A Study of Scrap Rubber Devulcanization and Incorporation of Devulcanized Rubber into Virgin Rubber Compounds

by

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I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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ABSTRACT

In this era of rapid development and economic growth, waste management is of high concern for humans. According to statistics, a great amount of rubber waste materials are produced annually. The major amount of these waste rubber material comes from scrap tires. Only a few percent of the waste rubber materials are recycled and made into new products. Recycling of waste rubber has a certain problem: the crosslink structure of thermoset rubber.

Due to the presence of three dimensional crosslink structures in rubber products, they cannot be reprocessed by application of heat, like we do for thermoplastic materials. In order to recycle and reuse the vulcanized rubber we have to find a way to cleave the crosslink bonds. This technique which can break down the crosslink bonds in the rubber is called devulcanization.

Different devulcanization processes are utilizing heat, chemicals, ultrasound, and mechanical stresses in order to break down the crosslink structure of vulcanized rubber and convert the insoluble thermoset rubber into a soft and sticky material which can be processed and vulcanized again. Comparing various devulcanization processes, the thermo-mechanical devulcanization process which applies mechanical forces and heat to break down the crosslink network of rubber is very effective. One of the common ways to maintain the required shear stresses and mechanical forces to cleave and break down the crosslink structure of vulcanized rubber is utilizing the extrusion process.

In this research, twin screw extruders are preferred due to their modular designs which enable us to adjust the different levels of shearing on the material. In order to facilitate the extrusion process supercritical carbon dioxide is used. Supercritical carbon dioxide diffuses into the rubber particles during the devulcanization process and facilitates the process by expanding and softening the rubber particles.

In this research we have established a high throughput devulcanization process to produce devulcanized scrap tire rubber at an industrial scale. The effect of different process parameters on obtained devulcanized rubber properties, such as network structure, rheological properties, and physical and mechanical properties are studied. Results showed that in the range of our experiment design, the only effective parameter on crosslink density and Mooney viscosity of the devulcanized scrap tire is feed rate. Using Horikx theory, it was shown that the devulcanization mechanism for our scrap tire devulcanization process is a selective crosslink cleavage rather than a random chain scission.

The obtained devulcanized rubber was then incorporated in a virgin tire rubber compound and the impact of devulcanized rubber utilization on tire compound performance was studied. Results showed that incorporation of devulcanized rubber into a tire tread compound up to 30 percent does not deteriorate the tire tread properties in a significant manner.

Finally, a high throughput devulcanization process was established for scrap ethylene-diene-propylene (EDPM) rubber devulcanization. The effects of main process variables on the properties of the devulcanized EPDM rubber were studied. It was observed that crosslink density and Mooney viscosity of the devulcanized EPDM rubber are affected by the feed rate and screw speed in a significant manner.

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My parents, who have raised me and have been giving their love and support all the time,

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To Nikoo

To my family

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LIST OF SYMBOL AND ABBREVIATIONS

ASTM	American society for testing and materials
BR	Butadiene rubber
°C	Degrees Celsius
cm	Centimeter
cm^3	Cubic centimeter
CRD	Crosslink density
C–S–C	Monosulfidic crosslink
$C–S_2–C$	Disulfidic crosslink
$C–S_x–C$	Polysulfidic crosslink
dn.M	deciNewton metres
DOE	Design of experiments
DPTT	Dipentamethylene-thiuramtetrasulfide
EPDM	Ethylene propylene diene rubber
g	Gram
HDA	Hexadecylamine
hr	Hour
kg	Kilogram

Kn. m	KiloNewton. meter
Lb_f-in	Pound force - inch
m	Meter
MBT	2-Mercaptobenzothiazole
MBTS	Dimercaptobenzothiazole-disulfide
MDR	Moving die rheometer
MH	Maximum torque (rheometer)
ML	Minimum torque (rheometer)
ML(1+4)	Mooney viscosity after 1 minute of preheating and 4 minutes of measuring, measured with a large rotor
MPa	Megapascal
MU	Mooney unit
N	Screw speed
NR	Natural rubber
ODR	Oscillatory disk rheometer
phr	Parts per hundred rubber
PVI	Pre vulcanization inhibitor
Q	Feed rate
R^2	Goodness of fit
rpm	Rounds per minute

S	Sulfur
SBR	Styrene-butadiene rubber
SSSE	Solid-state shear extrusion
T	Temperature
t_{S2}	Scorch time
t_{90}	Optimum curing time
t_{xx}	Curing time at the percentages of maximum minus minimum torque
tan δ	Loss angle
TMTD	Tetramethylthiuram-disulfide
USA	United States of America
vs.	Versus
ZDBC	Zinc-dibutyldithiocarbamate
ZnO	Zinc-oxide
v_r	Polymer volume fraction of the swollen sample
V_s	Solvent molar volume

wt%	Weight percent
ν_e	Crosslink density
χ	Flory-Huggins interaction parameter
δ	Crosslinking coefficient

CHAPTER1. INTRODUCTION AND OBJECTIVES

1.1 Prefaces for setting the scene

In this era of rapid development and economic growth, waste management is of high concern for humans. According to statistics, a great amount of rubber waste materials are produced annually. A major amount of these waste rubber materials comes from scrap tires. Only a few percent of these tires are recycled and made into new products. Recycling of waste rubber has a certain problem: the crosslink structure of thermoset rubber.

Due to the presence of three dimensional crosslink structures in the rubber products, they cannot be reprocessed by application of heat, as can be done for thermoplastic materials. In order to recycle and reuse the vulcanized rubber we have to find a way to cleave the crosslink bonds. The technique which can break down the crosslink bonds in the rubber is called devulcanization.

Different devulcanization processes utilize heat, chemicals, ultrasounds, and mechanical stresses in order to break down the crosslink structure of vulcanized rubber and convert the insoluble thermoset rubber into a soft and sticky material which can be processed and vulcanized again.

Comparing various devulcanization processes, the thermo-mechanical devulcanization process, which applies mechanical forces and heat to break down the crosslink network of rubber, is very effective. One of the common ways to maintain the required shear stresses and mechanical forces to cleave and break down the crosslink structure of vulcanized rubber is utilizing the extrusion process.

In this research work, twin screw extruders are preferred due to their modular designs which enable us to adjust the different levels of shearing imposed on the material. In order to facilitate the extrusion process, supercritical carbon dioxide is used. Supercritical carbon dioxide diffuses into the rubber particles during the devulcanization process and facilitates the process by expanding and softening the rubber particles.

The aims of this research work were set as follows:

1. Establish and develop a continuous, high throughput, and stable devulcanization process.
2. Study the effect of key process parameters on the final properties of the devulcanized rubber.
3. Optimize the performance of the devulcanization process in order to obtain a useful product with high quality and optimum properties that can be used in new rubber products.
4. Evaluate the incorporation of devulcanized rubber in virgin rubber compounds in order to lower the material cost without considerable property loss.

1.2 Thesis outline

This thesis consists of nine chapters:

Chapter 2 is an introduction to rubber recycling and rubber devulcanization. General background and literature review about rubber devulcanization are brought up in this chapter.

Chapter 3 describes all the experimental methods and procedures which are used in devulcanized rubber preparation and analysis. Process parameters and procedures for our devulcanization process are described in this chapter. Furthermore, this chapter explains all the devulcanized rubber analysis methods that are used for characterization of the obtained devulcanized rubber in detail.

Chapter 4 introduces a continuous thermo-mechanical devulcanization process with supercritical CO_2, which is carried out on an industrial scale twin screw extruder. The main objectives that this chapter focuses on are: (1) How to establish a high throughput devulcanization process which is stable, and (2) Production of a devulcanized rubber that can be used in rubber products. Different properties of devulcanized rubber such as, crosslink density, curing behavior, and physical and mechanical properties were measured and reported in this chapter.

In *Chapter 5* the effect of different process parameters such as temperature, screw speed, and feed rate on the properties of the devulcanized rubber are studied. A statistical design is used to study the effect of process variables on the crosslink structure, gel and sol fractions and degree of devulcanization of devulcanized rubber. Rheological, physical and mechanical properties are also measured to evaluate how changing the process variables can affect these important properties. A fractional factorial design in three levels is used to study the effects of process variables. The main objectives that this chapter focuses on are:

1- Develop an experimental design to study the effect of main process variables on the properties of the devulcanized rubber
2- Analyze the experimental results using statistical methods to investigate how significantly these parameters and their interactions affect the output properties.
3- Derive a mathematical model using response surface methodology to optimize the process
4- Find out the optimum values for the process parameters to optimize the devulcanized rubber properties within the range of experiments

In *Chapter 6* the effects of incorporation of devulcanized rubber into a virgin tire tread compound on the final properties and performances of the tire tread compound are studied. This chapter explains how incorporation of up to 30% devulcanized rubber into a virgin tire tread compound can alter the rheological, physical and mechanical, cut and chip performance, and heat buildup of the tire tread compound.

And finally *Chapter 7* presents an attempt to devulcanize the EPDM rubber obtained from automotive waste weather strips. A statistical design is used to investigate the effect of process independent variables on the properties of the devulcanized EPDM rubber. The crosslink structure, gel and sol fractions and degree of devulcanization of the devulcanized EPDM rubber was evaluated. Rheological, physical and mechanical properties of the devulcanized EPDM are also measured in order to study how changing the process variables can affect these important properties.

CHAPTER 2   LITERATURE REVIEW

2.1 Outlook of waste rubber

In recent years the accumulation of waste materials has been a big problem for mankind and waste disposal management is of high importance. The problem is more serious especially for polymeric materials which due to their chemical structure cannot decompose easily in nature. Recycling of waste rubber is even harder and takes a very long time due to the three dimensional crosslinked structure and presence of different additives and stabilizers that make the recycling process very difficult. Finding a solution for recycling waste rubber has two important aspects: first to stop the wasting of valuable rubber material and second to prevent environmental pollution [1].

2.1.1 Vulcanized rubber and recycling

A rubber is a polymeric material which has an elastic behavior. This behavior is the result of the long chain characteristics of the rubber macromolecules. We can stretch the rubber at room temperature at least up to 100% of its original dimensions and it can come back to its original shape after releasing the stress. “Rubber materials are elastic, flexible, tough, and relatively impermeable to both water and air”[2]. Unvulcanized rubber does not have enough strength and dimensional stability to make it applicable for rubber products and it’s very sticky. “It becomes soft and sticky in hot temperatures and stiff and hard in cold temperature”[2]. Virgin rubber (before vulcanization) is considered a liquid, but the viscosity is very high so it may appear like a solid. After the vulcanization (curing) process, a network between the polymer chains forms and the rubber cannot flow anymore. The crosslinks bond the polymer chains together and they prevent chains to slip on top of each other [3].

In 1841, the vulcanization process was first invented by Charles Goodyear in USA. He discovered that sulfur in the presence of heat is able to bond the rubber chains together and make it a thermoset material with good elastic properties and high strength [2]. A year later an English scientist, Thomas Hancock, used the same process for vulcanization of the rubber.

Curing is a general definition which we can use for all kinds of thermoset polymers, but vulcanization is generally applied for elastomers or rubbers. The vulcanization process produces a chemical network between the rubber chains by bonding the chains together and increases the elasticity and dimensional stability of the polymer. Figure 2.1 is a schematic of the vulcanization process, in which sulfur bonds the rubber molecules to form a vulcanized network. These chemical bonds are formed by a group of sulfur atoms or a single sulfur atom, carbon-carbon bonds, an organic radical, an anionic cluster or a polyvalent metal ion [3].

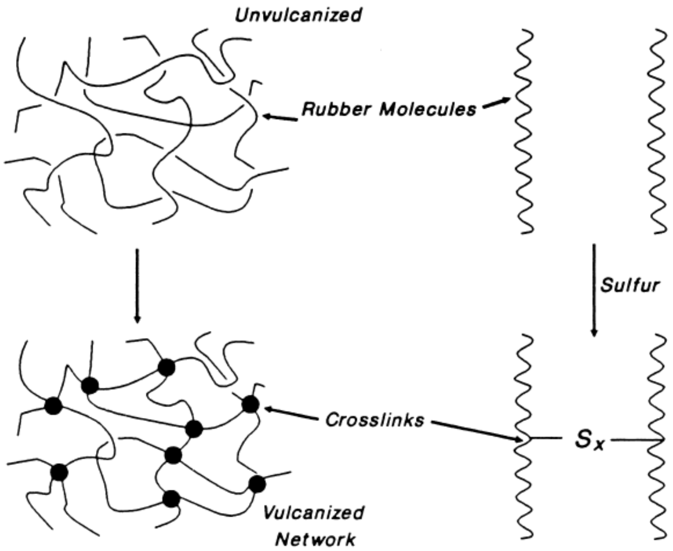


Figure 2.1: Network formation [3].

The presence of these chemical bonds and networks does not let the vulcanized rubber to be soluble in any kind of solvent and the rubber cannot flow by heating anymore. So, we cannot process and shape the rubber after vulcanization. Therefore it is essential to form the shape of a rubber product before the vulcanization process is complete [3]. As we discussed above, unlike thermoplastic polymers, we cannot recycle vulcanized rubber easily just by heating and molding it again. Consequently, most of the vulcanized rubber products become a waste material after their useful life [4].

2.1.2 Historical development of rubber recycling

Rubber recycling is not a recent issue and its history goes back to more than 100 years ago when rubber was a very precious material and resources were very scarce. The cost of an ounce of rubber in 1910 was the same as the cost of an ounce of silver. But after production of synthetic rubber the capacity of rubber production increased and the price of rubber decreased.

In the 1900's rubber products were made from fifty percent reclaim rubber but by the end of the 1950's, it became only one fifth and by the 1980's less than 1% of rubber consumption consisted of reclaimed rubber [4]. The development of synthetic rubber and the steel belted radial tires decreased the capacity of rubber recycling dramatically and these new tires became scrap tires themselves. Because of their high quality and presence of fibers and steel belts, the recycling process for these tires became very expensive and difficult [4].

2.1.3 Current market

Statistics in 2005 for the USA show that nearly 7/8 of the scrap tires in the U.S. were used in end-use markets [5]. These statistics show that annual generation of tires in 2005 is around 299 million tires and the end use market consumed about 259 million tires. The statistics show that there is an eight – fold increase in percentage of consuming of scrap tires by the end use market annually since 1990 (figure 2.2) [5].

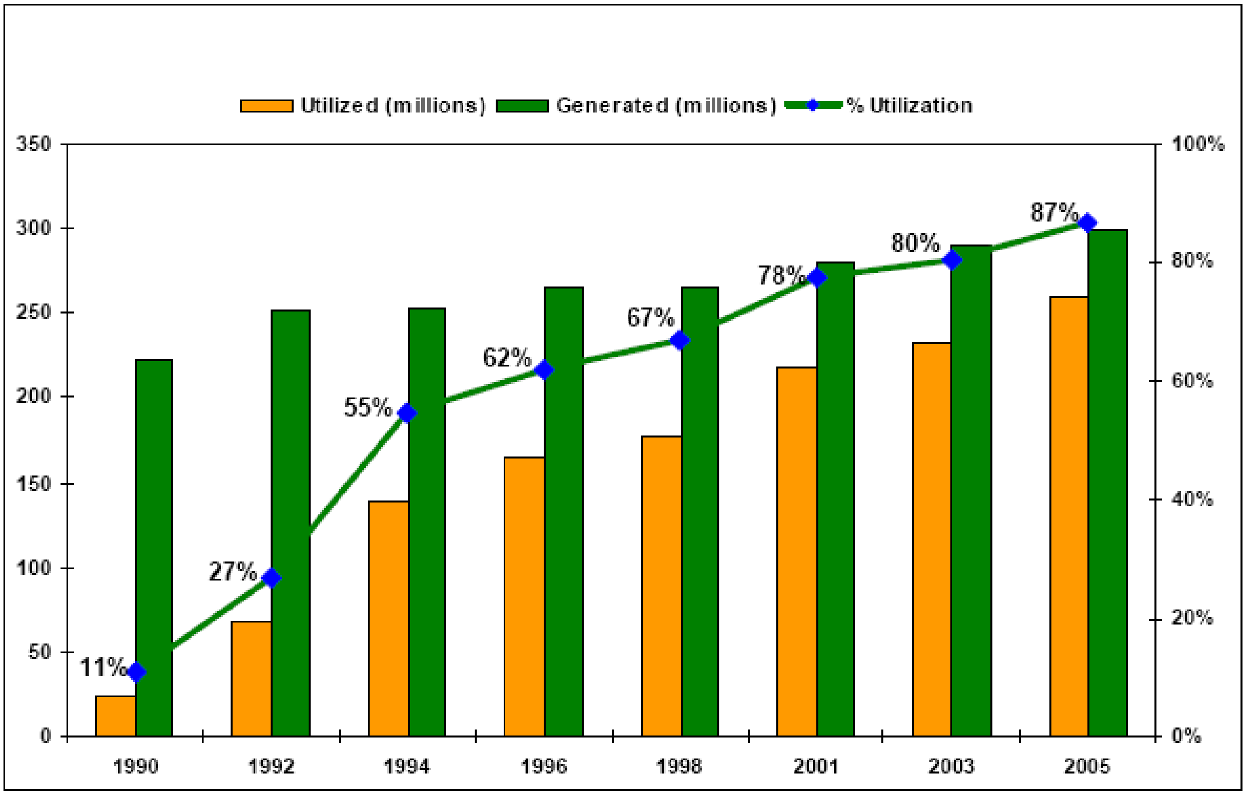
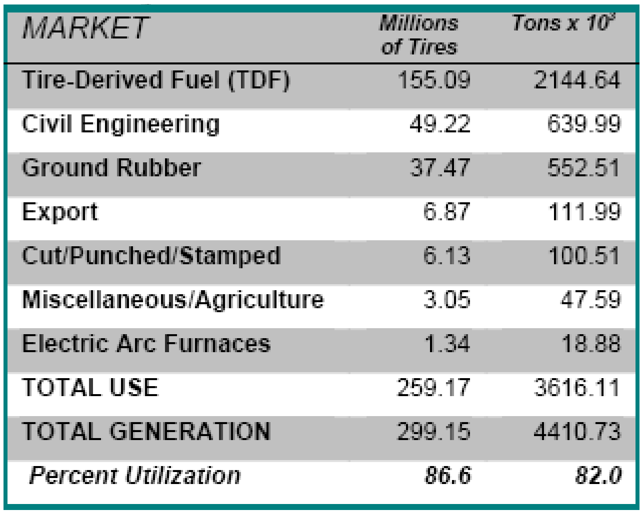


Figure 2.2: US scrap tire management trend [5].

A variety of different markets are using scrap tires, including tire-derived fuel, civil engineering and ground rubber applications. TDF (Tire–derived fuel) applications consumed about 52 percent of total scrap tire or 155 million scrap tire in U.S in 2005. Since the price of fuel is increasing, TDF market is growing very fast due to new improvements in application of TDF and its reliable delivery.TDF is a very good alternative for coal because it is more economical and cleaner[5].

Another big consumer for scrap tires is the civil engineering market. This market has consumed about 16 percent of total scrap tires or 49 million tires in 2005. It uses the crumb rubber for road construction and other structural purposes.

Table 2.1: 2005 U.S scrap tire market [5]



MARKET	***Millions of Tires***	***Tons x 10^3***
Tire-Derived Fuel (TDF)	155.09	2144.64
Civil Engineering	49.22	639.99
Ground Rubber	37.47	552.51
Export	6.87	111.99
Cut/Punched/Stamped	6.13	100.51
Miscellaneous/Agriculture	3.05	47.59
Electric Arc Furnaces	1.34	18.88
TOTAL USE	259.17	3616.11
TOTAL GENERATION	299.15	4410.73
Percent Utilization	***86.6***	***82.0***

Almost 12 percent or 38 million tires in 2005 have been consumed by ground rubber products. Ground rubber can be utilized in safety floorings for playgrounds and sports fields. It can be used in rubber compounds for producing new rubber products.

Another market for ground rubber products is the asphalt market. This market utilizes the ground rubber for modification of the asphalt binder used in road paving [5]. More recent statistics show that the percentage of consuming of scrap tires in the end use market has increased and for an instance this percentage in 2007 was 89.3% compared to 87% in 2005 [6,7]. Similar to the previous statistics, still the TDF application is accounted as the biggest market for scrap tire consumption. The market share for this application increased to 54% in 2007. Demand for ground rubber market has increased but the market development for this application was slow. Figure 2.3 shows U.S scrap tire deposition in 2007. Ground rubber product application has the second highest share after TDF application in 2007 [6, 7].

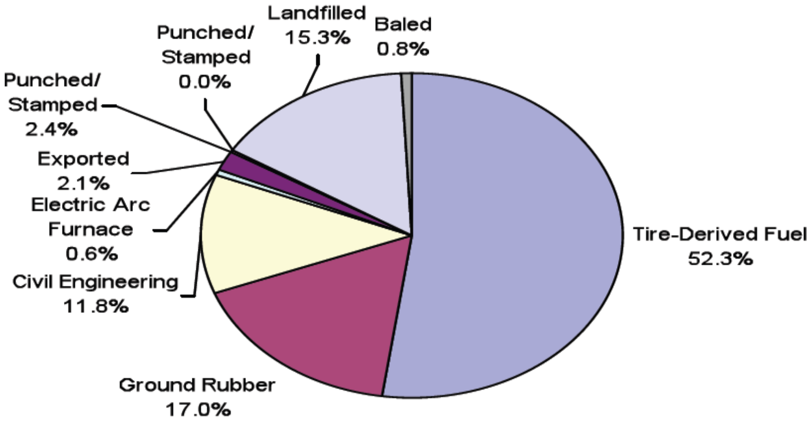


Figure 2.3: 2007 U.S scrap tire deposition (in millions of tires) [7]

2.2 Crumb Rubber: Production methods and applications

2.2.1 Production methods and properties

Grinding the vulcanized rubber is one of the easiest ways for rubber recycling. There are several techniques for preparation of crumb rubber. Different methods have different effects on particle size and particle shape and therefore, different influences on mechanical properties of crumb rubber. In the following, we discuss the common techniques for grinding vulcanized rubber.

