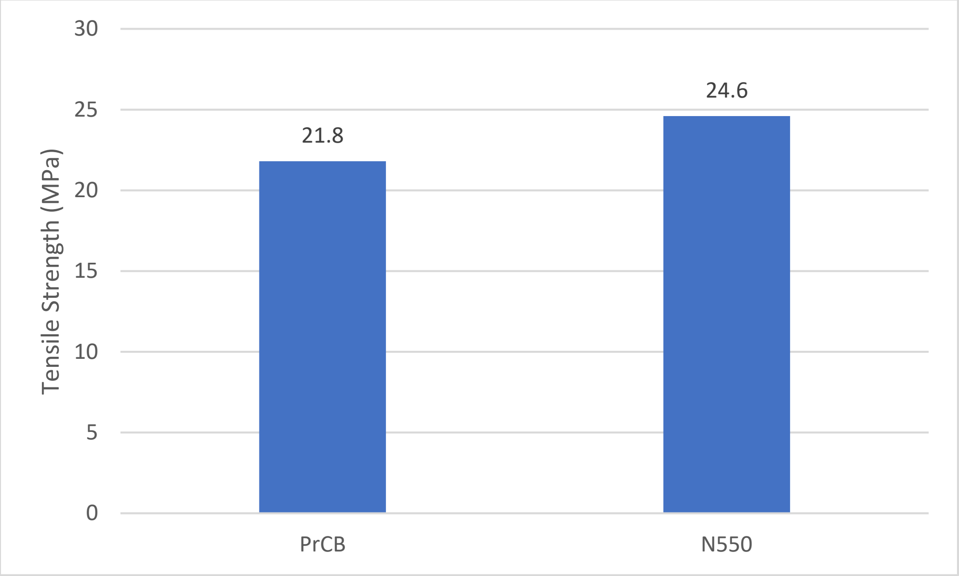


Figure 69 - Tensile Strength of PrCB vs N550 Virgin Carbon Black

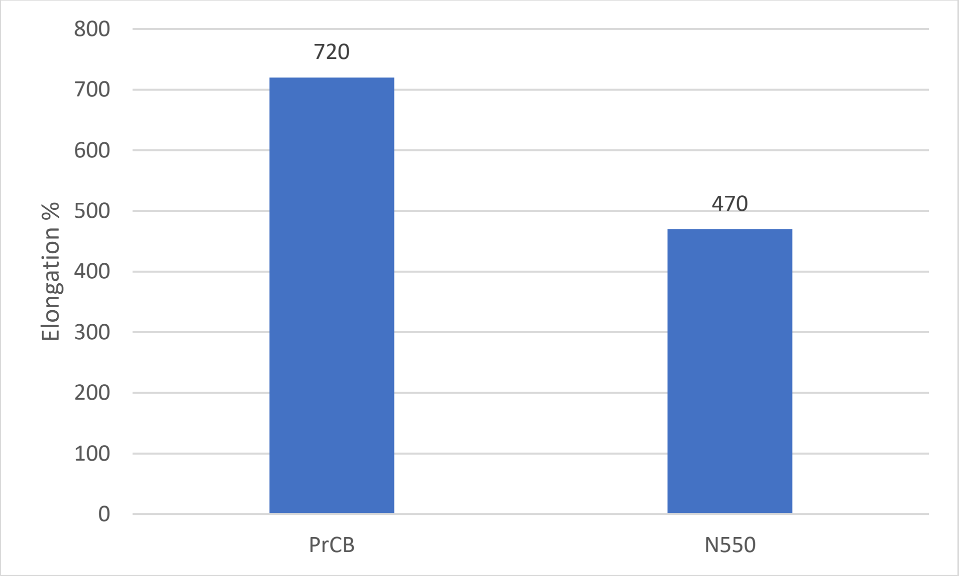


Figure 70 - Elongation % of PrCB vs N550 Virgin Carbon Black

Although it is not correct to directly compare the values of tensile strength and elongation for the CrCB to the PrCB in this test due to the different formulations, we can look at the % change of both materials vs the virgin N550 carbon black to assess performance.