Ambient grinding process

Ambient grinding process is a mechanical process in which the vulcanized rubber is broken down by mechanical forces in ambient temperature. Two-roll cracker-type mills or high-powered shear mills are the common machines which are usually incorporated in ambient grinding process (Figure 2.4).

The type of the mill and the number of times that we pass the vulcanized rubber through the nip-gap of the mill, can determine the final particle size and particle size distribution of the crumb rubber. Normally, in the first stage we have a size reduction in the order of 10-40 mesh and for the second stage we can produce a crumb rubber with particle size in the order of 80 mesh [8, 9]. There are eight types of different cutting and grinding equipment: (1) knife hogs (2) primary granulators (3) secondary granulators (4) raspers (5) primary crack mills (6) secondary crack mills (7) finishing mills (8) micro mills [8, 9] .In case of grinding the scrap tires we need two more stages to separate the metal and fibers from the crumb rubber. In order to separate the metals a magnetic separator is utilized in this process. Using an air blowing separator can remove the fibers and lighter materials from the crumb rubber [4, 7].

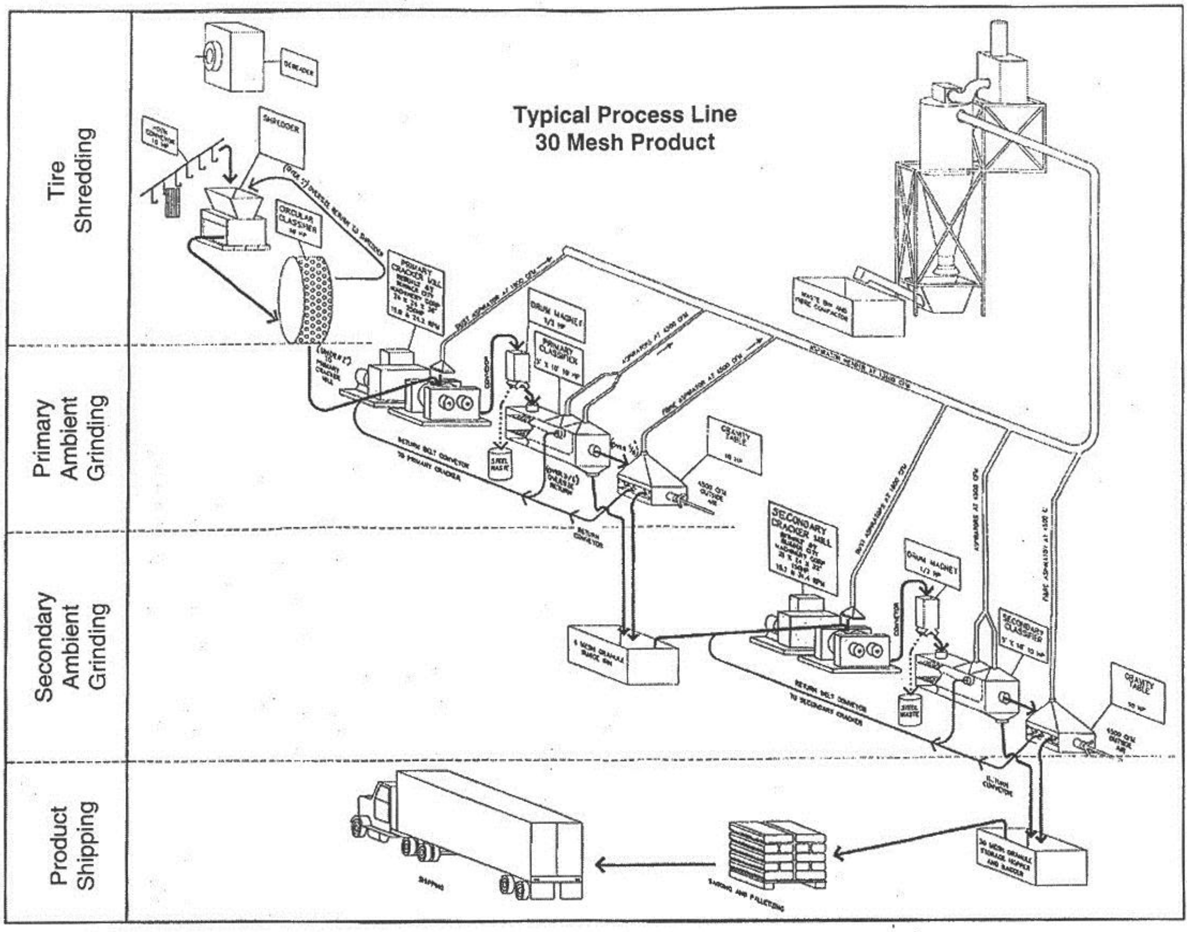


Figure 2.4: typical two-roll mill ambient grinding system [7].

The ambient grinding process has several advantages. The running cost is relatively low and the system is very simple and easy to service. This process has two disadvantages. First, a great amount of heat is generated which can oxidize and degrade the crumb rubber, and second the process becomes very costly if producing very fine mesh size crumb rubber is required.

Cryogenic grinding process

The cryogenic grinding process is basically carried out by first freezing the rubber shreds in a chiller by using liquid nitrogen and then crushing the frozen rubber by an impact mill (Figure 2.5). The brittle frozen rubber is ground into finer particles with mesh size in the order of 40 to 60. After the crushing step, the crumb rubber must be dried in order to remove the moisture and then the fibers and steel can be removed by the same procedure explained in ambient grinding process. This process can produce a rubber crumb with smaller particle size in a faster and cleaner way [4, 7].

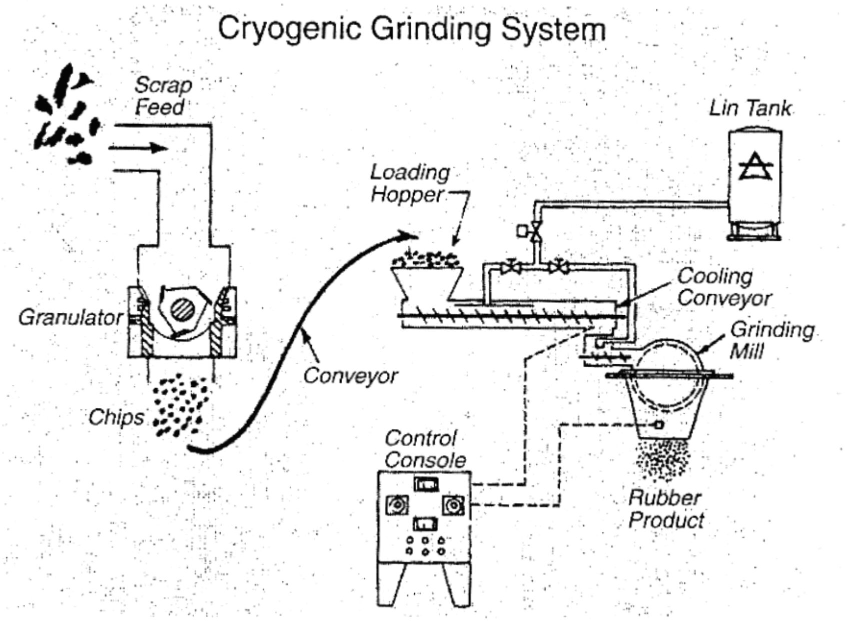
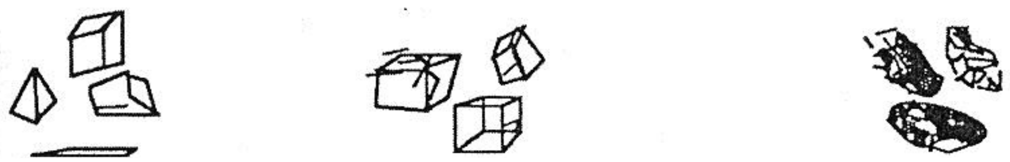


Figure 2.5: Basic cryogenic process layout [7].

Ambient and cryogenic techniques have different effects on the shape, size, size distribution and surface characteristics of the crumb rubber particles. As we see in figures 2.6, the morphology and surface structure of the crumb rubber obtained from these different processes are different. The crumb rubber obtained from the ambient grinding process has an irregular shape with a rough surface.



CRYOGENICS
-Glass like Surfaces
(Very limited surface area)
-Irregular Shapes
-limited Particle Ranges
(-40 mesh)

GRANULATION
-Slightly fractured Surfaces
(Limited Surface Area)
-Rectangular Shapes
-Very Limited Particle Ranges
(-10 mesh)

MILLED, EXTRUDED, GROUND
-Highly Fractured Surfaces (porous)
(High Surface Area)
-Irregular/Rhombic Shapes
-Very Wide Particle Ranges
(-80 mesh)

Figure 2.6: Crumb rubber surface morphology comparisons [7]

The surface of cryogenically grounded rubber is relatively smooth and the particle size distribution has a broad range. These differences can affect the properties of the final crumb rubber. The crumb rubber obtained from the ambient process has better physical properties for bonding. In terms of removing the fiber and steel residue, the cryogenic process produces a cleaner rubber crumb. The capital cost for a cryogenic process plant is lower in comparison with the ambient process, but using the liquid nitrogen and the extra drying step for removing the moisture from the crumb rubber increase the operating cost [8].

Table 2.2 shows a comparison of physical properties between cryogenic ground rubber and ambient ground rubber. Fiber and steel content is about 0.5 % and 0.1 %, respectively, for ambient ground rubber, while those contents are not found in cryogenic ground rubber. The shape of particles is regular for cryogenic ground rubber in contrast with ambient ground rubber which has an irregular particle shape. Table 2.3 shows the particle size distribution for two different 60 mesh ground rubber which are obtained from ambient and cryogenic grinding process. Data show that the distribution of particle size is broader for cryogenic ground rubber.

Table 2.2: Comparison of Ambient and Cryogenically Ground Rubber [8]

Physical Property	Ambient Ground	Cryogenic Ground
Specific gravity	Same	Same
Particle shape	Irregular	Regular
Fiber content	0.5 %	Nil
Steel content	0.1 %	Nil
Cost	Comparable	Comparable

Table 2.3: Particle size distribution of 60 mesh Ground Rubber [8]

Amount Retained	Ambient	Cryogenic
30 mesh	2 %	2 %
40 mesh	15 %	10-12 %
60 mesh	60-75 %	35-40 %
80 mesh	15 %	35-40 %
100 mesh	5 %	20 %
Pan	5-10 %	2-10 %

Wet grinding process

This process consists of adding water as a lubricant and cooling agent to small chips of rubber and then grinding the rubber by a flour type grinding mill. This method is able to produce a very small size crumb with mesh size from 60 to 120 and the final material is very clean. Another similar process is solution grinding, in which, a solvent is used instead of water [4].

Extrusion

In this process rubber powder is produced by using a twin-screw extruder. The vulcanized rubber is passed through the extruder and ground by the high shear stress and temperature in the extruder. The process is capable of converting a material having particle size of few millimeters to a powder having an average particle size of some hundred microns. Since the surface of rubber powder is degraded due to excess temperature during this process, appropriate cooling is necessary to reduce the degradation effects [7].

Another process has been developed by Arastoopour and Bernstein [10], utilizing a single screw extruder. This process is called solid–state shear extrusion (SSSE). A single screw extruder (Figure 2.7) grinds the vulcanized rubber to very fine rubber particles with average diameter in the order of 40 to 60 µm. The shape of the rubber particles is very irregular and the size distribution is very wide. It was reported that the SSSE-made rubber powder has a surface area three times higher than that of the cryogenically crumb rubber. Crosslink density measurements showed that the crosslink density of the SSSE-made rubber powder is much lower than the feed material, showing partial devulcanization due to sulfur-sulfur bonds breakage during the extrusion process.

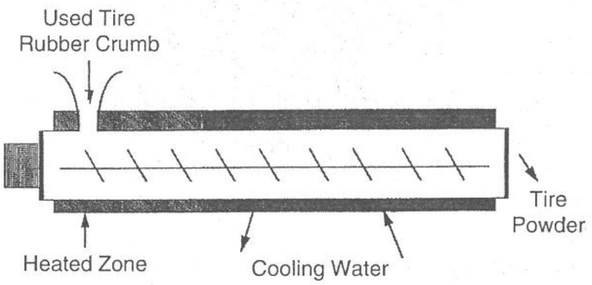


Figure 2.7: Typical Solid state shear extruder [9].

2.2.2 Applications of crumb rubber

The crumb rubber market has grown during the last decade. This market consumed about 807.5 thousand tons scrap tires in 2007 [7]. There are several applications for crumb rubber.

Crumb rubber application in asphalt

Using the crumb rubber in asphalt binders is one of the recent interesting research areas. Utilizing the crumb rubber improves the performance and durability of asphalt pavements. There are two different processes which are used to produce the rubberized asphalt; dry and wet processes [8].

In the dry process, the crumb rubber is premixed with aggregates and then the mixture is added to the asphalt aggregate. The wet process consists of, first mixing and reacting the crumb rubber (15-22 wt %) with asphalt bitumen and then introducing the mixture in to the hot mixer alongside the aggregates [8]. Efficient mixing and content of rubber in the mixture are important factors which can affect the properties and performance of the asphalt material. The rubberized asphalt has better short and long term performance and improved properties (i.e. ductility, skid resistance, under icy condition, crack resistance and noise reduction) [7].

Crumb rubber in sport and playground surfaces

One of the major applications of crumb rubber is in sport and playground surfaces. The crumb rubber exhibits a very good resilience and durability in sport and playground floorings. It can be used for flooring of children playground surfaces, jogging tracks, tennis and indoor football courts, athletic tracks, swimming pool surroundings etc. Some companies produce rubber crumb pads and tiles by bonding the crumb rubber with polyurethane or latex binder [8].

Rubber products

Several investigations have been done for utilizing the crumb rubber in rubber compounds. Rubber crumb can be used in rubber compounds as filler in order to produce new rubber products. Adding the crumb rubber into the rubber compounds has many different effects on processing and rheological behavior, cure characteristics and mechanical properties. There are many publications that have reported these effects.

Ghosh et al. [11] reported that the Mooney viscosity, Mooney scorch time and shear viscosity of fluoro-rubber compounds shows a marginal increase by adding flourorubber vulcanized powder and the presence of fluoro-rubber vulcanized powder in the fluoro-rubber compound can marginally increase the tensile strength, modulus and hardness while the tear strength decreases.

Jacob and co-workers [12, 13] studied the effect of ground EPDM vulcanizate on properties of EPDM rubber compounds. Their results showed that addition of ground rubber into the compound increases the Mooney viscosity and decreases the Mooney scorch time. They reported that the presence of crumb rubber in the EPDM compound increases the stress-strain properties and tear resistance.

Cure behavior of rubber compounds can be affected by the addition of crumb rubber. Scorch time, optimum cure time, rate of cure and state of cure of the rubber compound change when we introduce the crumb rubber into the rubber compounds [8]. Table 2.4 shows typical applications for crumb rubber.

Table 2.4: Typical applications for crumb rubber [8].

Industry	Applications
Road and Rail Applications	• Rubber modified bitumen • Acoustic barriers • Road base • Portable traffic control devices • Ripple strips and speed bumps • Rail crossings, sleepers and buffers
Construction & Industrial	• Foundation material • Industrial flooring & footpaths • Anti-static computer mats • Acoustic barriers • Sprayed up roofing, insulation • Adhesive sealants • Mounting pads and shock absorbers • Membrane protection • Airfield runways • Shoe soles • Children’s playground surfacing
Automotive	• Filler in new tire manufacture • Tire retreads • Solid and pneumatic tires

	• Oil spill absorber • Floor mats, mud flaps, molded protection strips • Special friction brakes • Automotive door and window seals • ALLTRACK segmented earthmoving tires • Gaskets • Adhesive sealants • Spray able sealant for automobile wheel housings • Vehicle bumper bars
<u>Industrial</u>	• Flexible foam • Rollers • Pond liners • Compression molding compound • Extrusion compounding for rubber products • Injection molding compound • Solid tires for industrial equipment • Conveyor belts
<u>Rural and Landscaping</u>	• Flooring • Watering systems, rubber hosing • Agricultural pipes • Flower pots, wall hangers, pot plants • Animal bedding

Packaging	- Filler - Bags - Recycling bins
Sporting	- Flooring - Sporting fields, athletic tracks, tennis courts, etc - Gymnasium flooring and matting

2.2.3 Testing and quality assurance

Tire-derived materials (TDMs) are the materials which we make from scrap tires. TDMs consist of different type of material depending on the process we utilize to recycle the scrap tires. Crumb rubber materials (CRMs) are one of the highly refined portions of the TDMs which are produced by size reduction processes [8].

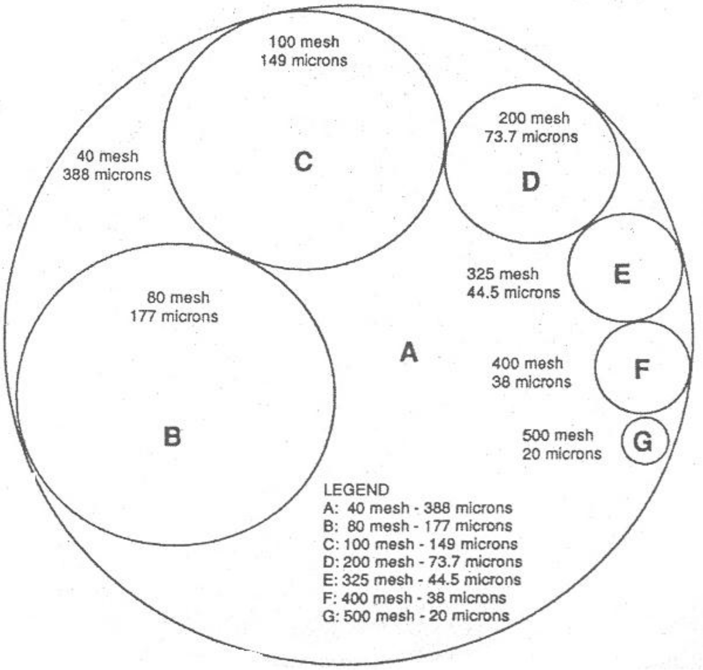


Figure 2.8: Relative particle size comparison [8]

The size range of crumb rubber starts from below 2 millimeters or 2000 microns or 10 mesh. Rubber particles with a size of less than 180 microns (80 mesh) are called crumb rubber powder. Figure 2.8 compares the various particle sizes and table 2.5 shows a sieve comparison of different rubber particles [8].

The U.S standard Tyler screen is defined to measure the crumb rubber particle sizes. The opening between the wires of a screen is called mesh. Generally we use this term to describe the crumb rubber particle size. A greater number of mesh means a greater number of openings in a fixed surface area, have a finer particle size of crumb rubber. 40 mesh means that there are 40 holes per 1 square inch of surface area.

Passing the crumb rubber through the screen or mesh in the production process determines the size of the crumb rubber. Usually two numbers are used to express the crumb rubber size. The first number has a minus sign (-) which refers to material that has passed the mesh screen. The second one has a plus (+) symbol and shows the size of particles that has not passed the screen. Figure 2.9 shows the glossary of terms for inch to mm to mesh

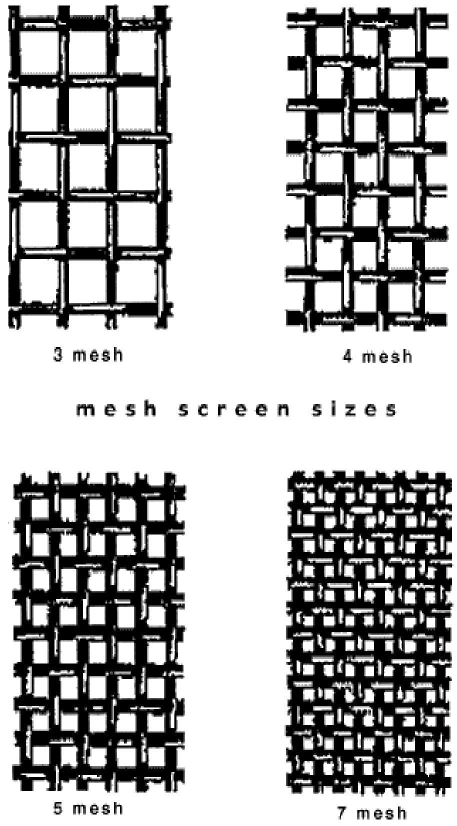
Table 2.5: Sieve comparison table [8]

Major Grade size Categories	Designation Size (inch) or Sieve (Mesh)	Mm (millimeters)	Microns (1000×mm)	Inches
Fuel Grade size	2”	50.000	50,000	2.000
	1-1/2”	37.500	37,500	1.500
	1”	25.000	25,000	1.000
	3/4”	19.000	19,000	0.750
	5/8”	16.000	16,000	0.625
	1.2”	12.500	12,500	0.500
	7/16”	10.938	10,938	0.438
	3/8”	9.520	9,520	0.375
	5/16”	7.930	7,930	0.313
	1/4” or 3	6.350	6,350	0.250
Coarse Grade Sizes	3.5	5.660	5,660	0.223
	4	4.760	4,760	0.187
	5	4.000	4,000	0.157
	6	3.360	3,360	0.132
	7	2.830	2,830	0.111
	8	2.380	2,380	0.094
	10	2.000	2,000	0.079
	11	1.840	1,840	0.072
	12	1.680	1,680	0.066
	14	1.410	1,410	0.056
	16	1.190	1,190	0.047
	18	1.000	1,000	0.039
Fine Grade Sizes	20	0.840	840	0.0331
	24	0.736	736	0.0290
	30	0.590	590	0.0232
	35	0.500	500	0.0197
	40	0.420	420	0.0165
	45	0.350	350	0.0138
	50	0.297	297	0.0117
	60	0.250	250	0.0098
	70	0.210	210	0.0083
	80	0.177	177	0.0070
Ultra Fine ™ Grade sizes	100	0.149	149	0.0059
	120	0.125	125	0.0049
	140	0.105	105	0.0041
	150	0.099	99	0.0039
	165	0.091	91	0.0036
	170	0.088	88	0.0035
	200	0.074	74	0.0029
	230	0.062	62	0.0024
	250	0.058	58	0.0023
	270	0.053	53	0.0021
	325	0.044	44	0.0017
	400	0.037	37	0.0015

Inch to mm to Mesh Glossary of terms

Inch - 1/36th of a yard, 25.4 millimeters
Millimeter - 1/1000th of a meter, .0394 inch
Screen - a meshed wire fabric mounted on a frame for the purpose of separating coarser from finer parts
Mesh - the opening between the wires of a screen

Sieve - the device which includes the frame and the screen used for separating coarser from finer parts
Classifier Screen - the screens or sieves that are mounted in a production piece of equipment to separate the desired size of crumb from the other sizes, and recycle the other for the purpose of further size reduction
Testing Screen or Sieve - a small, hand-held sieve made for testing the product coming off the classifier screen



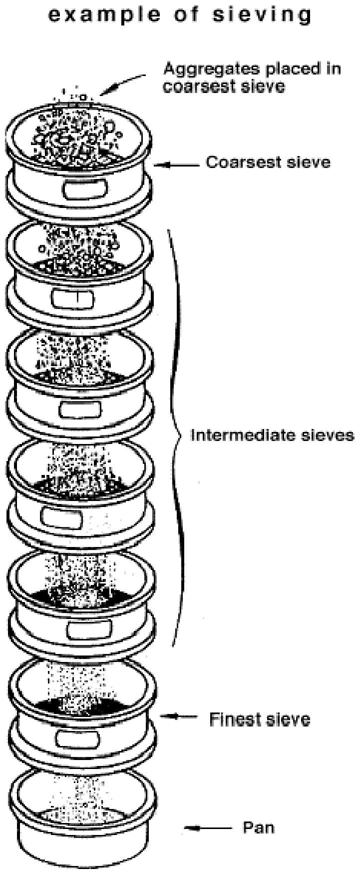


Figure 2.9: Detailed illustration of mesh definition [8].