Table 17 - Comparative Performance of PrCB and CrCB vs N550 Virgin Carbon Black

Performance Relative to N550 Carbon Black		
	Tensile Strength	Elongation %
PrCB	-11%	53%
CrCB	-43%	36%

The tensile strength drop-off for CrCB is greater when compared with PrCB and although the elongation at break appears to show better performance for the CrCB, that is not the case. The elongation % at failure for CrCB is estimated at 617% at a stress of 11.6 MPa versus 720% at 21.8 MPa for the PrCB. The CrCB would have had significantly longer elongation if it was capable of a 21.8 MPa tensile strength. This would lead to the conclusion that the current version of CrCB has reinforcement that is below that of PrCB. However, as we have seen CrCB's performance can be sensitive to the individual rubber compound ingredients and CrCB's performance may equal PrCB's in the dock fender application test. Despite this, PrCB has more consistent performance across multiple applications than CrCB (64). Again, it is likely that the CrCB surface area and morphology must be improved before it can have consistent performance across multiple applications like PrCB and virgin CB. Further work is needed to determine the extent of improvement possible for CrCB performance.

5.3.5 Chloramine Devulcanized Rubber

As mentioned previously, much work remains to be done to properly determine the value of the CdR recovered from the chloramine process. The work on CrCB has progressed at a quicker rate due to the relative ease of its extraction from the post reaction solution versus the challenges that have been faced in extracting the CdR. The following section outlines the current status of CdR and shows the testing required to properly evaluate it.

5.3.5.1 Current Status of CdR

Extracted CdR has been evaluated with NMR, FTIR, and TGA as shown in Chapters 3 and 4. These results show a that the CdR has the same function groups as the input rubber and a high molecular weight, though likely lower than the input rubber based on TGA decomposition temperatures. Future testing should include both analytical and physical testing as outlined below

Analytical Testing

1. Molecular Weight by Gel Permeation Chromatography
2. Glass Transition by DSC
3. Mooney Viscosity

Physical Testing

1. Shore A Hardness
2. Rebound Resilience
3. Tensile Strength
4. Elongation %
5. 100% / 300 % Modulus

These tests were taken from a technical data sheet for virgin SBR and are the minimum that would be required to evaluate the material properly.

The limiting factor in this work has been the aqueous CdR extraction process. Though extraction has been successfully shown on the lab scale in 1-5 g samples, efforts to create a pilot scale extraction process to generate kg of CdR has been difficult due to the nature of the aqueous solution and the process.

Two extraction methods have been explored at pilot scale. The first was a combination nanofiltration-centrifugation process. This successfully produced small amounts of CdR yet concentrated impurities from the devulcanization reaction, chloramine size reactions, and had relatively low yield.

Figure 71 - CdR Recovered from Nanofiltration-Centrifugation Process

The second extraction method attempted on a pilot scale was a foam fractionation process that used the surface tension reducing properties of the aqueous CdR to froth and foam the solution. The foam was captured and dried to produce a rubber product. The process in its initial state had relatively low yield, however the yield was increased by the addition of a surfactant that increased production rate. Unfortunately, the surfactant remained in the rubber after extraction at relatively high quantities and appeared to inhibit re-vulcanization of the material. Figure 72 and Figure 73 show the pilot scale foam process and material recovered from it, respectively.

Figure 72 - Pilot Scale Foam Fractionation Process

Figure 73 - CdR Recovered from the Foam Fractionation Process

Approximately, 500 g is required to complete a proper set of physical testing which includes mixing, compounding, curing, cutting of coupons, and then completion of the various tests. Further development work is needed to develop a proper pilot scale extraction process to recover purified CdR in quantities that allow it to be further tested.