2.3 Methods for rubber devulcanization

The term devulcanization refers to a process in which the crosslink bonds in the vulcanized rubber cleave totally or partially. By cleaving these crosslink bonds, the vulcanized rubber is able to be revulcanized and utilized again like a virgin rubber material. In order to have better properties, it is preferable to avoid main chain scissions during the devulcanization process. Figure 2.10 shows the molecular structures of virgin raw rubber, vulcanized and, devulcanized rubber.

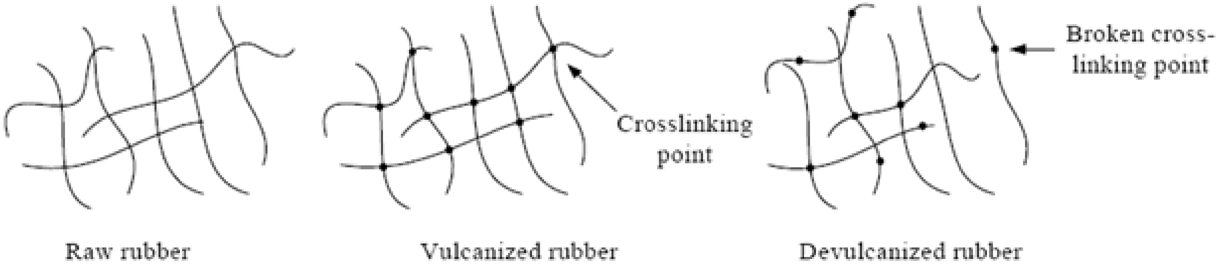


Figure 2.10: The difference of molecular structures between virgin raw rubber, vulcanized and devulcanized rubber [14].

2.3.1 Thermo-Mechanical Devulcanization Process

In the thermo-mechanical devulcanization process, shear and elongational stresses are used to break down the crosslink bonds. Extruders and open mills are common equipments which are suitable for this purpose. The process usually involves heating to increase the cleavage performance of crosslink chemical bonds. However, shear and elongational stresses alongside high temperature can easily break down the main chains of polymer which results in a significant decrease in molecular mass and poor physical properties. In order to cleave the crosslink bonds selectively, the characteristics of equipment and the processing parameters are very important [9].

Mouri et al. published a number of papers [16, 17, 18 and 19] regarding the thermo-mechanical devulcanization of EPDM rubber crumb. A new continuous devulcanization technique, based on a shear flow reaction control technology, is utilized to break down the EPDM crosslink bonds selectively. The process is carried out in a twin screw extruder and effects of various parameters, like screw geometry, screw speed and processing temperature were investigated.

The screw configuration controls the reactor fill factor, rubber residence time, internal rubber pressure, mixing force and shearing force. High shearing deformation alongside high hydrostatic pressure results in a better devulcanization performance. By optimum designing of the screw, they produced a continuous sticky strand of devulcanized rubber [16, 17].

In another paper [18], they investigated the devulcanization process inside the twin screw extruder. They removed the screw during the devulcanization process and took samples from five different points of screw (Figure 2.11).

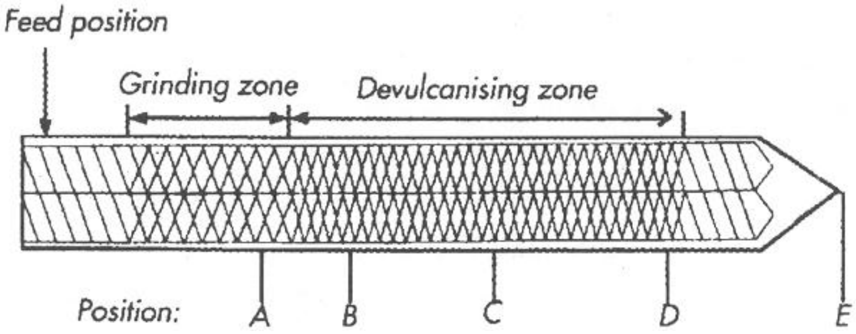


Figure 2.11: Sampling positions for devulcanized rubber [18].

The experiment was done in a constant feed rate of crumb rubber (10kg/hr), at three temperatures (200, 240 and 280 ˚C) and three different screw speeds (100, 200 and 400 rpm). Figure 2.12 shows the gel fraction and effective network chain density of different samples. The results show, as the devulcanization process proceeds from position A to position E, the gel fraction decreases and the crosslink structure becomes weaker. Mouri et al. [19] also analyzed the changes in crosslink structure during the devulcanization process. The proposed mechanism for the devulcanization process shows that the heat, at the first step, converts the poly/di-sulfide crosslink bonds into the mono sulfide crosslink bonds as seen in figure 2.13.

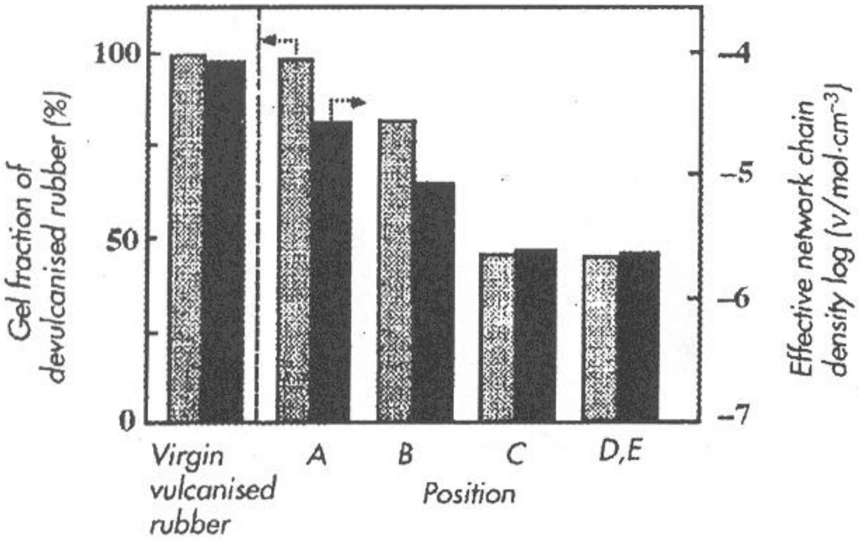


Figure 2.12: Gel fraction of devulcanized rubber and its effective network chain density [18].

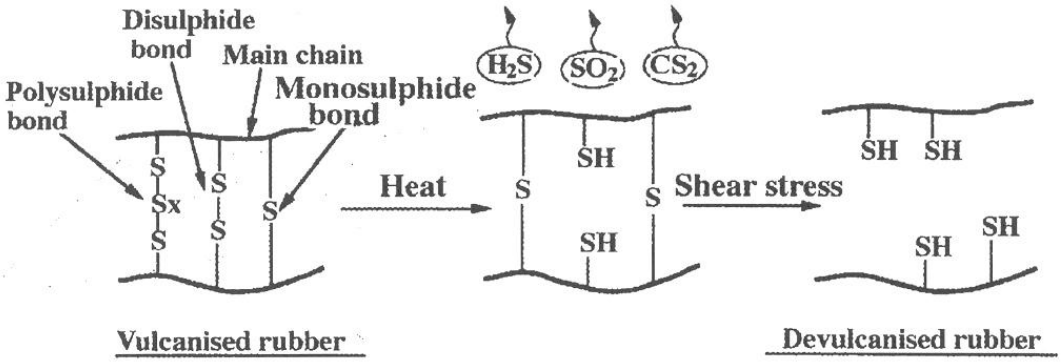


Figure 2.13: Mechanism for crosslink bonds breakage [19].

"With the breakdown of sulfide crosslinks the sulfur atoms of the crosslinks are separated from the rubber molecules and converted into low molecular sulfur compounds such as hydrogen sulfide and sulfur dioxide" [19].

Another study was done by Fukumori et al. [20]. They developed the same technology which was presented by Mouri et al. before. They utilized a 30 mm twin screw extruder and optimized the devulcanization process by adjusting different parameters like shear stress, temperature and internal pressure. They tried three different screw configurations, three different temperatures and two different screw speeds. Measuring the sol fraction of devulcanized rubber can give us a good sense of the devulcanization performance. The relation between the Mooney viscosity and sol fraction shows a very good correlation (Figure 2.14). Since the Mooney viscosity is an easy parameter to measure, they monitor the devulcanization performance by measuring the Mooney viscosity during the different experiments. Figure 2.15 shows the optimum process parameters for obtaining the suitable range of Mooney viscosity [20].

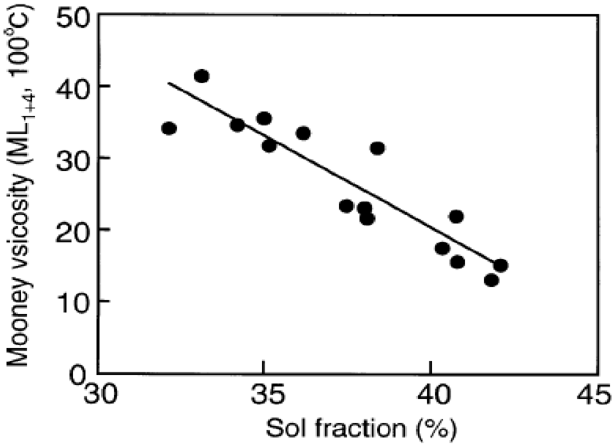


Figure 2.14: Relation between Mooney viscosities and sol fraction for SBR-based rubber [20]

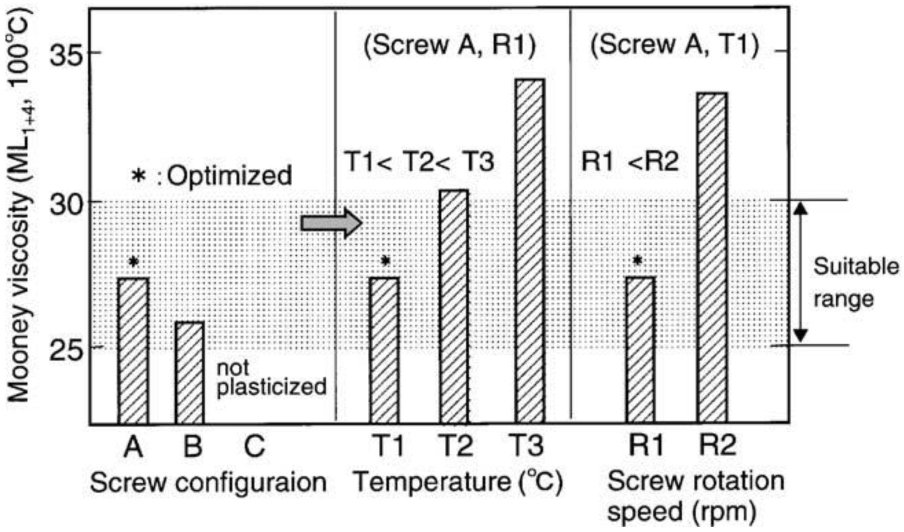


Figure 2.15: Relation between Mooney viscosity and process parameters for SBR-based rubber [20]

Figures 2.16 and 2.17 show the results for tensile strength and elongation at break for SBR and NR compounds containing the devulcanized SBR-base and NR-base rubber. The results show that adding 30 phr of devulcanized rubber into the virgin rubber compounds will reduce the tensile strength and elongation at break up to 10 % compared to 100% virgin rubber compounds [20].

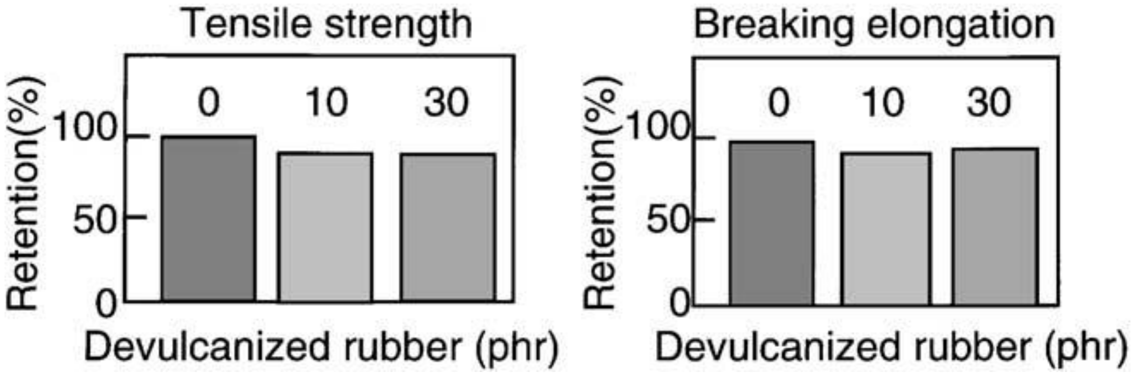


Figure 2.16: Tensile properties of NR compounded with devulcanized NR-based rubber [19].

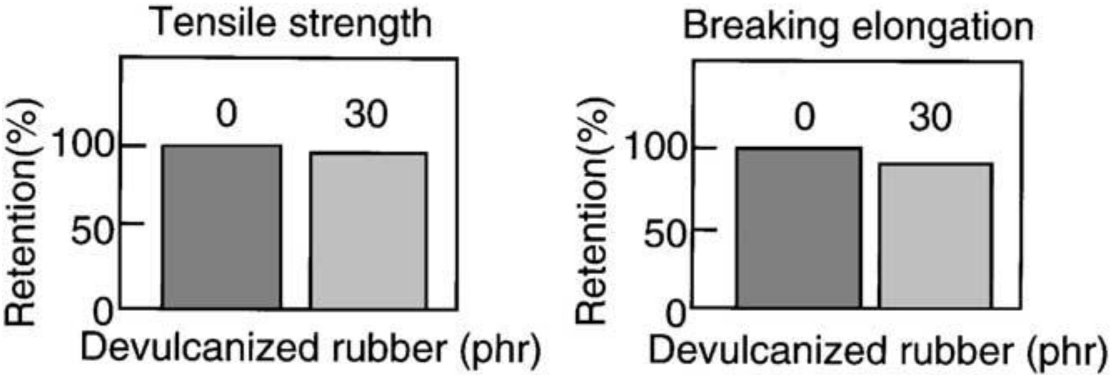


Figure 2.17: Tensile properties of SBR compounded with devulcanized SBR [19]

Figure 2.18 shows the results of actual road test for truck tires containing 10 % of devulcanized NR-based rubber. After 200,000 Km running, the tires containing the devulcanized rubber showed similar behavior in term of tread wearing, compared to the standard new tires [18].

Tzoganakis and Zhang developed and patented a new thermo-mechanical devulcanization process by using supercritical carbon dioxide in a twin screw extruder [4, 21, and 22]. Carbon dioxide acts as a processing agent to facilitate the devulcanization process. It is dissolved into the rubber particles and swells them and makes them easier to extrude.

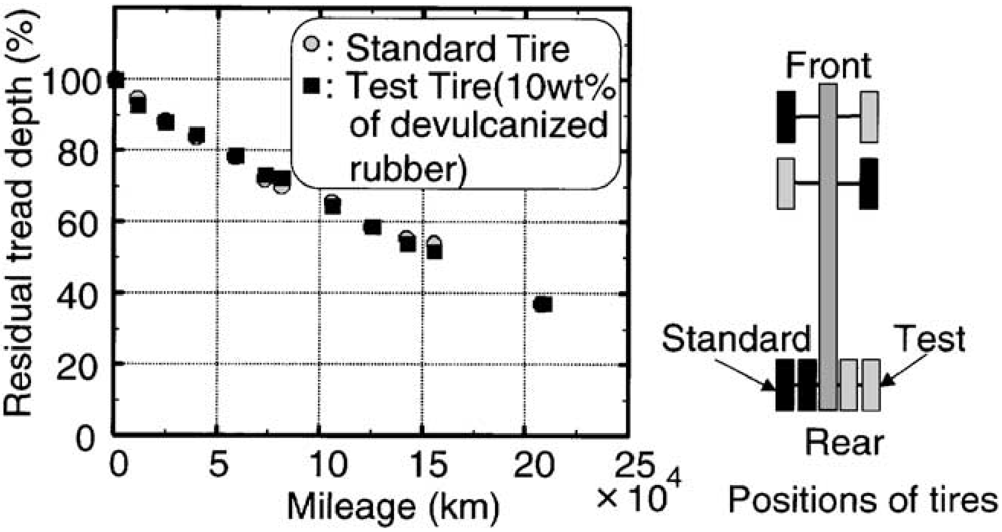


Figure 2.18: Changes in tread depth for standard and test truck tires during actual road tests [20]

Figure 2.19 shows the dependency of degree of devulcanization on the injected CO_2 concentration. Presence of $scCO_2$ results in an increase of soluble fraction at the beginning, but as shown, the CO_2 concentration has a very small influence on the soluble fraction of devulcanized rubber [21]. Low molecular weight part is extracted by acetone extraction and mainly consists of rubber additives such as oil, resins, and low molecular weight material and also the small molecules of rubber which are generated due to polymer degradation. Sol fraction is free rubber chains that are not attached to the rubber network and is extracted by toluene swelling. In this research the soluble part is defined as the sum of the low molecular weight fraction and sol fraction.

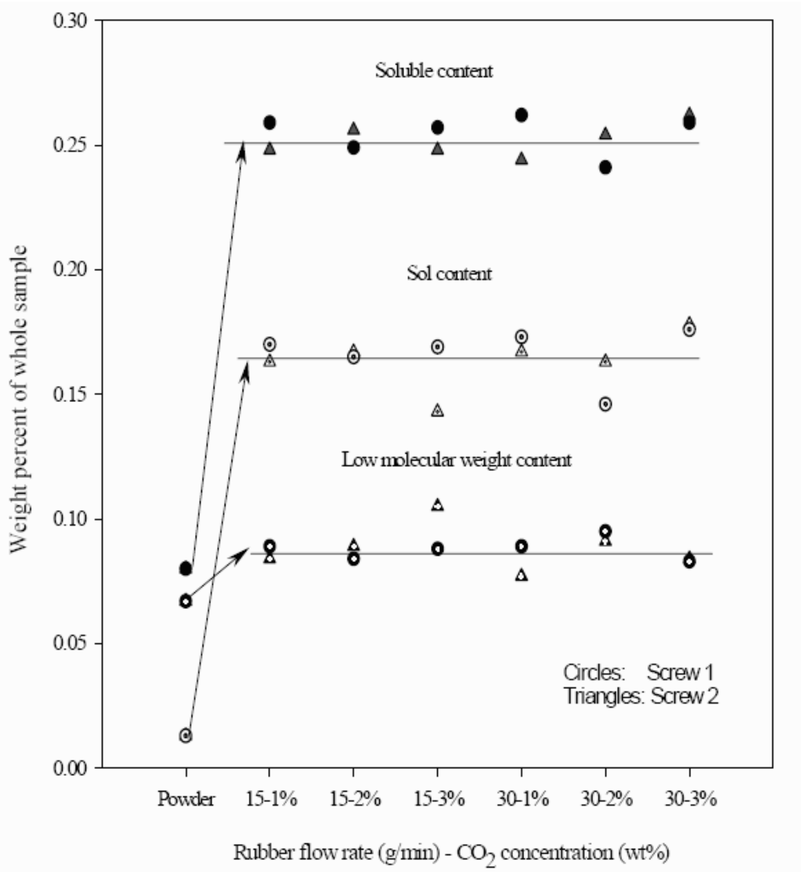


Figure 2.19: Degree of devulcanization at 250°C [21].

Figure 2.20 shows the processing temperature and screw speed effects on the soluble, sol and the low molecular weight contents of devulcanized rubber. The results show that increasing the screw speed will increase the shear rate and as a consequence the devulcanization performance increases [21].

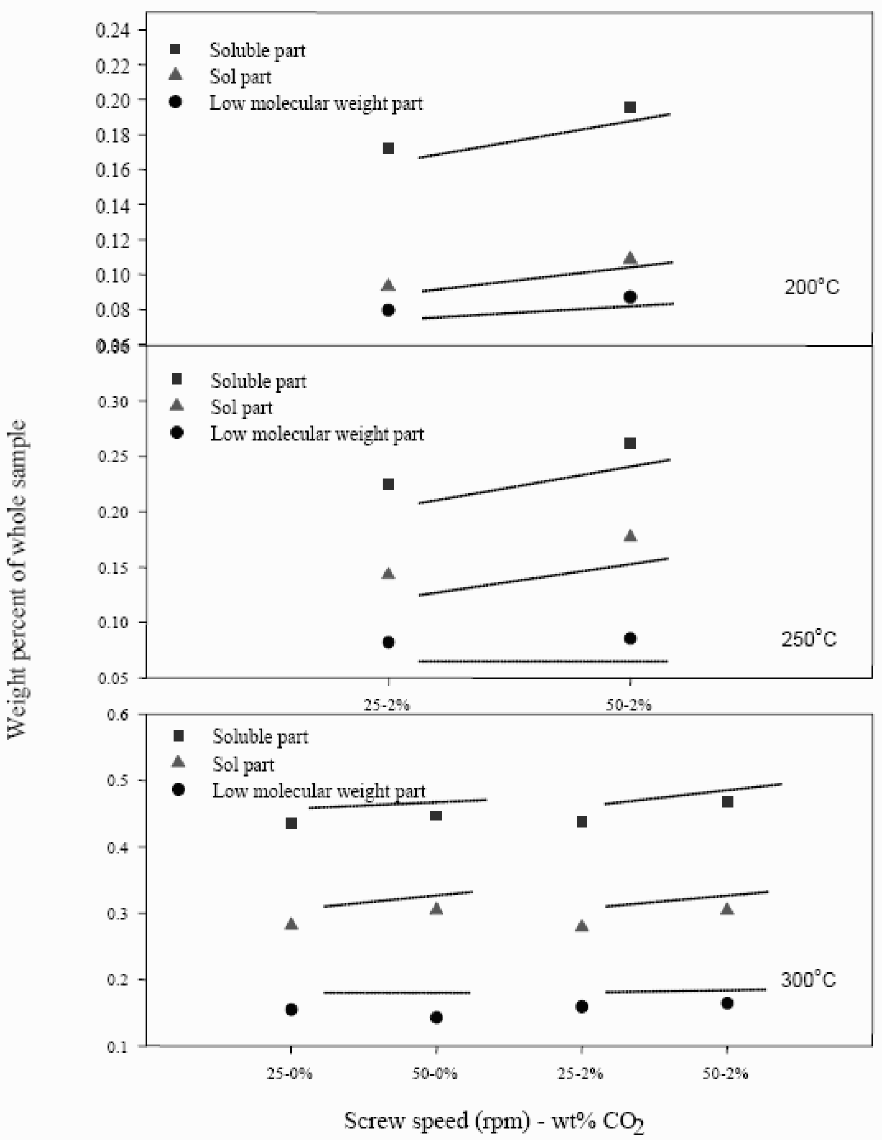


Figure 2.20: Devulcanization degree for 80 mesh crumb at different screw speeds (15 g/min, 2wt%CO2 concentration, and screw 1) [21]

Figure 2.21 shows the effect of temperature on the soluble part, sol part and low molecular weight part of the devulcanized rubber. From figure 2.21, it can be seen that the soluble content increases by increasing the temperature from 200°C to 300°C [21].

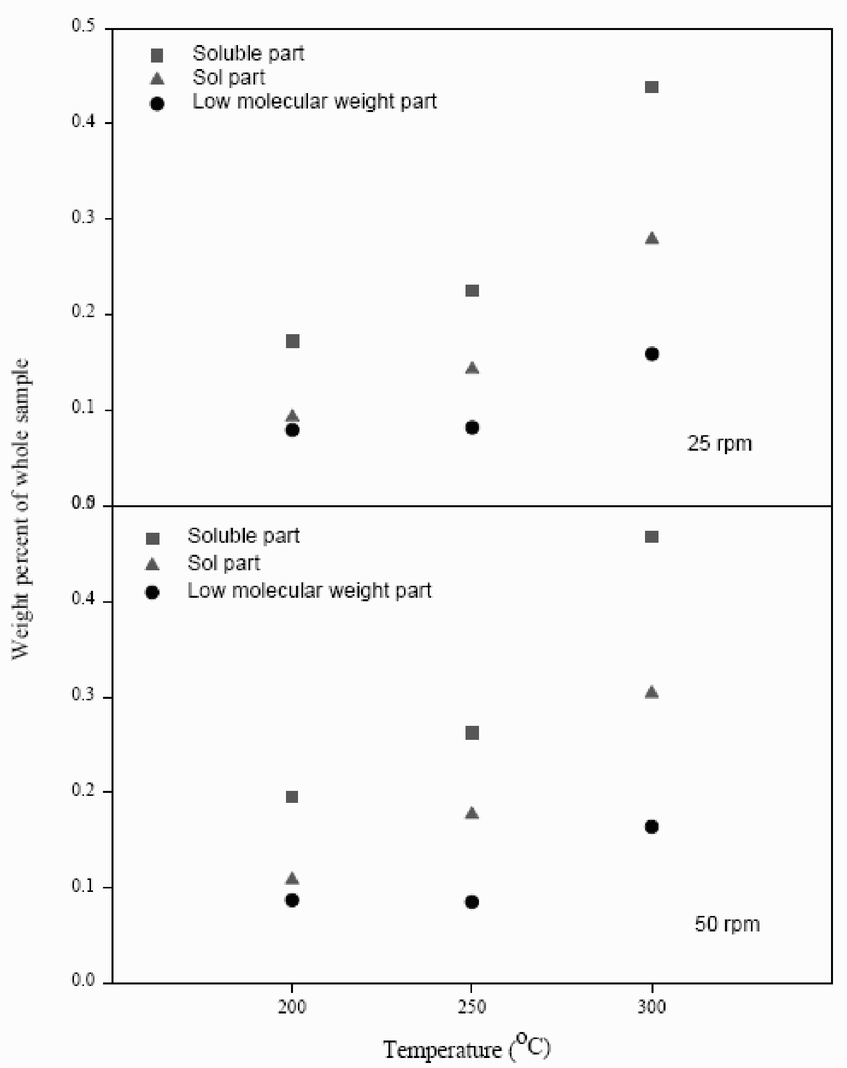


Figure 2.21: Devulcanization degree for 80 mesh crumb at different temperatures (15 g/min, 2wt%CO2 concentration, and screw 1) [21]

2.3.2 Mechano-Chemical Devulcanization Process

In 1995 Shekhar and Komar presented a new devulcanization process, using De-Link material to devulcanize vulcanized rubber. The process was carried out by blending the De-Link with crumb rubber in a two-roll rubber mill or in an internal mixer, like Banbury mixer. De-Link in presence of shear force can cleave sulfur crosslinks and the product would be an unvulcanized rubber or "De-Vulc" (Figure 2.22) [23].

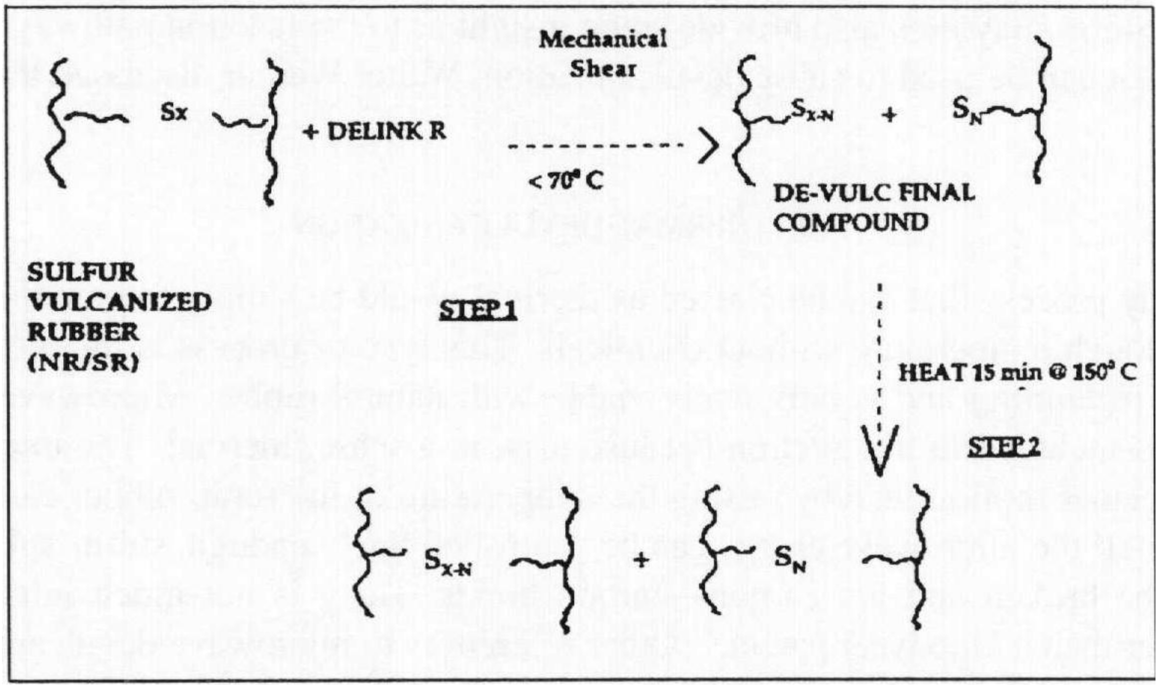


Figure 2.22: Possible devulcanization mechanism [23].

De-Vulc can be vulcanized again in the presence of heat and pressure without adding any new curing agent. This process is applicable for different types of vulcanized rubber, like NR, BR, SBR, EPDM, NBR and CR. [23]

De et al. [24, 25] devulcanized a sulfur cured natural rubber by using two levels for two different devulcanization agents. They milled these compounds at two different temperatures and two different milling times. The chemical devulcanization agents were diallyl disulfide and a vegetable product named RRM (renewable resource material). The sol and gel fraction, molecular weight of sol fraction and Mooney viscosity were determined. (Table 2.6) [24]. The sol fraction shows a gradual increase with milling time for both temperatures and Mooney viscosity decreases with milling time for both temperatures.

Table 2.6: Effects of Concentration of Reclaiming Agent, Milling Time, and Temperature on Sol Content, Mol Wt of Sol, and Mooney Viscosity [24]

	Milling at 40 C						Milling at 60 C					
	15 Min Milling			35 Min Milling			15 Min Milling			35 Min Milling		
Reclaiming Agent	**% Sol**	**Mol WT× 10^{-4}**	**Mooney Viscosity**	**% Sol**	**Mol WT× 10^{-4}**	**Mooney Viscosity**	**% Sol**	**Mol WT× 10^{-4}**	**Mooney Viscosity**	**% Sol**	**Mol WT× 10^{-4}**	**Mooney Viscosity**
10 g RRM	**21.0**	**0.28**	**200.0**	**26.5**	**0.80**	**83.5**	**18.0**	**0.51**	**97.9**	**28.0**	**1.05**	**61.5**
20 g RRM	**19.8**	**0.27**	**200.0**	**27.0**	**0.83**	**85.6**	**22.4**	**0.50**	**200.0**	**29.0**	**1.68**	**76.7**
2 g DADS	**24.5**	**0.49**	**107.2**	**31.0**	**1.35**	**58.5**	**25.0**	**0.38**	**54.1**	**29.0**	**0.98**	**26.2**
4 g DADS	**23.0**	**0.49**	**145.5**	**32.0**	**1.41**	**62.4**	**23.0**	**0.94**	**89.9**	**32.3**	**1.38**	**51.8**

Table 2.7 shows the effect of devulcanization on tensile properties. The values for tensile strength, elongation at break and hardness of the revulcanized samples are less than those of virgin rubber vulcanizates.

Table 2.7: Tensile Properties of Re-vulcanized NR samples [25]

Nature of the Vulcanizate	**Tensile Strength (MPa)**	**Elongation at Break (%)**	**Shore A Hardness**	**Swelling Value (Q)**	**Weight Loss After Eq. Swelling (%)**
Vulcanized NR	**22.88**	**500**	**66**	**2.99**	**1.79**
Reclaim by RRM	**4.34**	**283**	**34**	**5.52**	**2.98**
% Retention	**19.00**	**57.0**	**51.5**	**184.0**	**-**
Revulcanized NR	**3.52**	**300**	**33**	**6.60**	**3.31**
Reclaim by DADS					
% Retention	**15.40**	**60**	**50**	**220.7**	**-**
Reclaim NR, fresh NR blend [a] **(RR: NR = 40 : 60)**	**19.13**	**150**	**75**	**2.5**	**3.57**
% Retention	**83.60**	**90**	**114**	**84**	**-**

[a] Formulation (phr): RR:40; NR (RSSI):60; Zno: 5; stearic acid: 2; CBS: 1; sulfur: 1.75; carbon black: 32; vulcanized at 150 °C for 5.75 min.

Jalilvand and co-workers [26] studied the devulcanization of EPDM in the presence of diphenyl di-sulfide as a devulcanization agent by using a twin screw extruder. Percent of devulcanization, sol fraction, Mooney viscosity and curing behavior of devulcanized EPDM was evaluated. They reported that the Mooney viscosity and sol fraction strongly depended on the barrel temperature and that shear stress has an important role on percent devulcanization.

Sutanto and co-workers [27, 28] performed a series of studies on devulcanization of EPDM rubber in both batch and continuous processes using an amine as the devulcanizing agent. In their first paper [27], they modeled the kinetics of EPDM devulcanization in a batch mixer using the hexadecylamine (HDA) as a devulcanizing agent. The effect of the process parameters such as temperature, shear rate, concentration of devulcanization agent, and devulcanization time on the degree of decrosslinking was studied. The derived model was verified with experimental results and it was shown that the model can predict the de-crosslinking degree quite adequately. In the second publication [28] they used an experimental design to study the responses of continuous devulcanization processes. They used the scrap EPDM roofing sheet and also the scrap EPDM profile as the starting material. Devulcanization of EPDM rubber was done in a twin screw extruder using the HDA as a chemical agent. The measured response was the degree of devulcanization of the rubber and they studied the effect of the feed rate, screw speed, and the temperature of the extruder barrel. It was shown that the conversion is higher at the higher temperature and higher shear rate. On the contrary, a lower flow rate can give us a higher conversion [27].

2.3.3 Ultrasound devulcanization

Another important method for rubber devulcanization is ultrasound devulcanization process. In order to break the carbon-sulfur and sulfur-sulfur chemical bonds, the ultrasound devulcanization process uses a high energy level ultrasound source. “An ultrasonic field creates high frequency extention-contraction stresses in various media” [1]. In a continuous ultrasound devulcanization process, an extruder is utilized for passing the crumb rubber through a narrow gap between the stationary die and the vibrating horn [4]. There are three different types of ultrasonic devulcanization reactors, coaxial, barrel and grooved barrel ultrasonic reactors [8] (Figure 2.23).

The c*oaxial reactor* consists of an extruder and a coaxial ultrasonic die attachment. There are a power supply, an acoustic convertor, booster, and a cone-tipped horn in the ultrasonic system. When the rubber crumb flows in the gap of the die the horn vibrates longitudinally and the material is exposed to the ultrasonic waves which propagate vertically to the flow direction. The ultrasonic waves help devulcanize the rubber material passing through the die gap [8].

Two ultrasonic horns with rectangular cross section were attached in to the extruder barrel in the b*arrel ultrasonic reactor*. The rubber is forced to pass through the gap between the horn and the screw [8]. A *Grooved barrel ultrasonic reactor* is almost similar to the Barrel reactor and the only difference is the presence of two helical channels which are made on the barrel surface. "Rubber flows into the helical channels and passes through the gap created between the rotating shaft and the tip of the horns, where devulcanization takes place” [8].

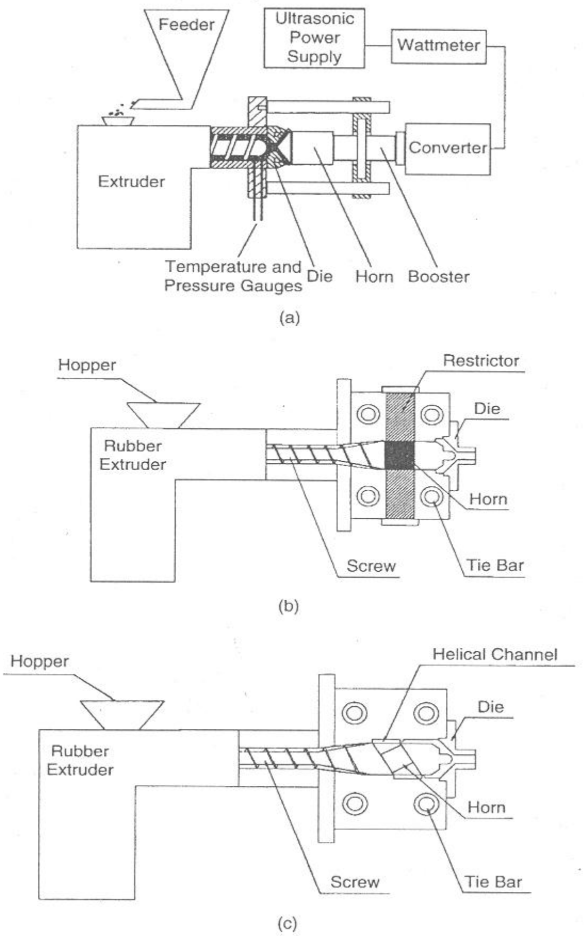


Figure 2.23: Schematic representation of coaxial (a), barrel (b), and grooved barrel (c) reactors [8].

In 1973, Pelofsky patented the first ultrasonic rubber devulcanization process. The process consisted of immersing rubber particles into a liquid and uses an ultrasonic energy source to cleave the rubber bulk and dissolve it into the liquid [1].

Okuda and Hatano patented another ultrasonic devulcanization process for NR in 1987. They achieved a reclaim rubber with properties close to the original rubber by subjecting the vulcanized rubber to 50 Hz ultrasonic energy for 20 min [1].

Many efforts have been done by Isayev and coworkers in this area. They have published a number of papers regarding the continuous ultrasonic devulcanization processes. Levin et al.

[29], studied the effect of crosslink type on the ultrasound devulcanization of SBR vulcanizates. They devulcanized SBR vulcanizates in a continuous ultrasonic process under various processing conditions. Then they evaluated the total crosslink density, proportion of polysulfidic crosslinks, gel fraction and glass transition temperature. They showed that increasing amplitude and decreasing the gap clearance will increase the degree of devulcanization.

It was reported that the ultrasonic devulcanization of SBR will increase the glass transition temperature. They found that ultrasonic waves break up different kinds of chemical bonds (polysulfide, di/mono sulfide) selectively and cleavage of polysulfide crosslink bonds is predominant in this process.

Ultrasonic devulcanization of EPDM was studied by Yun et al. [30]. They utilized the ultrasonic grooved barrel reactor to devulcanized the carbon black-filled EPDM. They measured the dynamic viscoelastic properties and cure behavior of revulcanized EPDM. The gel fraction, crosslink density, and mechanical properties were determined in this work. It was reported that the grooved barrel reactor has two times more output compared to coaxial ultrasonic reactor. Comparing the degree of devulcanization of carbon black-filled and non-filled EPDM shows that the physical and chemical bonds beteen EPDM rubber and carbon black, consume certain portion of ultrasonic energy which results to less degree of devulcanization for carbon-filled EPDM rubber in the same condition. A study of the dynamic viscoelastic behavior shows that the uncured virgin EPDM is less elastic than devulcanized EPDM and virgin vulcanized EPDM is more elastic than revulcanized EPDM rubber.

2.3.4 Other devulcanization processes

There are many other different devulcanization techniques for rubber. Some of them are discussed here:

Thermo-chemical Process

In this process crosslink breakage is carried out by a combination of heat and chemical reagents. The most famous and oldest process of this kind is the “Pan Process” [9].

First the Pan Process consisted of heating the rubber with steam for 48 hours. Later adding the chemical reagents reduced the processing time to 5-10 hours. Another process is the digester process in which the ground rubber is mixed with alkali, water, plasticizing oil and chemical peptizers. The devulcanization process takes place by heating the mixture in an autoclave for 5-24 hours. [9]

Microwave Process

In the microwave devulcanization method a certain amount of microwave energy with specified frequency is needed to cleave the crosslink bonds of vulcanized rubber. The presence of polar groups in the waste rubber is essential to absorb the microwave energy and generate the sufficient heat required for the devulcanization process. Most of the time, this process involves extrusion and mixing [1].

Biological Process

In this technique, biological attack cleaves the sulfur bonds in the vulcanized rubber. Recently a new method has been patented [9] using a chemolithiotrop micro-organism in order to devulcanize the rubber powder surface. Another attempt has been done [9] by using the bacteria from genus Nacardia and Thiobacillios for devulcanization of NR and SBR.

In the biotechnological devulcanization processes, the vulcanization takes place on the surface of the rubber only and the percent of devulcanization is very low. The modified surface of the rubber powder facilitates the compounding of the devulcanized rubber powder with virgin rubber due to better bonding between the surface of the powder and the virgin rubber chains.

Because of the mentioned limitations and long processing time (~40 days), biotechnological devulcanizaton processes are still far beyond industrial applications.

2.4 Supercritical Fluids (SCFs)

None of the gaseous and liquid solvents show the unique properties of supercritical fluids. They are the best substitutes for harmful solvents which are commonly used in different industries. For example, organic solvents can be replaced by supercritical fluids in different polymer processing systems. When the pressure and temperature of a substance increase over the critical value, a one-phase homogeneous fluid forms [31].

It seems that a supercritical fluid is a high pressure gas but there is a big difference here: a supercritical fluid never liquefies under any pressure as long as its temperature remains above its critical value. So there is no phase separation for a substance whose temperature and pressure are above the critical value [31]. Figure 2.24 shows the phase diagram of a fluid. In the supercritical region of the phase diagram there is one-phase, homogeneous fluid [32]. The properties of a supercritical fluid can be tuned easily by adjusting the pressure of the fluid. The density can be adjusted by manipulation of pressure between a wide range from gas to liquid values. Other properties like viscosity and diffusivity can be adjusted as well. This makes supercritical fluids to be very useful in polymer processing.