5.4 Conclusions and Future Work

Chapter 5 presented results for analytical and physical CrCB testing and compared those results against both virgin carbon black and PrCB. The results of the analytical testing show that the CrCB particle size and surface area correspond to a N990 grade carbon black. However, when tested in rubber compounds, the reinforcement capability varied. The NR/SBR test against an N550 control showed loss of performance for CrCB versus the control. Yet, when tested against N650 carbon black in a Dock Fender application, the reinforcement of CrCB at 100% loading was nearly unchanged versus the N650 control. Thus, although interfacial area and morphology play a significant role in reinforcement of all rubber fillers, CrCB performance may depend on other mechanisms, including sulfur crosslinking to the residual CrCB polymer content. Overall, we concluded that the CrCB was graded between N660 and N990 carbon black. This grading is general and CrCB may have unknown sensitivities to ingredients used in the rubber compound recipes that cause poor performance. However, there are a significant number of rubber applications where CrCB may be appropriate, especially dock fenders where it already shows great performance. These results provide evidence to support that the chloramine devulcanization process can contribute to a more sustainable future for rubber goods.

Despite these positive results, significant future work remains to make CrCB a more consistent, high performing product. Chapter 4 showed that polymer content was reduced with repeated treatments of micronized rubber / CrCB with chloramine. Particle size also decreased with subsequent treatment, indicating that future versions of CrCB may have greater performance. Future work should focus on determining the maximum reduction of CrCB polymer-carbon black ratio and then evaluating particle size, morphology, surface area and compounded physical properties for that material.

Chapter 5 also discussed the status of chloramine devulcanized rubber (CdR). The CdR has been evaluated for chemical structure, but not molecular weight and compounded physical properties. Future work should focus on developing a high yield pilot scale aqueous extraction process for CdR and then evaluating the tensile strength, 100% / 300% modulus, elongation % at break, hardness, and rebound of the resulting polymer material. This future work will allow the CdR product to be evaluated versus virgin rubber and other methods of devulcanization.

CHAPTER 6 – CONCLUSIONS AND FUTURE WORK

6.1 Conclusions on Chapter 3 - Chloramine Devulcanization Efficacy

The research in Chapter 3 sought to expand on initial research done in 2012-2013 and show that devulcanized rubber could be produced by exposing rubber to a solution of chloramine. Micronized rubber was exposed to chloramine solutions over the course of a 30-day test. A liquid-liquid extraction was performed using acetone to extract a malleable, formable, polymeric material. The recovered CdR visually was observed to have a high viscosity and had the appearance of a high molecular weight material. Molecular weight characterization was not completed on the sample. Characterization was performed using FTIR, C-NMR, and H-NMR and showed the presence of alkane, alkene, and aromatic functional groups associated with styrene butadiene rubber. From this evidence, we concluded that devulcanization occurred due to the chloramine solution exposure and this CdR material was being released into the aqueous solution. Additionally, we concluded that the presence of carbon-carbon double bonds in the CdR indicated that the CdR could mixed in new rubber applications and revulcanized.

6.2 Conclusions on Chapter 4 - Chloramine Physical Mechanism and Rate

The work in Chapter 4 expanded on the work in Chapter 3 by analyzing both the CrCB and CdR recovered from chloramine devulcanization. This products analysis was then used to propose a physical mechanism for the devulcanization and breakup of the rubber particle. The reaction rate of the chloramine-rubber system was then analyzed to estimate whether the reaction is rate limited or diffusion limited. The work was completed in partnership with Arduro Sustainable Rubber Inc, which is currently working to commercialize chloramine devulcanization technology.

Analysis of the CrCB powder recovered from the continuous chloramine devulcanization pilot plant at Arduro showed that CrCB has a particle size ranging from 0.5-20 µm. TGA analysis showed that the CrCB still contained residual polymer but that the chloramine devulcanization had reduced the polymer-to-carbon black ratio from 1.54 in the input micronized rubber to 0.89. A solid-liquid solvent extraction (SLE) process using xylene was used to further reduce the polymer-to-carbon black ratio to 0.46. Liquid-liquid extraction (LLE) with xylene was also used to extract CdR from the aqueous post reaction CdR solution. TGA analysis was performed on the solids recovered from both SLE and LLE extractions and showed both contained SBR and NR. The TGA onset temperatures for the SBR and NR weight loss were lower than for the input material and virgin material referenced in literature suggesting a decrease in molecular weight.

Using the SEM and TGA characterizations on both CrCB and CdR, we proposed a physical mechanism for the breakup of the rubber particle. Aqueous chloramine diffuses from the outside of the micronized rubber particle moving towards the center. Since the rubber is a 3-dimensional matrix with carbon black primary particles and aggregates dispersed throughout the polymer lattice, the aqueous chloramine, with diffusion driven flow, has its highest flow rate and concentration in the channels between carbon black aggregates and lowest concentration and zero flow at the polymer-carbon black interface. This flow pattern combined with higher crosslink density near the polymer-carbon black interface, creates unsymmetrical devulcanization, with more sulfur cross-linkages broken in the channels between carbon black aggregates than near the interface. With the sulfur crosslinks removed in the area of least reinforcement, cracks begin to form in rubber matrix and the rubber particle breaks apart. Thus, we concluded that it was possible that further treatment with chloramine could cause additional particle breakup and reduction of the polymer-carbon black ratio in the CrCB.

Finally, the reaction rate of the chloramine-rubber system was analyzed to show whether the system is rate limited or diffusion limited. Using an auto-decomposition rate model for chloramine loss and the diffusivity of chloramine into SBR, the Thiele modulus was calculated for the chloramine-SBR system at different pH, temperature, and chloramine concentrations. This analysis showed that at pH ranges between 6.55 and 7.55, where chloramine is unstable, the reaction is extremely diffusion limited. However, at pH 8.3 the reaction is rate limited and becomes more rate limited at higher temperatures (up to 80 °C). At a pH 8.5, 85 °C, and 100 ppm concentration, the Thiele modulus was calculated to be 0.79. Higher concentrations of chloramine showed that the reaction moved to be more diffusion limited. This analysis was performed using an auto decomposition model and chloramine diffusivities developed for water quality at lower concentrations and temperatures than were analyzed in our modeling. It is expected that the extrapolated data may not yield the confidence level shown in literature, but the available model is useful to show trends and indications of where the reaction is more rate limited versus diffusion limited.

6.3 Conclusions on Chapter 5 – Testing of Materials from Chloramine Devulcanization

The work from Chapter 5 focused on the analytical and physical testing of chloramine recovered carbon black (CrCB) provided by Arduro Sustainable Rubber. CrCB was tested in virgin carbon black (vCB) analytical testing methods NSA, STSA, and OAN, and COAN. NSA and STSA values were 8.2 m^2/g and 7.6 m^2/g, respectively. The OAN and COAN tests were not run due to the excessive torque on the OAN testing unit. This result was likely due to the polymer content of the CrCB limiting its ability to absorb oil.

CrCB was first compounded and vulcanized in a general NR/SBR formulation versus an N550 carbon black control and then compounded in dock bumper, dock fender, and tarp strap applications against an N650 control. After compounding, the Tensile strength, elongation % at break, Shore A hardness, and tear strength were evaluated for performance against the control samples. CrCB showed poor performance against the control in dock bumpers and tarp straps, medium reinforcement against the control in the NR/SBR compound, and great performance against the N650 carbon black control in the dock fender application. This inconsistent performance across applications led us to concluded that the performance was partly due to relatively large particle size (0.5-20 µm) and smooth surface morphology and also due to some unknown mechanisms, possibly sulfur crosslinking with the residual polymer on the CrCB. The CrCB was graded between N660 and N990 carbon black with the caveat that application testing is needed for each product within those grades to determine if CrCB is an appropriate fit. It is likely that CrCB performance can be increased with additional chloramine treatment to further remove polymer content and reduce particle size. It may be possible to expose the carbon black aggregates and primary particles with sufficient chloramine treatment, which would allow the CrCB to reach a maximum performance approaching that of the carbon black grade of the input material.