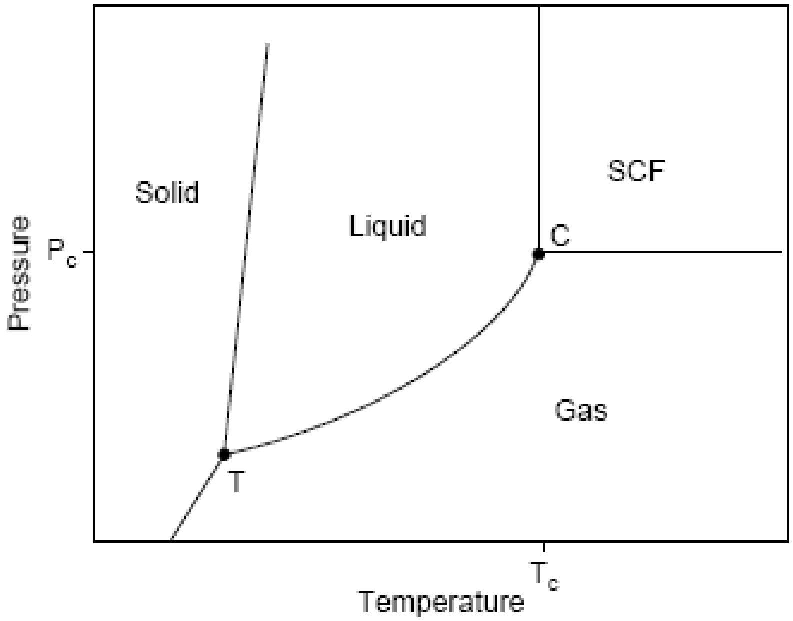


Figure 2.24: P–T phase diagram of fluid: (1) T, triple point (2) C, critical point [32]

Table 2.8 shows a comparison between supercritical fluid, liquid and gas physical properties [4, 31].

Table 2.8: General ranges of selected physical properties of Gases, Supercritical Fluids and Liquids [4]

	Density (g/ml)	***Diffusivity (cm2/s)***	***Viscosity (g/cm.s)***	***Surface Tension (dynes/cm)***
Gas	$(0.6\text{-}2)\times10^{-3}$	0.1-0.4	$(1\text{-}3)\times10^{-4}$	0
Supercritical Fluid	0.2-1.0	$(2\text{-}7)\times10^{-4}$	$(1\text{-}9)\times10^{-4}$	0
Liquid	0.6-1.6	$(0.2\text{-}2)\times10^{-5}$	$(0.2\text{-}3)\times10^{-2}$	30-60

It can be seen that the density of supercritical fluids is in the order of liquid densities but SCFs have a higher diffusivity value (one order of magnitude higher).The viscosity of supercritical fluids is similar to that of gas viscosity and the surface tension value for both of them is zero [4].

Applications of SCCO$_2$ in polymer processing

Supercritical CO$_2$ (critical temperature = 31.06°C and critical pressure = 73.8 bar) is a cheap, non-flammable and non-toxic material and it can be removed from the polymer very easily, at the end of the process. No further expensive and time consuming solvent extraction process is required for SCCO$_2$ removal [32].Besides being environment friendly, scCO$_2$ exhibits numerous unique properties. When scCO$_2$ diffuses in to the polymer matrix, it swells and softens the polymer and changes the physical properties. The plasticization of polymers by scCO$_2$ plays a major role in polymer processing operations. “These include viscosity reduction for polymer extrusion and blending, enhancement of the diffusion of additives through polymer matrices for impregnation and extraction, enhancement of monomer diffusion for polymer synthesis, foaming of polymers, and changes in polymer morphology due to induced crystallization”[31]. Figure 2.25 shows the effect of scCO$_2$ on glassy polymers.

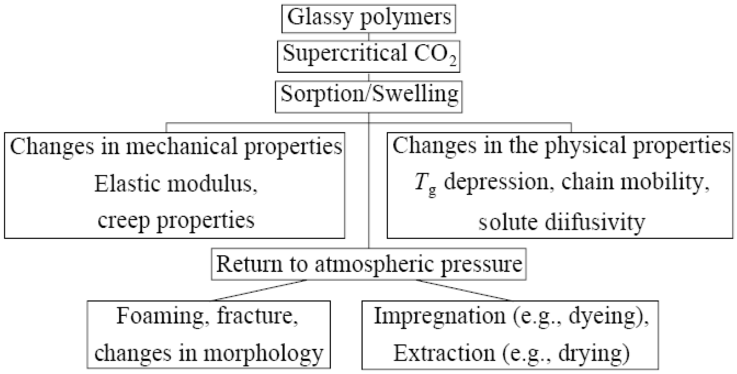


Figure 2.25: Effect of SCCO$_2$ on glassy polymers [31].

Chen et al. (1995) used supercritical H_2O and CO_2 for depolymerization of tire and natural rubber [33]. They put the 30 mesh crumb tire rubber and natural rubber in an autoclave using a supercritical atmosphere of CO_2 and water. The temperature was 380°C and the pressure was 276 bar. Figure 2.26 shows the schematic of the process.

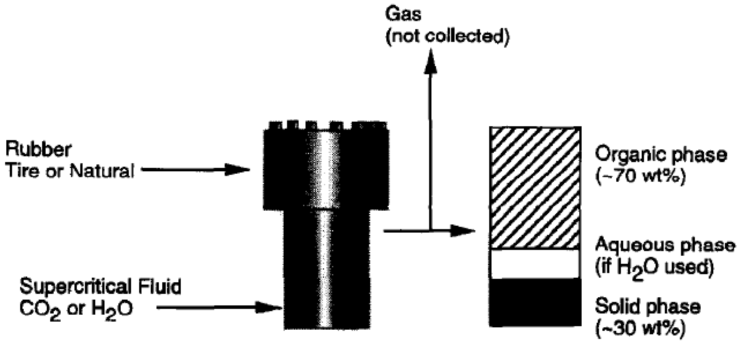


Figure 2.26: Schematic of materials generated from supercritical water depolymerization of tire rubber [33].

They reported that the reaction time and supercritical fluid type can affect the degree of depolymerization. The behavior of natural rubber and tire crumb were different in this process and the product resulted from tire crumb had higher molecular weight [33].

Kojima et al. [34] developed a chemical devulcanization process by using supercritical CO_2. They used diphenyl disulphide as a devulcanizing agent in order to devulcanize unfilled polyisoprene rubber vulcanized samples. It has been reported that in the presence of $scCO_2$, the devulcanizing agents can penetrate and diffuse into the vulcanized samples easier and the devulcanization process takes place more efficiently [34].

Tzoganakis and Zhang [4, 21, and 22] developed and patented a continuous devulcanization process by using scCO2 in a twin screw extruder. The process was described in more detail in the section 2.3.1 (thermo-mechanical devulcanization). This is a very simple process that requires small amount of $scCO_2$ and relatively small residence time in an extruder.

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CHAPTER 3 EXPERIMENTAL METHODS

3.1 Procedures

3.1.1 Devulcanization of crumb rubber

Crumb rubber is fed into the twin screw extruder in order to perform the devulcanization process. Supercritical CO_2 is injected in the extruder to swell the rubber crumb particles and facilitate the devulcanization process. As a consequence, waste rubber can be processed under mechanical deformation at various operating conditions that may lead to different degrees of devulcanization. The extruder machine that is used in this research is a 50 mm (L/D = 40/1) twin screw extruder from Leistritz. Using a computer system, all process variables such as barrel temperature and screw speed can be adjusted by the extruder operator. A loss-in-weight feeder is used to automatically feed the rubber crumb into the extruder hopper. The feed rate can be adjusted by the operator.

3.1.2 Experimental variables

Screw configuration

The screw configuration plays a major role in the devulcanization process. Selecting an appropriate screw element configuration enables us to control the pressure acting on the material inside the extruder and the level of shear and extensional forces working on the crumb rubber.

Rubber crumb mesh size

Different mesh size of rubber crumbs is tried, in order to investigate the effect of feeding particle size on the properties of devulcanized material.

Feeding rate

During the devulcanization process volatiles are generated due to breakdown of the chemical structure of crumb rubber and due to evaporation of oils. These volatiles can blast out of the exit of the extruder periodically and make the process unstable. Control of the feeding rate is one of the options that can help us to control the process stability. Feeding rate has an effect on the material pressure inside the extruder which is an important factor to control the devulcanization performance. Achieving a higher throughput is one of our goals to maintain a higher production rate of devulcanized material to make the process economically reasonable.

Screw speed

The screw speed controls the shear rate in the process and consequently affects the devulcanization performance and process stability.

Temperature

Selecting appropriate temperature for the devulcanization process can help for the cleavage of sulfur bonds in the vulcanized rubber. Excess heating may result in degradation of rubber and low physical properties of the product. In order to achieve the best devulcanization performance, the temperature must be adjusted in the extruder.

3.2 Characterization methods for molecular properties

3.2.1 Crosslink density and degree of devulcanization measurements

In order to characterize the performance of the devulcanization process we calculate the network crosslink density of several samples. The procedures for crosslink density and degree of devulcanization measurements are described in ASTM D6814-02 standard [1].

For the first step, the low molecular weight components must be removed by acetone extraction using a Soxhlet apparatus for 16 hours. Then the samples are dried at 70±2 °C in an air oven, for 16±1 hours. After drying we need to cool down the samples down to room temperature while they are kept in a dessicator.

Subsequently, swelling of the rubber samples is conducted by immersing the dried samples in toluene for 72 h. The toluene must be refreshed every 24 hours. After 72 hours the solvent is removed and samples are "pat dried" immediately, using a soft paper towel. Then samples are weighed in a closed, tarred, weighing bottle. Later the cap of the bottle is removed and the sample is placed in a ventilated air oven at 70±2 ^{0}C overnight until it dries to constant weight. After drying the sample must be removed and cooled down to room temperature in a dessicator. Later, the weight of the dried sample is measured and recorded [1].

The Flory-Rehner equation [2] is used for the calculation of crosslink density as follows:

$$\vartheta_e = \frac{-[\ln(1-V_r)+V_r+\chi_1 V_r^2]}{[V_1(V_r^{\frac{1}{3}}-V_r)/2]} \qquad (3.1)$$

where V_r, χ_1 , V_1, and ϑ_e are the rubber volume fraction in the swollen sample, rubber-solvent interaction parameter, molar volume of solvent and the crosslink density (effective number of chains in a real network per unit volume) of the rubber sample [2].

The rubber volume fraction V_r is calculated using the following relation:

$$V_r=\frac{(\text{weight of the dry rubber})/(\text{density of dry rubber})}{\frac{\text{weight of the dry rubber}}{\text{density of dry rubber}}+\frac{\text{weight of the solvent absorbed by sample}}{\text{density of solvent}}} \qquad (3.2)$$

Density of the rubber sample was measured using an electronic densitometer , model EW-3000 SG from Advanced Rubber Testing Technologies. It basically measures the weight of the rubber in the atmosphere and while it is immersed in water. Using the buoyancy role the density of the rubber can be calculated. Following the crosslink density determination, the percent devulcanization can be determined by using the following equation:

$$\%\,Devulcanization = [1 - \left(\frac{Crosslink\ density\ of\ devulcanized\ rubber)}{Crosslink\ density\ of\ control\ crumb\ rubber)}\right)] \times 100)] \quad (3.3)$$

3.2.2 Acetone extraction [3]

Acetone extraction was conducted using a Soxhlet apparatus in order to separate the low molecular weight content such as free sulfur, acetone soluble plasticizers, processing oils or waxes, organic accelerators, and fatty acids. Also bituminous substances, vulcanized oils, high molecular mass hydrocarbons, and soaps can be removed by acetone extraction. Figure 3.1 shows the Soxhlet extraction apparatus, which consists of an electric heater, 500ml round boiling flasks, extraction tubes, and a condenser. The electric heater has three positions for three 500 ml round flasks. The heating rate can be adjusted using an electrical controller located on the right side of the heater. The acetone boils and evaporates and when it gets to the condenser it cools down, condensed by the cool water which is circulating in the condenser. Condensed acetone drips on the samples, placed in a white cellulose extraction “thimble”, and washes the sample. Acetone extracts the acetone soluble contents and siphones back into the boiling flask again. This procedure must be continued for 16 ± 1 hr according to ASTM D 297 to completely remove all acetone extractable contents from the rubber sample. After extraction, the sample is removed from the extractor and dried overnight in a ventilated oven at 72°C. The difference between the weight of the sample before extraction and after drying gives us the weight value of acetone soluble contents which was present in the sample. By dividing this value over the total weight of the rubber before extraction and multiplying by 100 we can find out the percentage of acetone soluble part of the rubber sample.

Figure 3.1: Soxhlet extraction apparatus

3.2.3 Sol and gel contents measurements

After acetone extraction, the sol and gel part of the rubber is separated by swelling the rubber sample in toluene. The gel part is the fully crosslinked part or some of the polymer chains which are still attached to the network from one side (in case of devulcanized rubber) and cannot be dissolved by toluene. The fraction of rubber sample which consists of free polymer chains that can be dissolved in toluene is called the sol fraction. By immersing the rubber samples in toluene for 72 hours we can separate the sol and gel fraction of rubber. We can also use the Soxhlet extraction with toluene to separate the sol and gel fraction but there is a very small difference (2-3%) between Soxhlet extraction and immersing in solvent as previously reported [4,5].

After 72 hours we remove the sample from toluene and put it in an air ventilated oven at 72°C over night to dry it to constant weight. The sol and gel fractions can be calculated using this equation:

$$Sol\ fraction(\%) = \frac{weight\ before\ swelling - weight\ of\ dried\ sample}{weight\ before\ swelling} \times 100 \qquad (3.4)$$

$$Gel\ fraction\ (\%) = 100 - Sol\ fraction\ (\%) \qquad (3.5)$$

3.2.4 Crosslink structure analysis

Determination of the types and percentages of the sulfur crosslinks in a sulfur-vulcanized rubber network is an essential step for the analysis and characterization of the rubber crosslinked network [6].

Using special chemical probes, we can specifically cleave particular types of crosslinks in the rubber network. By measuring the crosslink density of the rubber network before and after treatment, we are able to find out the percentage of each type of sulfur crosslink which is present in the rubber network [6].

Saville and Watson have described the procedure for chemical reagent preparation for selective crosslink cleavage of poly-sulfide bonds at room temperature. They used a solution of propane-2-thiol (0.4M) and piperidine (0.4M) in n-heptane. This solution reacts with polysulfide bonds which results in the complete cleavage of polysulfide bonds while di-sulfide bonds remain unaffected [6], [7].

In another publication by Campbell [8] the use of more reactive thiol reagent system is described. This thiol probe solution (hexanthiol (1.0M) in piperidine) is able to cleave both polysulfide and di-sulfide bonds in the rubber network according to reaction schemes 3.6 and

3.7. Hexanthiol ($C_6H_{13}SH$) reacts with the di-sulfide bond in the rubber network (R'SSR') and cleaves the di-sulfide crosslink. Finally another hexanthiol molecule reacts with $C_6H_{13}S_2R'$ (second reaction in reaction scheme 3.6) and forms another R'SH. The thiol probe solution cleaves the S-S bond and leaves a SH group on each rubber molecule [8].

$$\begin{aligned}&RSH\ (\text{Hexanthiol}) + R'SSR'(\text{di sulfide rubber crosslink}) \leftrightarrow RSSR' + R'SH\\ &RSH + RSSR' \leftrightarrow RSSR + R'SH\end{aligned} \qquad (3.6)$$

For polysulfide bonds we can see the exactly same reaction (similar to di-sulfide cleavage) in which hexanthiol ($C_6H_{13}SH$) reacts with the SS_x bond and cleaves the polysulfide crosslinks. Depending on the number of sulfur molecules present in the poly sulfide bond, this reaction continues until all sulfur molecules react with hexanthiol and leave a SH group on every rubber chain molecule (reaction scheme 3.7) [8].

$$\begin{aligned}&RSH + R'SS_xSR' \leftrightarrow RSSR' + HS_xSR'\\ &(2X\text{-}1)\ RSH + HS_xSR' \leftrightarrow RSSR' + XH_2S + (X\text{-}1)\ RSSR\\ &RSH + RSSR' \leftrightarrow RSSR + R'SH\end{aligned} \qquad (3.7)$$

In order to evaluate the content of each crosslink type in our crosslinked network we need to prepare three thin (1mm thickness) specimens for each sample.

All samples must be continuously extracted in acetone for 16 hours using Soxhlet apparatus (ASTM D296-90) and then immersed in pyridine for 24 hours. All samples must be dried to constant weight after extraction. The extracted specimens are divided into 3 groups: first group (G1) for determination of total crosslink density, second group (G2) for di+mono sulfide crosslink density and finally the last one (G3) for mono-sulfide crosslink density [7-9].

For estimation of di+mono sulfide crosslink density, samples from group 2 (G2) are pre-swollen in n-hexane at room temperature. After 16 hours swelling, n-hexane is removed and a reagent solution of propane-2-thiol (0.4M) and piperidine (0.4M) in n-hexane is poured on the rubber sample. In the beginning the solution is clear but after 2 hours of immersion it becomes a dark brown solution (probably due to presence of carbon black in the rubber sample). After treatment completion (2 hours), the sample is removed and dried to constant weight. This procedure cleaves all polysulfide crosslinks while mono and di sulfide bonds remain intact [7-9]. In order to determine the mono sulfide crosslink density, another chemical probe is used to treat the samples from group 3 (G3). This chemical reagent is a solution of hexanthiol (1.0M) in piperidine. Usually for 1 gram rubber sample, 50 ml of solution is required. Since our rubber samples were 2 grams in weight, we poured 100 ml of the reagent solution on each sample. The chemical reagent is able to cleave both poly and di sulfide bonds in 48 hours at room temperature. After 48 hours when the treatment is completed, samples are removed and dried to constant weight [8-9].

Finally, by swelling all three group samples in toluene, crosslink density values, ϑ_e for each sample can be obtained. Poly sulfide crosslink density value can be calculated by the subtraction of the (di + mono sulfide) crosslink density of G2 samples from the total crosslink density obtained from G1 samples. The difference between the crosslink density of G2 samples (di + mono sulfide) and G3 (mono-sulfide) can give us the crosslink density of the di-sulfide bonds. Having all crosslink density values for all three different sulfur bonds, one can calculate the percentage of each crosslink type in the rubber network [9].

3.3. Rheological characterization methods

3.3.1. Mooney viscosity [10-11]

In the rubber industry, the unvulcanized compound must be mixed and processed using different mixing and processing equipment, such as Banbury mixers, mills, and extruders. Measuring rheological properties can help us to assess the processability of the unvulcanized rubber compound. They basically show how the rubber compound responds to the force and temperature that is experienced in the mixing and processing step.

One of the most popular instruments for evaluation of rheological properties of the unvulcanized compound is the shearing disk viscometer or Mooney viscometer. Mooney viscometer is able to measure the relative viscosity of uncured rubber compounds. For Mooney viscosity measurement, the specimen is placed in a shallow cylindrical cavity in which a rotor (a metal disk) rotates. By measuring the required force to rotate the rotor at the test temperature, Mooney viscometer reports the viscosity of the compound in Mooney units. This value is a relative viscosity which is an indication of the resistance to flow of the rubber compound at the test temperature [10].

ASTM D-1646 describes the standard test procedure for Mooney viscosity measurement. The viscosity value is reported for a specific test temperature and the most common test temperature is 100°C (212°F). To start the test, the sample must be placed below and above the rotor. The rotor is then placed back to the cavity and by pushing the start button, measurement starts [11]. Figure 3.2 shows an example for a typical Mooney viscosity curve and the outcome results.

Results are usually reported as a number which is followed by ML 1+4 (100°C). Letter M indicates Mooney, L indicates the use of large rotor, 1 shows that the preheat period is 1 min, 4 stands for four minutes test duration, and 100°C is the test temperature. The minimum measured value is reported as the Mooney viscosity of the sample. For example the Mooney viscosity value in figure 3.2 is reported as 32 M.U.

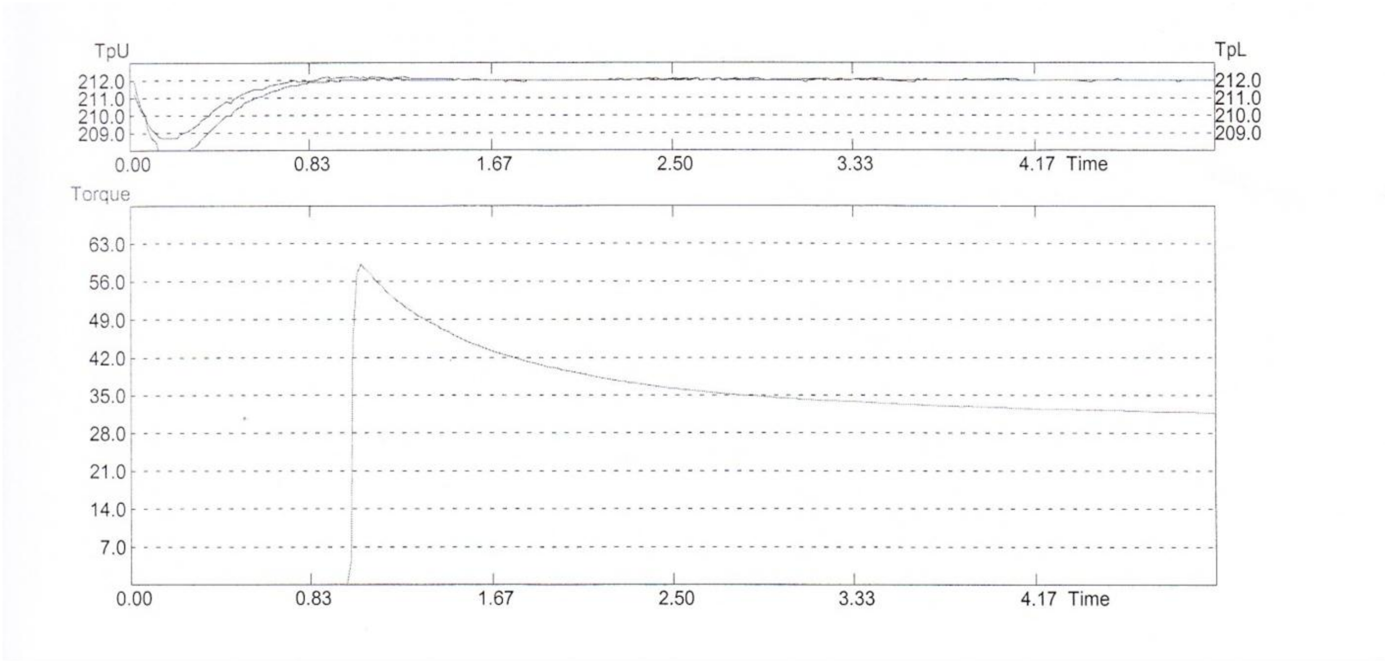


Figure 3.2: A typical Mooney viscosity graph

3-3-2 Oscillatory disk rheometer (ODR) and Moving die rheometer (MDR) [10, 12]

ODR test

Curing characterization of a rubber compound is measured by using an oscillatory disk rheometer (ODR). ASTM D-2084 describes how this machine evaluates the curing behavior of an uncured rubber compound until it cures completely. The main difference between an ODR machine and a Mooney viscometer is that the Mooney viscometer measures the rheological properties of the compound at the processing temperature while ODR measurements take place in the curing temperature of the rubber compound [12].

The ODR test starts by setting the desired curing temperature and follows by inserting the test specimen in the shallow cavity of the machine. After closing the die and sealing the cavity under pressure, the rubber flows and surrounds the bi-conical disk which is present in the cavity (figure 3.3). The disk starts to oscillate back and forth and imposes shear strain to the test specimen. The rubber specimen starts to cure and as a consequence the shear modulus and stiffness of the sample increases. The required force/torque to keep the disk to oscillate is measured as a function of time. The test stops when the selected time by the operator is reached. A typical ODR curve is shown in figure 3.4. This test evaluates the bulk viscosity, scorch time, cure rate, and the state of the cure of the rubber compound.

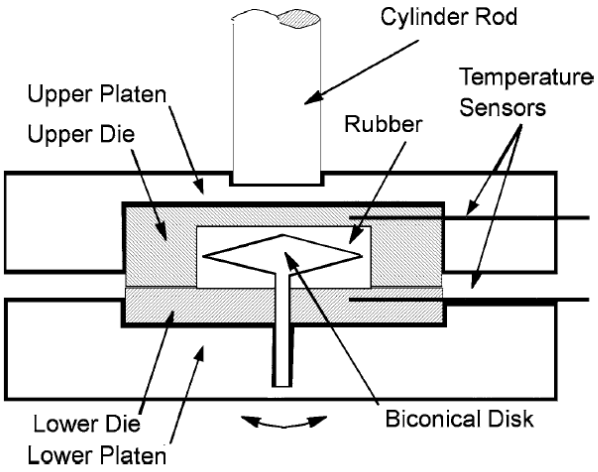


Figure 3.3: ODR cavity and rotor [12].

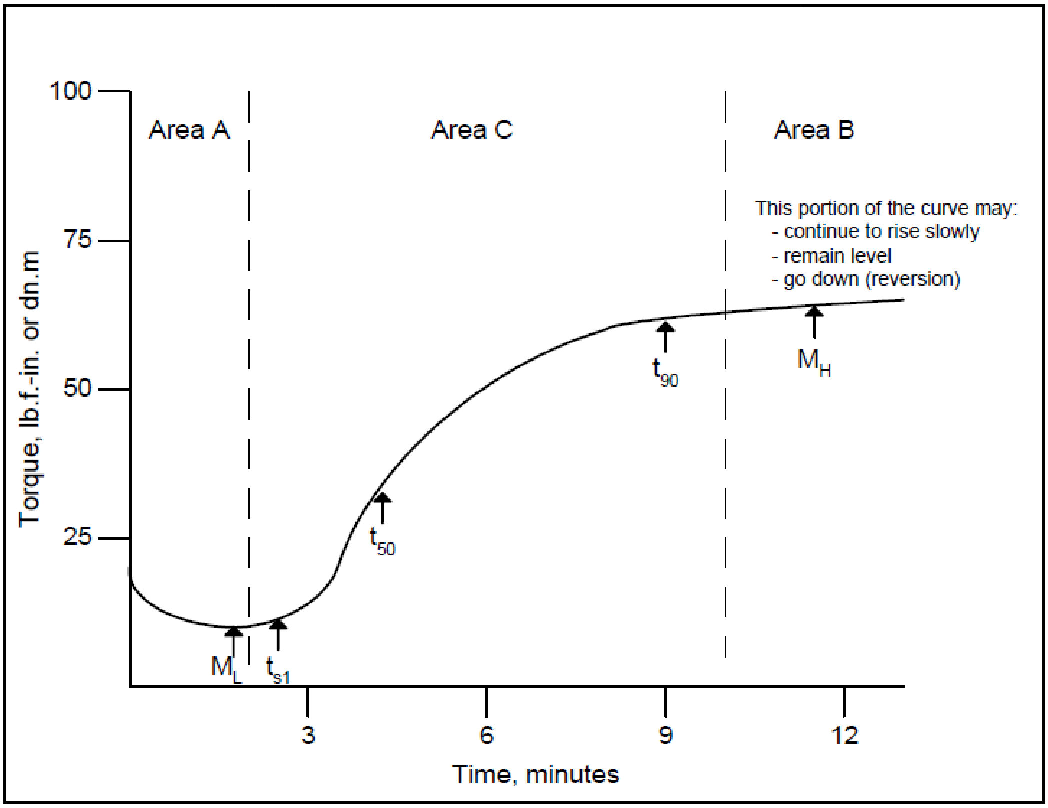


Figure 3.4: A typical ODR curve [10].

Typical output values from the ODR machine are listed below [10]:

1- ML: minimum torque or a measurement of the bulk viscosity of the compound. This value is in a very good correlation with Mooney viscosity.

2- MH: maximum torque or the highest value for the torque during the rheometry test. This value is an indication of modulus and is related to the cure state of the cured rubber.

3- t_{s1}: scorch time or the required time that torque reaches about 0.1 Nm above the minimum torque. Any flowing or forming process for the rubber compound must be finished by this time at the cure temperature.

4- t_{50} and t_{90}: the required time to get to the 50% and 90% curing. t_{90} is also defined as the optimum cure time or the time in which vulcanization process for a rubber compound completes.

MDR test

The moving die rheometer (MDR) is a modern version of the ODR machine. Instead of the oscillatory disk which we had in the ODR machine, for MDR there are two dies and the rubber sample is inserted in the space between them. The upper die is connected to a torque meter which measures the torque that transfers from the rubber sample, while the lower die oscillates. MDR basically provides the same type of information that is described for ODR and there is a very strong correlation between the output results from two machines. MDR usually provides a higher repeatability and it has a very fast thermal recovery. Compared to ODR machines, MDR machines are more expensive [10].

3.4 Characterization methods for mechanical properties

3.4.1 Sample preparation

Using a batch mixer (Haake mixer), sulfur and curing chemicals are added to the devulcanized rubber. Devulcanized samples are milled later to achieve a more uniform sample using a lab scale two roll mill. Standard slabs are prepared later by pressing and curing the devulcanized rubber using a standard slab mold and hot press. According to ASTM D 3182, dimensions of a standard slab are 150 by 150 by 2-mm.

3.4.2 Tensile properties [10, 13, 14]

One of the most common tests in the rubber industry is the tensile test. In this test a tensile machine pulls a rubber specimen until it breaks and records the force and the extension value at the time of rupture. Since rubber samples usually show a very high extension value, Hooke's law is not applicable for this case. ASTM D-412 describes the procedure for specimen preparation and test conduction for tensile properties of rubber materials in detail [14].

Tensile strength is defined as the stress required breaking the test specimen. This stress can be calculated from the applied force value at the time of rupture, divided by the cross sectional area of the original sample. In the rubber industry it is expressed using different units such as pound force per square inch, kilogram per square centimeter, or mega Pascal (MPa).

The maximum strain value, at which the rubber specimen breaks, is defined as the ultimate elongation or elongation at break value. It is obtained by measuring the distance between the benchmarks at the time of the rupture and is expressed as the percent of extension from the benchmark distance on the sample before the extension [13].

The tensile strength that is required to pull the specimen to a certain elongation value such as 100%, 200%, or 600% is defined as the tensile modulus. Tensile modulus is reported as modulus at 100%, or modulus at 300% and, etc. [10]. Although many different shapes can be used as the tensile test specimen (such as o-rings, straight strips, rings, and etc.), the most common specimens for tensile tests are dumbbells. Dumbbell shape specimens can be cut in different standard sizes and ASTM D-412 has described all the specifications in detail. A dumbbell specimen is usually cut from a cured standard test slab using a dumbbell die. The thickness of a slab must be in the range of 2.0±0.2 mm (0.08±0.008in.). Figure 3.5 shows the dimensions of the tensile test dumbbell specimen.

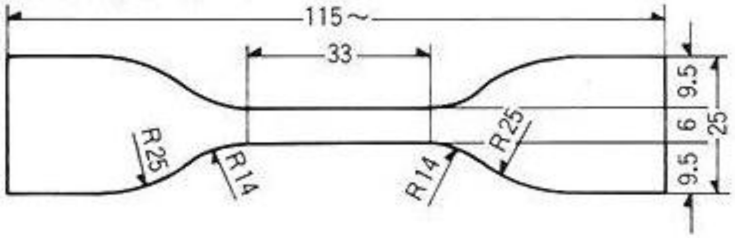


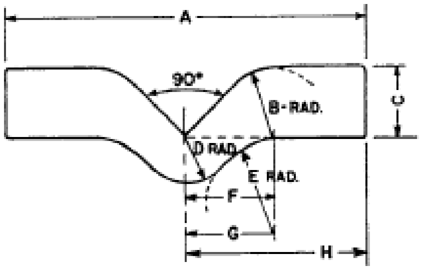
Figure 3.5: Die C (ASTM D412) tensile dumbbell specimen (dimensions are in mm)

The dumbbell specimen is gripped to the tensile machine's jaws in order to start the test. As the test starts, the tensile machine (tensiometer) applies 500±50 mm/min extension on the specimen until the rupture occurs. The machine stops and reports the tensile strength, ultimate elongation, and tensile modulus automatically. The average of three to five measurements is usually reported for tensile property values [14]. Picture of the tensile machine (Monsanto model 500) that we used for this research is shown in figure 3.6.

Fig 3.6: Tensile testing machine (Monsanto model 500 located in Airboss)

3.4.3 Tear strength

The resistance of the rubber sample to tear propagation is defined as tear strength and is expressed by the force required to tear a test specimen per unit of the specimen thickness. The common units which are used for tear strength are pounds per inch, kilograms per cm, and kilo Newton (KN) per meter [10]. ASTM D 624 describes the standard test method for sample preparation and test conduction for tear strength measurement of rubber materials. It is appropriate to mention that the tear strength can be influenced by many parameters, such as, sample anisotropy, strain size, and the specimen size. Therefore, the obtained results from each tear measurement are only useful to be compared with the same particular test in the same conditions. Tear strength specimens are cut from a standard slab, using a special tear die. ASTM D624 has described the dimensions of three different tear dies. Among those dies, die C (figure 3.7) is more common and we have used that die for our tear strength measurements. When the specimen is prepared it should be clamped to the tensiometer jaws. As we start the machine it pulls the specimen to a point that it tears completely. The required force to tear the sample per unit of the specimen thickness is reported as its tear strength value [15].



DIE C

Dimensions	A	B	C	D	E	F	G	H
Value (mm)	102±0.50	19±0.05	19±0.05	12.7±0.05	25±0.05	27±0.05	28±0.05	51±0.25

Figure 3.7: Tear strength Die C [15]

3.4.4 Hardness measurement [10, 13, 16]

Hardness measurement is a very quick and easy test which can be done by using inexpensive equipment. Hardness durometer shore A is usually used for hardness measurement of rubber products. It is scaled from 0 to 100; 0 is for extremely soft material and 100 is for a very hard rubber material. ASTM D 2240 describes the standard test method for hardness measurement for rubber materials [10, 13, and 16].

Figure 3.8 is an actual picture of a shore A durometer. A penetrator, which is attached to a spring, is pressed against the rubber surface. Depending on the hardness of the sample, the depth of the penetration and the exerted force to the spring varies. The hardness of the material can be calibrated against the penetration force and depth [10, 13].

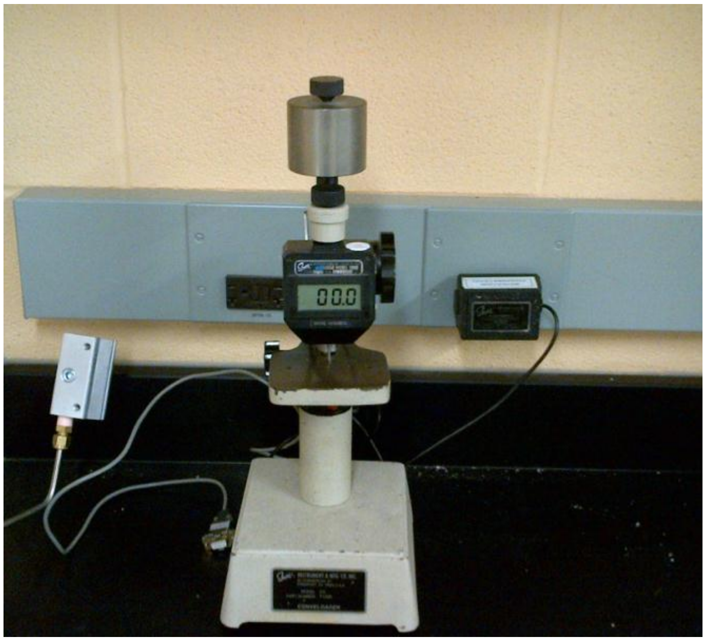


Figure 3.8: Hardness durometer (Shore A)

3.4.5 Permanent set [10, 13, and 17]

The permanent deformation of a rubber sample which has been under a compressive force is known as compression set or permanent set. A high set value shows that the rubber sample cannot recover to its original state after being subjected to compressive tension and this is usually not desirable. It becomes more critical in some situations that the rubber product is expected to maintain its sealing properties when it is under compression [10, 13]. ASTM D 395 describes the standard test method for compression set measurement. Button shape specimens are more common for the permanent set test. The original thickness of the specimen is measured carefully before it goes under compression. Using the compression set device (figure 3.9), a specimen is compressed to a certain thickness (50% for example). Usually this test is conducted at elevated temperatures (70°C is more common) for a test period between 22 hrs to 70 hrs. When the test is done, the specimen must be removed immediately and cool down in room temperature for half an hour. Final thickness must be measured carefully and percent of permanent set can be calculated by the following formula [17]:

$$Compression\ Set\ (\%) = \frac{[t_0 - t_2]}{[t_0 - t_1]} \times 100 \qquad (3.8)$$

$t_0 = Original\ thickness$, $t_1 = Thickness\ of\ the\ spacer$, $t_2 = Final\ thickness$

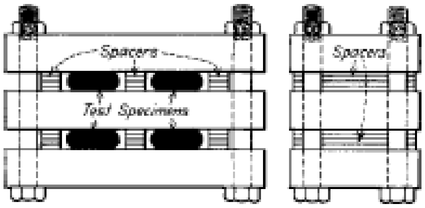


Figure 3.9: Compression set type B device [17]

3.4.6 Heat buildup [10, 18]

In this test the rubber specimen is subjected to an oscillating compressive stress and the heat generation (temperature rise) by the rubber sample is measured. Flexometers are used to generate the oscillating stress and measure the temperature rise (figure 3.10).

This test implies how effectively our sample performs, in terms of heat generation, during its service life when it is subjected to a dynamic force. Although there is no correlation between the real heat buildup behavior of the rubber material in its real service life and what we obtain from this accelerated test, it can still help us to have an estimation of relative heat generation quality of different compounds [10, 18].

Figure 3.10: BF Goodrich flexometer machine [18]

3.4.7 Cut and chip test

Cutting and chipping resistance of rubber compound can be evaluated by a cut and chip tester machine. A rubber specimen in the form of a disk is placed on a rotary shaft. At a specified frequency, a standard knife impacts the specimen for a specified period of time. The mass loss and diameter reduction of specimen is measured and reported in percent. Lower mass loss and diameter reduction shows that the rubber compound has a good resistance when it is subjected to sharp edges during its service life. This test is a common test for tire tread compounds including passenger tires but it is mostly used for off-road, truck, and mining tires in which the tire is subjected to harsh mechanical forces and sharp surfaces [19]. In figure 3.11, the left picture is a BF Goodrich cut and chip tester and the right picture shows a cut and chip specimen after testing from two different sides.

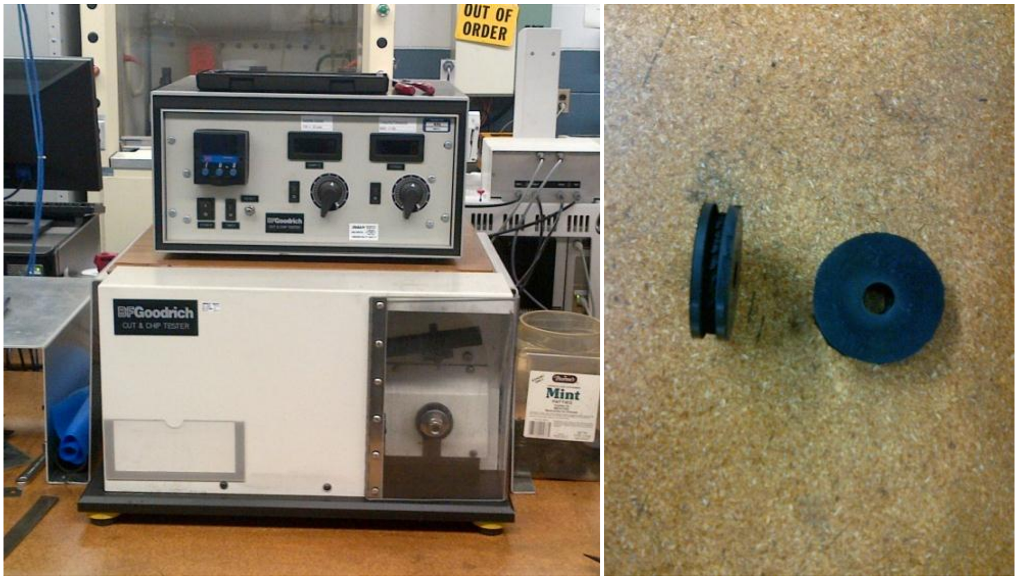


Figure 3.11: BF Goodrich cut and chip tester (left) and cut and chip specimen after test (right)

3.5 List of Equipment

Table 3.1 shows a summary of the equipment which have been used in this research work.

Table 3.1: Summary of equipment

Name of equipment	Model/Company	Specifications
Twin screw Extruder	HP 50 (Leistritz)	Co-rotating, fully intermeshing, L/D= 40/1 screw diameter = 50 mm, forward conveying elements (pitch= 20,30,45 mm) Bilobal kneading discs with possible stagger angles of -30˚,-60˚,30˚ ,60˚,and 90˚
Melt Batch Mixer	Rheomix 3000 attached to Rheocord 90 (Haake)	Batch mixer, torque rheometer, roller blades, process up to 200 g polymer per batch
CO$_2$ gas injection system	Isco Model 260D	Maximum pumping pressure = 7500 psi Constant pressure and constant flow rate modes
Hot Press	Pasadena Hydraulics	Temperatures up to 300 C, pressure up to 240 MPa
Soxhlet extraction apparatus	KNOTES /with Friedrich condenser	Capacity = 500 ml
Heater	Glas-col	Three position heater Flask size = 500 ml 120 V, 180 W,1.5 A
Rheometer (MDR)	Alpha technologies, KPA 2000	Oscillating Frequency = 1.67 Hz Temperature range: RT to 200^{o}C
Two roll mill	Farrel	Roller Bearing 12”× 12” Lab Mill
Tensiometer	Instron 3365	Load capacity = 5 KN Max speed = 1000 mm/min Min speed = 0.01 mm/min
flexometer	BF Goodrich	Temperature= 23 to 120 °C Frequency = 10 to 30 Hz
Mooney viscometer	Alpha technologies, MV 2000	Rotational speed = 2 rpm Max temperature = RT to 200 °C
Hardness durometer	Instrument & MFG Co / Durotronic 2000	Shore A Durometer

3.6 Materials

Two different types of scrap rubber were used in this research: scrap tire tread rubber, and scrap automotive weather strips. The source of scrap tire rubber is anonymous and depends on the type of tire. It usually is a mixture of different rubber materials, such as natural rubber, poly butadiene rubber, and styrene butadiene rubber. The source of our automotive weather strips was the rejected products from a weather strip manufacturing line, made from ethylene-propylene-diene monomer rubber or EPDM rubber. Both scrap tire rubber and scrap EPDM rubber were supplied in the form of rubber crumb. More information about the different types of crumb rubbers used up in this research is brought in table 3.2.

Table 3.2: Crumb rubber information

Type of crumb rubber	Source	Mesh size	Grinding method
Tire tread	Scrap tires	60 mesh	Wet processing
Tire tread	Buffing dust	20 mesh	Buffing byproduct
EPDM rubber	Scrap weather strips	8-10 mesh	Ambient grinding

In this research work, different chemicals also were used for rubber curing and characterization. A complete list of all the chemicals that were used in this research is presented in table 3.3.

Table 3.3: List of different chemicals used.

Name of the chemical	Purpose of application	Supplier
Zinc oxide	Rubber curing (activator)	Fisher scientific
Stearic acid	Rubber curing (activator)	Fisher scientific
TBBS	Rubber curing (accelerator)	Sunboss
OBTS	Rubber curing (accelerator)	Sunboss
PVI	Rubber curing (retarding agent)	Sunboss
MBT	Rubber curing (accelerator)	Cooper standard
MBTS	Rubber curing (accelerator)	Cooper standard
DPTT	Rubber curing (accelerator)	Cooper standard
TMTD	Rubber curing (accelerator)	Cooper standard
ZDBC	Rubber curing (accelerator)	Cooper standard
Sulfur	Rubber curing (cross link agent)	Sigma Aldrich
Toluene	Solvent (rubber swelling test)	Sigma Aldrich
Hexane	Solvent (network analysis)	Sigma Aldrich
Acetone	Solvent	Sigma Aldrich
Piperidine	Reagent (network analysis)	Sigma Aldrich
n-hexanthiol	Reagent (network analysis)	Sigma Aldrich
Propanethiol	Reagent (network analysis)	Sigma Aldrich

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CHAPTER 4 CONTINUOUS DEVULCANIZATION OF SCRAP RUBBER

4.1 Introduction

Recycling has been one of the major concerns for the last few decades and it has been addressed by many researchers around the world. Polymer recycling and rubber recycling in particular, have drawn even more attention for two main reasons: it takes a very long time for a polymeric material to be degraded in the environment, and the price of polymeric materials, especially raw rubber, has increased in the past few years. In order to protect the environment and also conserve resources, it is of high importance to find new solutions for rubber recycling that are more efficient and practical.