Chapter 5 also briefly explored the status of chloramine devulcanized rubber (CdR) analytical and physical testing. Limited testing has been completed to-date due to the technical challenge of extracting the CdR from the aqueous solution at pilot scale and the need to produce approximately 1 kg of material to complete physical testing. Two extraction methods, nanofiltration with centrifugation and foam fractionation have been explored, but both methods tested were low yield and produced a rubber product containing high amounts of impurities.

6.4 Overall Conclusions and Recommendations on Future Work on Chloramine Devulcanization

Chloramine devulcanization research is in its infancy compared with pyrolytic carbon black recovery and other methods of devulcanization. It shows promise in its potential capability to recover a carbon black product, CrCB, and a devulcanized rubber product, CdR. Since chloramine does not appear to react with the carbon-carbon bonds in the polymer backbone, it is likely that the devulcanized rubber product could have higher molecular weight than other previous methods of chloramine devulcanization, but much work remains to further explore these materials. Despite this, the current chloramine devulcanization manufacturing process developed by Arduro produces a CrCB product that has value in the market and future versions of this process may be able to supply a high quality devulcanized rubber material, CdR.

Future work should focus on further developing the CdR material. It has been a challenge to effectively extract the CdR from the aqueous solution and this has led to slower progress in CdR than in CrCB. A proper extraction method should be discovered to allow for high yield, high purity production of CdR. This development would allow the CdR to be tested and characterized to a similar extent to CrCB. With sufficient material produced via an effective extraction method, applications testing in new rubber applications should be explored to further assess CdR's value in the market. Work should also focus on characterizing the molecular weight of CdR and evaluate effects of processing techniques like fluid shear, temperature, and chloramine concentration on the molecular weight.

Additional research should be completed to determine the extent that the polymer-carbon black ratio can be reduced in the CrCB. The current performance of CrCB is relatively low compared with vCB but the proposed mechanism indicated that sulfur crosslinks may still remain and that further reduction of polymer content in CrCB is possible. It is not known the extent to which this polymer can be removed but based on the possible covalent bonding occurring between the polymer and carbon black at the polymer-carbon black interface, it is unlike that the ratio can be reduced to zero. However, it is likely that additional polymer removal would further reduce particle size of the CrCB and improve surface morphology and overall reinforcement properties in rubber.

The chemical mechanism of devulcanization and the sulfur byproducts are not well understood. Additionally, the rate of reaction between chloramine and sulfur has not been well documented, especially in the chloramine rubber system. Future work should look to propose a mechanism for the chemical reaction and define its rate law and constant. It also may be beneficial to see if chloramine is altering the chemistry of functional groups on carbon black or rubber. Although literature and our research suggest that chloramine is unreactive with C-C and C=C bonds, further research is needed to confirm this.

6.5 Final Comments on Chloramine Devulcanization

The work in this dissertation is only the beginning of the development in the new field of chloramine devulcanization research. Like many other devulcanization technologies, it is imperfect and produces a mixed product, yet it may represent the best method to-date of creating value from waste rubber. My only hope is that this work serves as a useful starting point for future development. Ultimately, I think the success or failure of this devulcanization technology will be determined by whether a business like Arduro can execute upon the potential that exists in chloramine devulcanization and, as a part of that business, I look forward to taking part in the continued growth and development of this devulcanization methods.