One of the main sources of scrap rubbers is the automotive industry. Different rubber components such as tires, weather strips, shock absorbers, etc. are made and scrapped each year. Among those components, tire scraps have the highest share since they are bigger in volume and they are also changed more frequently.

The biggest issue for rubber recycling is the crosslinked structure of the thermoset rubber which makes it much more difficult to be recycled. A thermoset material cannot be melted and processed again like thermoplastics, due to the presence of the three dimensional crosslink network. We need to break down the crosslink bonds first, to be able to re-process and re-use the vulcanized rubber again. The process in which we cleave the crosslink bonds of rubber network selectively is known as devulcanization process. Different devulcanization processes utilize heat, chemicals, ultrasound, and mechanical stresses in order to break down the crosslink structure of vulcanized rubber and convert the insoluble thermoset rubber into a soft and sticky material which can be processed and vulcanized again [1].

In the thermo-mechanical devulcanization process, shear and elongational stresses are used to break down the crosslink bonds. Extruders and open mills are common equipment which are suitable for this purpose. The process usually involves heating, used to increase the cleavage performance of crosslink chemical bonds. However, shear and elongational stresses, alongside high temperature, can easily break down the main chains of the polymer, thus resulting in a significant decrease in molecular mass and poorer physical properties. In order to cleave the crosslink bonds selectively, the characteristics of equipment and the processing parameters are very important [2].

Mouri et al. published a number of papers [3, 4, 5 and 6] regarding the thermo-mechanical devulcanization of EPDM (ethylene propylene diene M-class) rubber crumb. A continuous devulcanization technique, based on a shear flow reaction control technology, is utilized to break down the EPDM crosslink bonds selectively. The process is carried out in a twin screw extruder and effects of various parameters, like screw geometry, screw speed and processing temperature were investigated. Another study was done by Fukomori et al. [7]. They further developed the same technology which was presented by Mouri et al. previously. They utilized a 30 mm twin screw extruder and optimized the devulcanization process by adjusting different parameters like shear stress, temperature and internal pressure. Tzoganakis and Zhang developed and patented a new thermo-mechanical devulcanization process by using supercritical carbon dioxide in a twin screw extruder [8, 9, and 10].

In this research, a continuous thermo-mechanical devulcanization process with supercritical CO_2 is carried out on an industrial scale twin screw extruder. In order to facilitate the extrusion process, supercritical carbon dioxide is used. Supercritical carbon dioxide diffuses into the rubber particles during the devulcanization process and facilitates the process by expanding and softening the rubber particles.

The main objectives of this research work were: (i) establish a high throughput devulcanization process which is stable, and (ii) produce a devulcanized rubber that can be used in various rubber products. Different properties of the devulcanized rubber such as, crosslink density, curing behavior, and physical and mechanical properties of devulcanized rubber were measured and are reported here.

4.2 Experimental

4.2.1 Material

The rubber material used in these experiments was a 60 mesh scrap tire tread crumb supplied by Edge Rubber in Pennsylvania. Supercritical carbon dioxide from Praxair Co. was used as a process agent in order to facilitate the devulcanization process.

4.2.2 Devulcanization process

Process Set up

A co-rotating and fully intermeshing twin screw extruder from Leistritz, was used to perform the devulcanization process. The twin screw extruder had a 50 mm screw diameter and an L/D ratio of 44:1 with eleven heating zones along the extruder barrel. Crumb rubber was fed into the twin screw extruder in order to perform the devulcanization process. Supercritical CO_2 was injected in the extruder to swell the rubber crumb particles and facilitate the devulcanization. Figure 4.1 shows a schematic of the process. The pressure of devulcanized material was monitored using a pressure transducer mounted on the extruder die. Supercritical carbon dioxide was supplied by a gas injection system. The pump was able to control either the pressure or the flow rate of the supercritical carbon dioxide, injected into the extruder barrel.

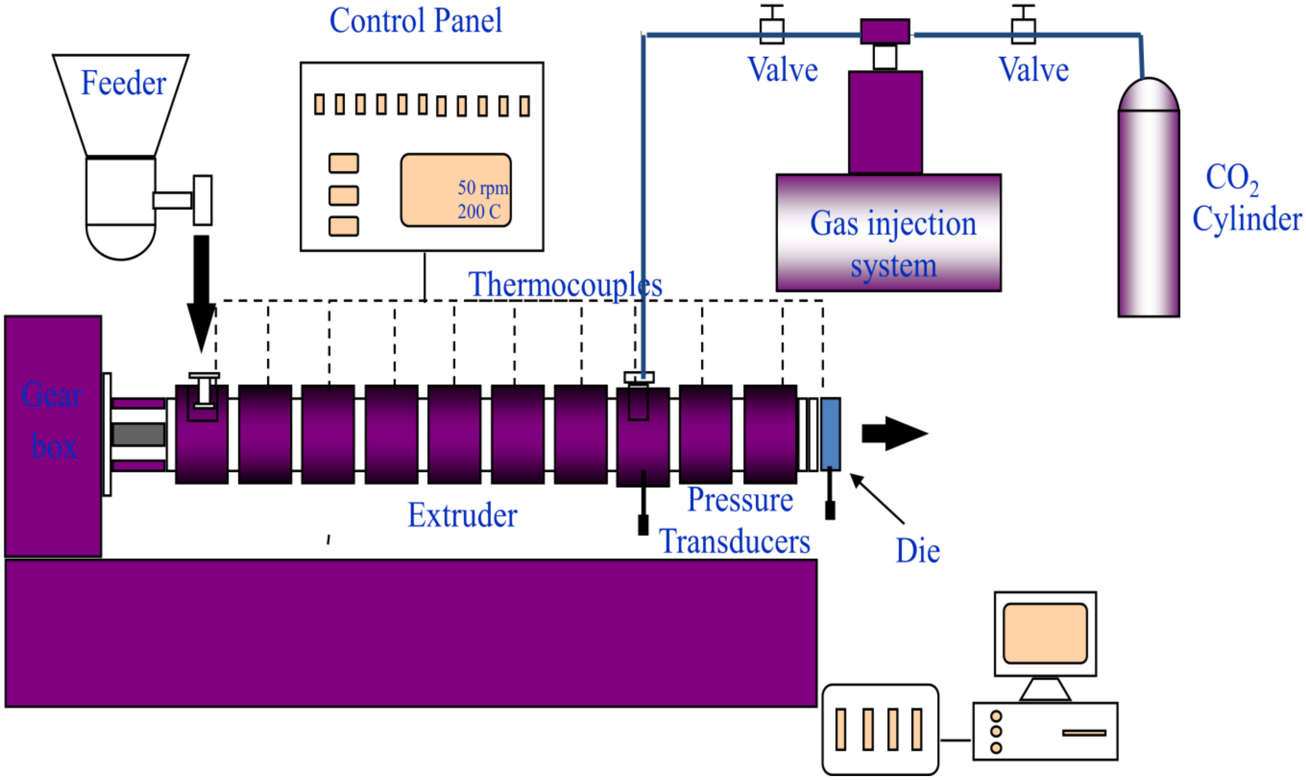

Figure 4.1: Schematic of the devulcanization process

Different screw configurations were tried by changing and replacing different screw elements such as kneading elements and conveying elements with different pitch size. In some cases we increased the numbers of kneading elements to increase the shear forces on the material.

Different conveying elements were used to convey the rubber along the extruder and in order to compress and decompress the rubber in the extruder barrel we used different pitch sizes for our conveying elements. To accomplish the objective of increasing the throughput, we tried different screw speeds and feed rates to maintain a continuous output and overcome the torque limitation.

4.2.3 Characterization techniques

Curing behavior

MDR rheometer was utilized to evaluate the curing behavior of the devulcanized rubber compounds. M_L (minimum torque*),* M_H (maximum torque*)* and t_{90} (optimum cure time) were measured according to ASTM D2084 [11].

Mooney viscosity

A Mooney viscometer was used in order to measure the Mooney viscosity of devulcanized samples. Using a large rotor, Mooney viscosity measurement is conducted at 100°C and MU (ML 1+4 @100°C) is reported for each sample in compliance with ASTM D 1646 [12].

Crosslink density measurements

In order to characterize the performance of the devulcanization process we calculate the network crosslink density of the devulcanized samples and of the starting crumb rubber, according to ASTM D6814-02 [13]. The Flory-Rehner equation is used for calculation of the crosslink density [14]:

$$\vartheta_e = \frac{-[\ln(1-V_r)+V_r+\chi_1 V_r^2]}{[V_1(V_r^{\frac{1}{3}}-V_r)/2]} \quad (4.1)$$

where V_r, χ_1 , V_1, and ϑ_e are the rubber volume fraction in the swollen sample, rubber-solvent interaction parameter, molar volume of solvent and the crosslink density of devulcanized sample and crumb rubber respectively.

The percent devulcanization can be determined by using the equation below:

$$\%\, Devulcanization = \left[1 - \left(\frac{Crosslink\ density\ of\ devulcanized\ rubber)}{Crosslink\ density\ of\ control\ crumb\ rubber)}\right)\right] \times 100 \quad (4.2)$$

Physical and mechanical property measurements

Using a Haake mixer, sulfur and curing chemicals were added to the devulcanized rubber according to Table 4.1. The devulcanized samples were milled later to achieve a more uniform sample using a lab scale two roll mill. Subsequently, standard slabs were prepared by pressing and curing the devulcanized rubber using a hot press at 160 °C for 10 minutes. Dumbbell shape specimens were cut from the cured standard slabs and the tensile strength and elongation at break were measured using an Instron tensiometer according to ASTM D 412-98a [15]. For each sample the average of three replicates was reported.

Table 4.1: Ingredients for re-vulcanization of devulcanized sample

Ingredients	***phr***
Devulcanized Rubber	100
Zinc oxide	3
Stearic Acid	1
OBTS	1.5
Sulfur	1.5

4.3 Results and discussions

4.3.1 Process set up

Set up a stable high throughput devulcanization process

In the beginning of the trials, screw #1 was set and the CO2 injection port was placed at the 7th zone of the extruder. For screw #1, it was not possible to achieve a stable process due to gas blow off from the die.

For the next trial we shifted the CO2 injection port to the 8th zone. We also changed the screw configuration to screw design #2, and added more kneading elements. This was done to increase the mixing capacity of the process to mix more CO2 gas with the rubber material and prevent gas blow offs. The process testing started with 10 lb/hr and 50 rpm and the throughput was increased to 50 lb/hr. Again we were not able to control the process and it was totally unstable. Screw was changed to screw design # 3 and it was tried to increase the mixing performance of the process and minimize the heat buildup which would result in the degradation of the rubber. At a low feed rate (20 lb/hr) we experienced a stable process but when we increased the throughput to 100 lb/hr it became unstable again. The screw design was changed again to #4, and the injection port was re-located to the 6th zone. We managed to increase the throughput to 100 lb/hr with a continuous devulcanized rubber extrudate coming out from the die in stable manner. More kneading elements were tried for screw design # 5 to increase the mechanical shear but stable process was not achieved. The die pressure was monitored to investigate the process stability. Figure 4.2 shows the die pressure variation as an example for an unstable process. Screw “#3” was utilized in this experiment and the barrel temperature was set at 200°C while the feeding rate and screw speed was 100 lb/hr and 100 rpm respectively. The process was totally unstable and material and gases were blasting out from the die exit periodically.

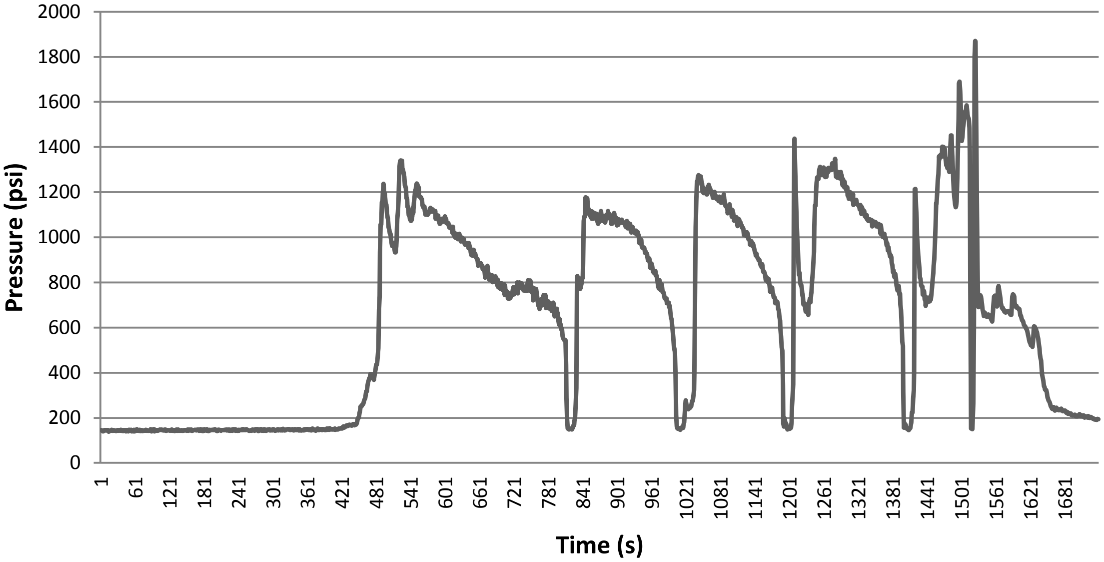

Figure 4.2: Pressure vs. time for an unstable devulcanization process. Screw configuration: #3, barrel temperature is 200 C, screw speed is 100 rpm, and feeding rate is 100 lb/hr.

Figure 4.3 shows the pressure variations in a stable process. In this process, material was coming out from the die exit in a continuous manner, and a relatively high production rate, i.e., 100 lb/hr, was achieved by selecting a proper screw configuration and process parameters. Samples were collected from different stable devulcanization processes in order to evaluate the properties of devulcanized material.

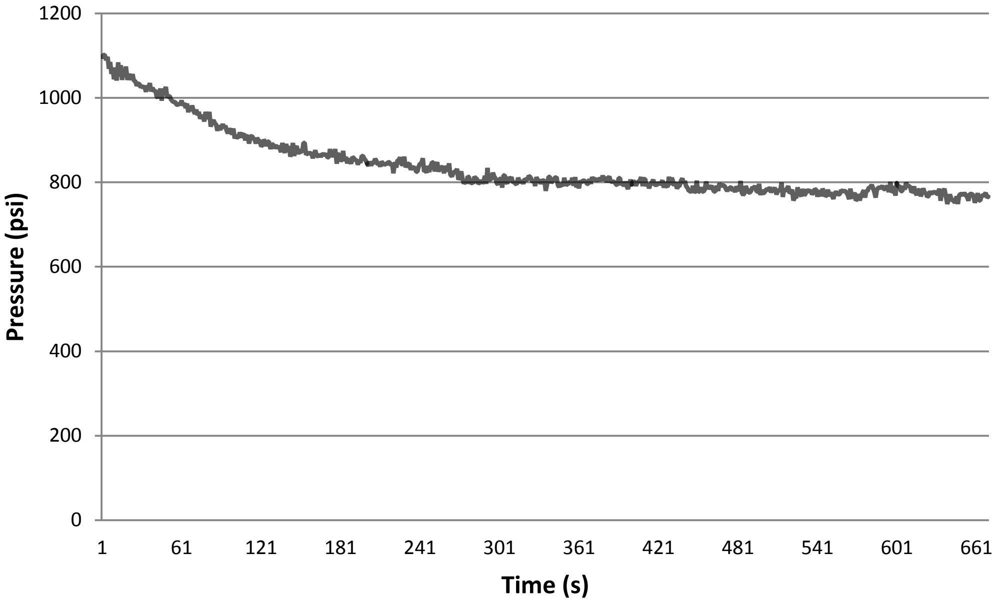

Figure 4.3: Pressure vs. time for a stable devulcanization process. Screw configuration: #4, barrel temperature is 200°C, screw speed is 100 rpm, and feeding rate is 100 lb/hr

Torque Analysis

Another limitation on increasing the throughput or feed rate is the torque value of the extruder driving motor. By increasing the feed rate, the fully filled length of the screw is increasing which results in higher torque demand for the screw rotation. Different models of TSE's depend on the size of the machine and also the capacity of the driving motor, and are capable of providing a certain maximum torque value. Our machine for this trial was a 50 mm HP twin screw extruder from Leistritz. A few tests were conducted to evaluate the effect of the different process parameters such as temperature, feed rate, and screw speed on the torque value of the TSE's motor.

Figure 4.4 shows how motor torque value changes with Q/N (feed rate divided by screw speed) for two different process temperatures (i.e., 140 and 180°C). Torque value increases when Q/N increases for both temperatures.

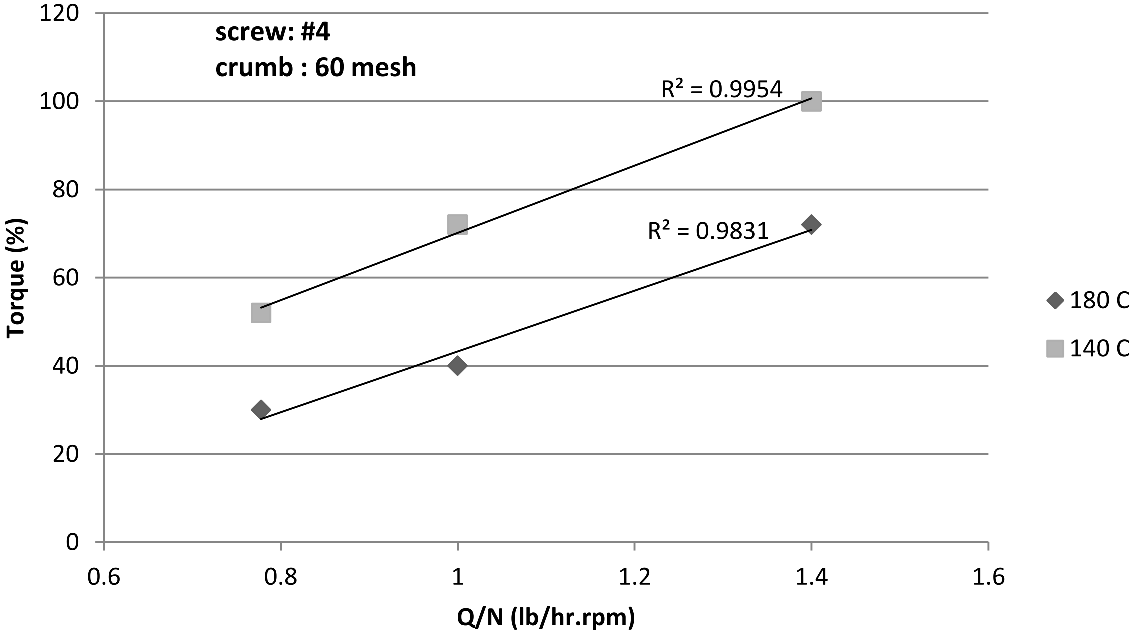

Figure 4.4: Torque vs. Q/N at two different process temperatures. Screw configuration: #4, material: 60 mesh rubber crumb

This means that either if we increase the feed rate at a constant rpm or if we decrease the rpm at a constant feed rate, torque increases. This is because when we increase the feed rate at a constant rpm, the fully filled length of the screw increases and therefore more torque is required to keep the extruder working. Similarly, when we decrease the rpm at a constant feed rate, we increase the residence time and as a result the fully filled length increases and the required torque increases. Increasing the process temperature from 140 °C to 180 °C decreases the viscosity of the rubber material inside the extruder and therefore decreases the torque value by ~ 28 %.

Figure 4.5 shows the effect of the screw speed on the torque value when the feed rate is constant. 60 mesh rubber crumb was used for this test and the temperature was set at 180 °C.

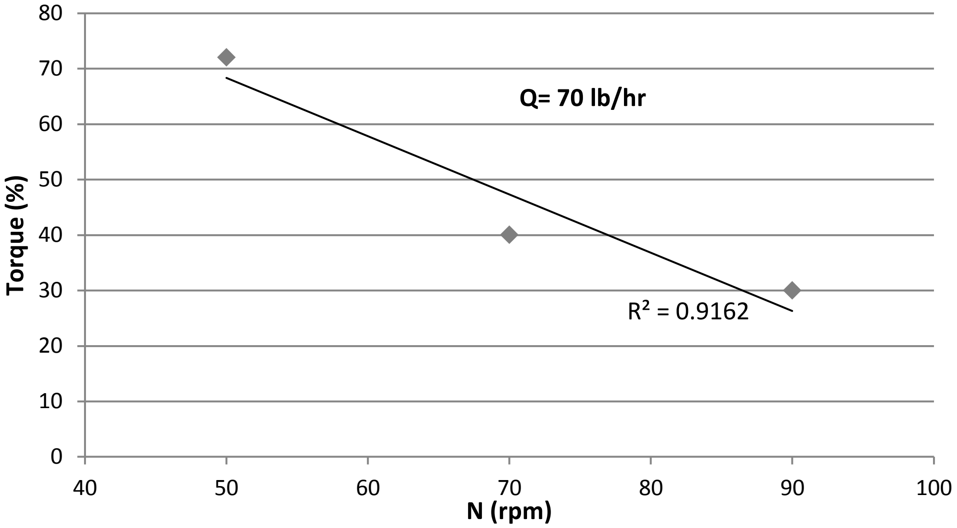

Figure 4.5: Torque vs. screw speed at constant feed rate (Q= 70 lb/hr). Screw configuration: #4, material: 60 mesh rubber crumb, and temperature: 180 °C

By increasing the screw speed from 50 rpm to 90 rpm the required torque decreases by almost 58%. As it was explained before, increasing the screw speed at a constant feed rate decreases the residence time and degree of fill in the extruder and as a result the required torque lowers.