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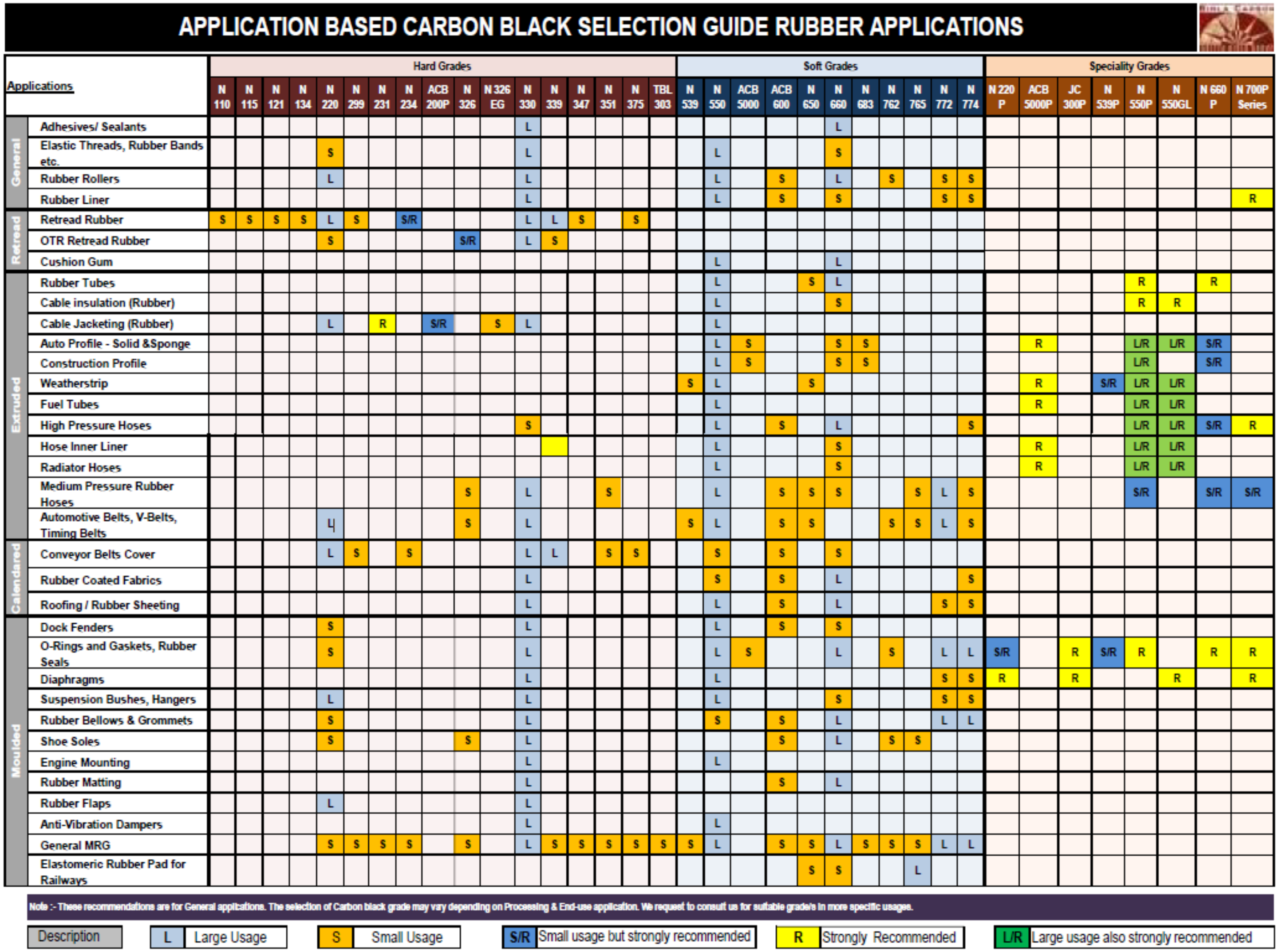
APPENDIX

Table 18 - Reported Values for Application Testing

		Control	X1 (100% CrCB)	X2 (50% CrCB)	X3 (25% CrCB)
Dock Bumper	Shore A Durometer	68.4	48.8	57.2	61.9
	Elongation %	305	473	377	293
	Tensile Strength (MPa)	9.1	1	3.7	5.6
	Tear Strength Die B (kN/m)	51.5	12.3	32.5	43.9
Dock Fender	Shore A Durometer	72.1	69.5	71.2	70.7
	Elongation %	272	299	307	319
	Tensile Strength (MPa)	7.9	8.4	8.5	8.6
	Tear Strength Die B (kN/m)	44.7	44.8	45	44.7
Tarp Strap	Shore A Durometer	61.3		50.6	57.6
	Elongation %	390		392	295
	Tensile Strength (MPa)	10.9		3.7	4.9
	Tear Strength Die B (kN/m)	43.3		23.4	32.6



APPLICATION BASED CARBON BLACK SELECTION GUIDE RUBBER APPLICATIONS

	Applications	Hard Grades																	Soft Grades											Speciality Grades							
		N 110	N 115	N 121	N 134	N 220	N 299	N 231	N 234	ACB 200P	N 326	N 326 EG	N 330	N 339	N 347	N 351	N 375	TBL 303	N 539	N 550	ACB 5000	ACB 600	N 650	N 660	N 683	N 762	N 765	N 772	N 774	N 220 P	ACB 5000P	JC 300P	N 539P	N 550P	N 550GL	N 660 P	N 700P Series
General	Adhesives/ Sealants												L											L													
	Elastic Threads, Rubber Bands etc.					S							L							L				S													
	Rubber Rollers					L							L							L		S		L		S		S	S								
	Rubber Liner												L							L		S		S				S	S								R
Retread	Retread Rubber	S	S	S	S	L	S		S/R				L	L	S		S																				
	OTR Retread Rubber					S					S/R		L	S																							
	Cushion Gum																			L				L													
Extruded	Rubber Tubes																			L			S	L										R		R	
	Cable insulation (Rubber)																			L				S										R	R		
	Cable Jacketing (Rubber)					L		R		S/R		S	L							L																	
	Auto Profile - Solid &Sponge																			L	S			S	S						R			L/R	L/R	S/R	
	Construction Profile																			L	S			S	S									L/R		S/R	
	Weatherstrip																		S	L			S								R		S/R	L/R	L/R		
	Fuel Tubes																			L											R			L/R	L/R		
	High Pressure Hoses												S							L		S		L					S					L/R	L/R	S/R	R
	Hose Inner Liner													🟨						L				S							R			L/R	L/R		
	Radiator Hoses																			L				S							R			L/R	L/R		
	Medium Pressure Rubber Hoses										S		L			S				L		S	S	S			S	L	S					S/R		S/R	S/R
	Automotive Belts, V-Belts, Timing Belts					L					S		L						S	L		S	S			S	S	L	S								
Calendared	Conveyor Belts Cover					L	S		S				L	L		S	S			S		S		S													
	Rubber Coated Fabrics												L							S		S		L					S								
	Roofing / Rubber Sheeting												L							L		S		L				S	S								
Moulded	Dock Fenders					S							L							L		S		S													
	O-Rings and Gaskets, Rubber Seals					S							L							L	S			L		S		L	L	S/R		R	S/R	R		R	R
	Diaphragms												L							L								S	S	R		R			R		R
	Suspension Bushes, Hangers					L							L							L				S				S	S								
	Rubber Bellows & Grommets					S							L							S		S		L				L	L								
	Shoe Soles					S					S		L									S		L		S	S										
	Engine Mounting												L							L																	
	Rubber Matting												L									S		L													
	Rubber Flaps					L							L																								
	Anti-Vibration Dampers												L							L																	
	General MRG					S	S	S	S		S		L	S	S	S	S	S	S	L		S	S	L	S	S	S	L	L								
	Elastomeric Rubber Pad for Railways																						S	S			L										

Note :- These recommendations are for General applications. The selection of Carbon black grade may vary depending on Processing & End-use application. We request to consult us for suitable grade/s in more specific usages.

Description					
	L	S	S/R	R	L/R
	Large Usage	Small Usage	Small usage but strongly recommended	Strongly Recommended	Large usage also strongly recommended

Figure 74 - Application and Usage Guide for Carbon Black Grades

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Recycling of styrene butadiene rubber and like materials

PCT/US2022/022729
Carbon black recovery methods and compositions comprising same

PROFESSIONAL SOCIETIES: AICHE, ASTM Intl