Figure 4.6 shows the TSE's motor torque vs. Q (feed rate), when Q/N remains constant. It can be concluded that increasing the feed rate does not affect the torque, if the Q/N value remains constant. Basically when we increase the feed rate and screw speed at the same time (to maintain constant Q/N value) we do not change the degree of fill, therefore the torque value remains constant. For this test, we managed to increase the feed rate up to 200 lb/hr.

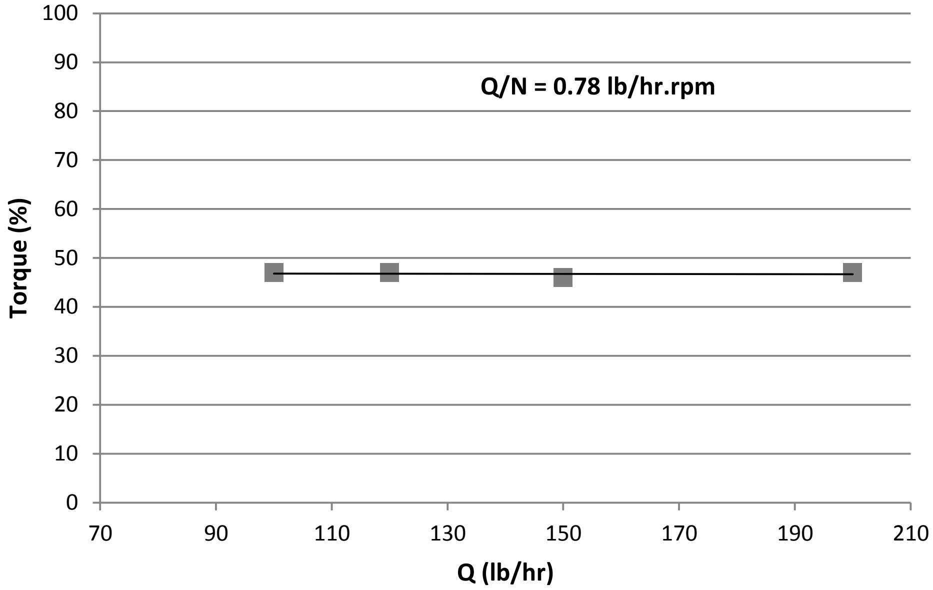

Figure 4.6: Torque vs. feed rate at constant Q/N (Q/N= 0.78 lb/hr.rpm, Screw configuration: #4)

4.3.2 Characterization of devulcanized rubber

Curing behavior of the devulcanized rubber

The moving die rheometer was used to evaluate the curing behavior of (1) devulcanized rubber without curing chemicals and (2) devulcanized rubber with added curing chemicals (according to Table 4.3). Both tests were conducted at 191 °C for 2 minutes. As shown in Figure 4.7, no rise in torque is observed during the MDR test for the sample without curing chemicals showing no vulcanization occurred in this sample. This test shows that no active sulfur has remained in the devulcanized sample and it cannot vulcanize by itself again. One can see that the devulcanized rubber can re-vulcanize again if it is mixed with the proper amount of curing chemicals including sulfur, accelerators, and activators. Table 4.2 shows the curing characteristic values for a devulcanized rubber sample. Screw speed, feed rate, and the process temperature for this sample were: 100 rpm, 100 lb/hr, and 180 °C respectively.

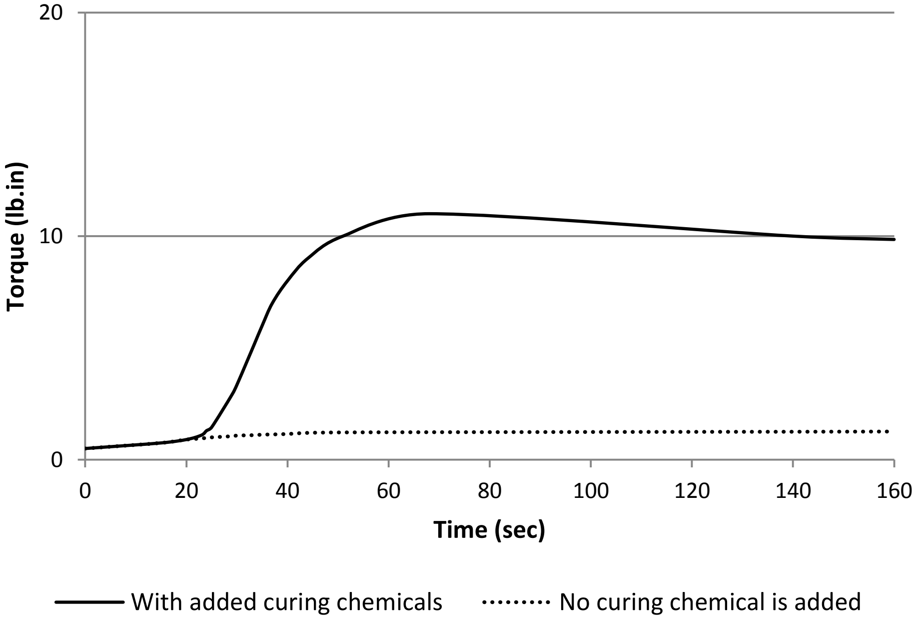

Figure 4.7: Curing behavior of devulcanized rubber with and without curing chemicals

Table 4.2 Curing characteristic values for devulcanized sample (Test temperature: 191 °C, Frequency: 1.667 HZ, and Strain: 0.50 degree)

Characteristic	Torque (lb-in)	Time (minute)
Min torque (ML)	0.664	0.083
Max torque (MH)	10.95	1.19
T_{s2}	2.664	0.457
T_{50}	5.769	0.54
T_{90}	9.905	0.75

Mooney viscosity

Figure 4.8 shows a Mooney viscosity graph for the devulcanized rubber sample. Devulcanized rubber obtained from our process was inserted into the Mooney viscometer cavity and the value of the torque versus experimental time (4+1 min) was measured at 100 °C (212 °F). The Mooney viscosity value for this devulcanized sample was 31.70 MU. The process conditions used for the production of this sample were: Screw speed: 100 rpm, feed rate: 100 lb/hr, and the process temperature: 180 °C.

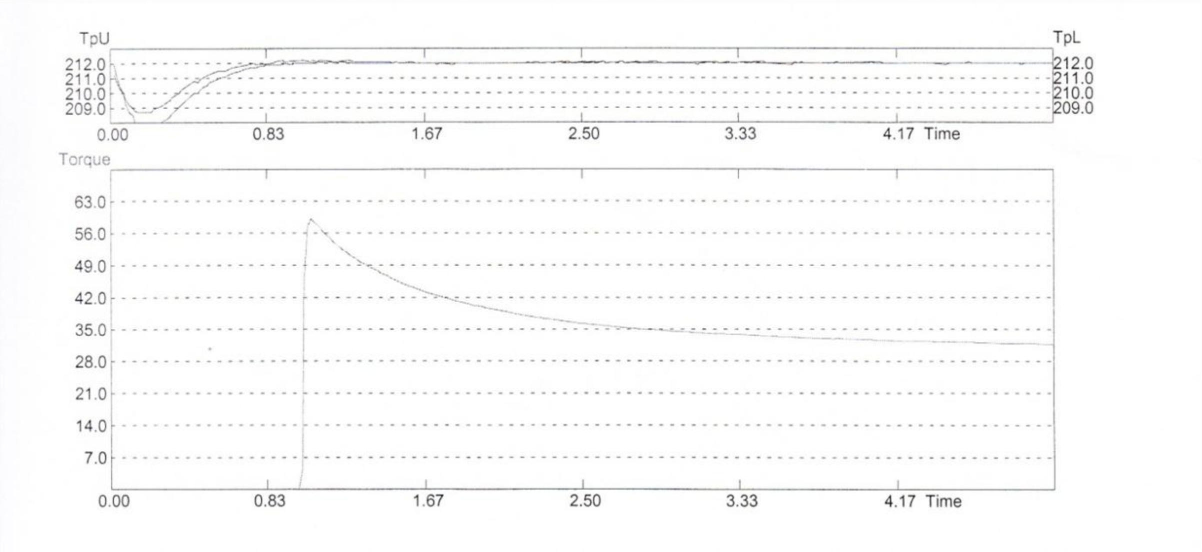

Figure 4.8: Mooney viscosity plot for devulcanized rubber (screw speed=100 rpm, feed rate=100lb/hr and temperature=180°C)

Figure 4.9 shows the effect of screw speed on the Mooney viscosity value of the devulcanized rubber when the feed rate and temperature were constant and equal to 70 lb/hr and 180 °C respectively.

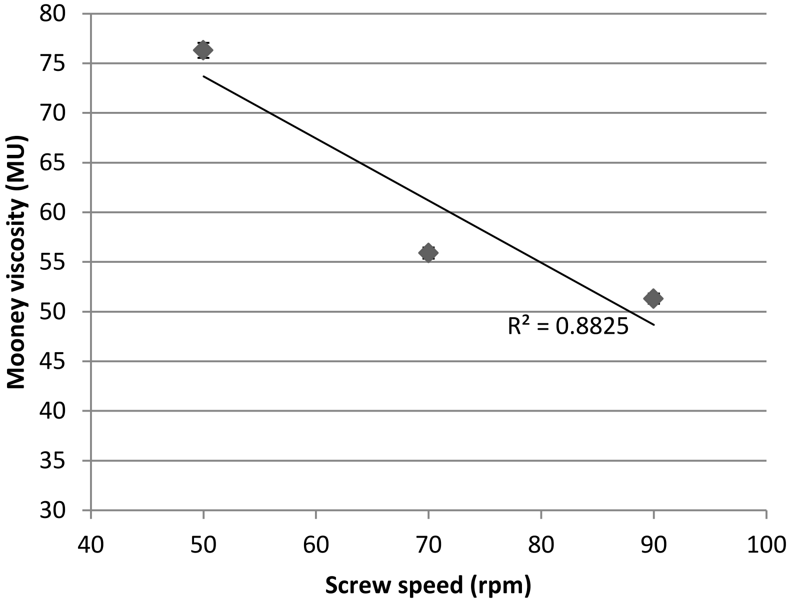

Figure 4.9: Mooney viscosity of devulcanized rubber vs. screw speed (rpm) when feed rate is constant and equal to 70 lb/hr. process temperature was 180 °C.

One can see that increasing the screw speed decreases the Mooney viscosity value of the devulcanized rubber. The reason is due to the fact that a higher screw speed imposes higher strain rate on the rubber material causing more devulcanization and chain scission that leads to lower Mooney viscosity. Figure 4.10 shows the effect of the feed rate on the Mooney viscosity of the devulcanized rubber at a constant screw speed (100 rpm) and temperature (180 °C). Increasing the feed rate from 40 lb/hr to 100 lb/hr seems to increases the Mooney viscosity. The rate of Mooney viscosity increasing for this range of feed rate is not high. When flow rates increases, fully filled lengths and hence the volume of the extruder occupied by the rubber increases, but overall residence time along the conveying section decreases. Lower residence time results in an increase in Mooney viscosity value.

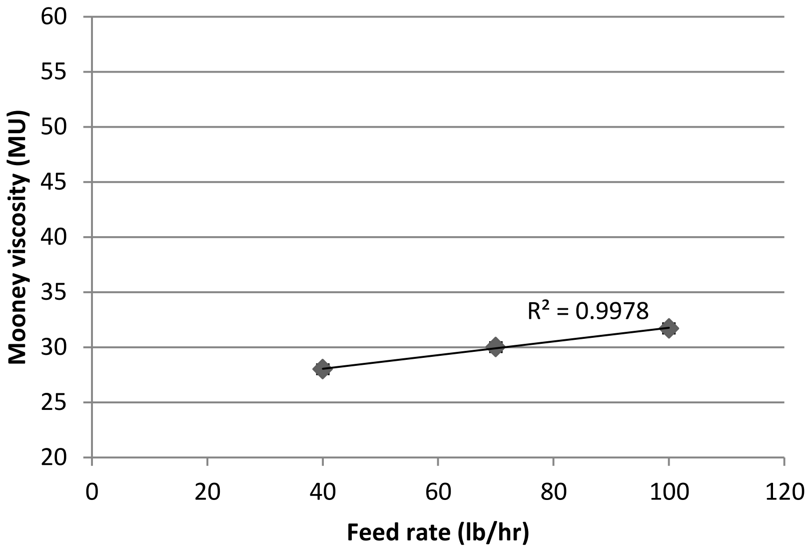

Figure 4.10: Mooney viscosity of devulcanized rubber vs. feed rate (lb/hr) when screw speed is constant and equal to 100 rpm. Process temperature was 180 °C.

Crosslink density and percent of devulcanization

Three different samples (s-1, s-2, and s-3) were collected at different screw speeds to evaluate the effect of devulcanization on the crosslink density value and percent of devulcanization of devulcanized rubber. The feed rate and the process temperature were 90 lb/hr and 180 C respectively. Figure 4.11 demonstrates the results for crosslink density measurements. It shows that crosslink density reduces from $10.67*10^{-4}$ for the 60 mesh rubber crumb to $4.08*10^{-4}$ for the s-1 sample. Further increase in screw speed results in a slight continuous reduction of crosslink density which is observable for s-1 to s-3 samples.

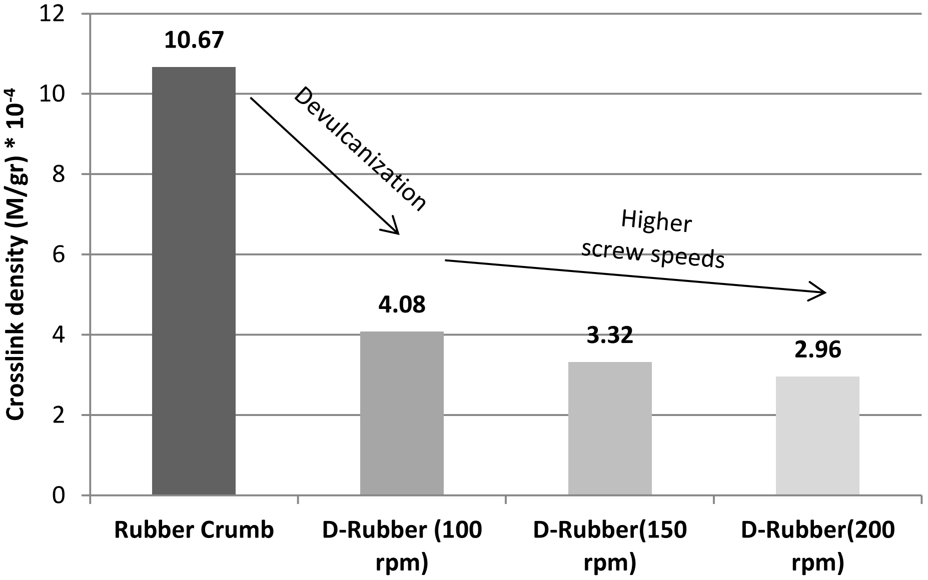

Figure 4.11: Effect of devulcanization on the crosslink density reduction of devulcanized rubber.

Figure 4.12 shows the crosslink densities of different types of crosslink bonds of the gel fraction as a function of screw speed at 180 °C and 90 lb/hr feed rate. A significant reduction (61%) of crosslink density value can be achieved when the screw speed is increased to 100 rpm which is mostly governed by decreasing the crosslink density of polysulfidic bonds. By increasing the screw speed further to 150 and 200 rpm the total crosslink density reduces by 68% and 72 % respectively compared to the starting crumb. Increasing the screw speed from 100 rpm to 150 and 200 rpm cleaves mostly the polysulfidic bonds and does not affect the mono and di sulfidic crosslinks significantly.

Mouri et al. [3-6] have shown that thermo-mechanical devulcanization of EPDM rubber decreases the crosslink density and the gel fraction of the rubber in a significant manner. They have also shown that during the devulcanization reaction, the effect of the heat first converts the polysulfide and di-sulfide crosslinks into mono sulfide crosslinks, and finally the mechanical forces break the monosulfidic bonds. Another study has shown that the amount of polysulfidic bonds decreases in a significant manner by only heat treatment, while the proportion of monosulfidic bonds increases significantly [16].

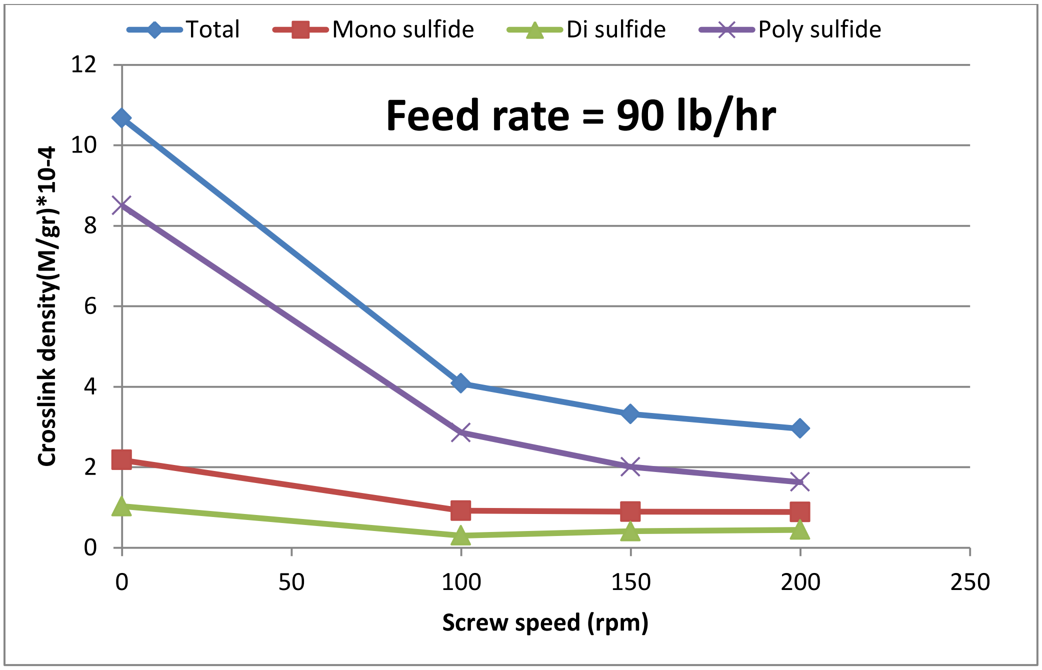

Figure 4.12: Total, Mono-sulfidic, Di-sulfidic, and Poly-sulfidic crosslink densities of the devulcanized rubber as a function of screw speed (Feed rate =90 lb/hr and temperature=180°C)

It must be mentioned that these reactions are very complicated and very hard to follow up, because all the sulfidic bonds including poly, di, and mono types, can transform to each other, or form cyclic sulfur structures during the devulcanization process [16].

Physical and mechanical properties of the devulcanized rubber

Tensile properties of the re-vulcanized sample, including tensile strength, elongation at break, and tensile modulus were measured and reported in table 4.3.

Table 4.3: Physical and mechanical properties of devulcanized rubber

Item	Value
Starting material	60 mesh tire tread crumb
Feed rate (lb/hr)	100
Screw speed (rpm)	100
Process temperature (°C)	120
Tensile strength (Mpa)	8.59±0.3
Elongation at break (%)	177±4
Modulus @ 100 % (psi)	494.5
Hardness (shore A)	66

The devulcanized rubber obtained from our devulcanization process has a Mooney viscosity comparable to virgin tire compound (30<M.U<50). As a result, it can be processed easily and mixed again with curing chemicals and re-vulcanized to form a new rubber product again. The physical and mechanical properties are inferior compared to a virgin compound, but are still acceptable for many applications, such as shoe soles, rubber mats, and etc.

4.4 Concluding remarks

1) Ground tire rubber crumb was devulcanized under stress in the twin screw extruder with supercritical CO_2. The devulcanization process which is described in this chapter is a continuous devulcanization process in which no chemical agent is used for crosslink bonds cleavage in the vulcanized rubber.

2) Using an industrial scale twin screw extruder, a reasonably high throughput of devulcanized rubber was obtained in the scale-up devulcanization process which was totally stable.
3) It is shown that throughput can be increased to an optimum level and Q/N and the process temperature are important parameters that can be adjusted to overcome the motor torque limitation.
4) The volatiles generated during extrusion can be controlled by using a proper set up for screw configuration and CO_2 injection zone.
5) The devulcanized rubber obtained from this process can be re-vulcanized again by adding curing agents, and it shows reasonable rheological, physical and mechanical properties

4.5 References

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CHAPTER 5. STUDY OF THE EFFECT OF PROCESS PARAMETERS ON PROPERTIES OF DEVULCANIZED SCRAP TIRE RUBBER

5.1 Introduction

A serious problem for the environment is the accumulation of scrap polymer material, especially scrap tires. In fact, compared to thermoplastic materials such as water bottles, it is way more difficult to recycle and reprocess a thermoset material like rubber. This is due to the presence of three dimensional crosslink networks in thermoset materials. According to statistics [1] the majority of scrap tires are burnt for tire-derived fuel applications, which not only cause air pollution but also waste the valuable rubber material. Considering the fact that the price of raw rubber (both natural and synthetic) is increasing, the best solution for scrap tires is recycling or more specifically devulcanization of scrap tire rubber. Many researchers have tried different devulcanization methods in which the crosslinked rubber network is cleaved by using mechanical forces, chemical reagents, ultrasonic waves, or thermal treatments. Adhikari et al. [2] have described different devulcanization methods for scrap tire rubber. Fukumori et al. [3] have utilized a thermo-mechanical devulcanization method to generate a high quality devulcanized rubber from scrap tires. They incorporated 10% of the obtained devulcanized rubber into a truck tire tread and observed satisfactory results. Maridass and Gupta [4-6] have published a number of papers regarding devulcanization of scrap rubber using a lab scale counter rotating twin screw extruder. They have used response surface methodology to optimize the performance of their devulcanization process. They used a central composite rotatable design for two variables, screw speed and barrel temperature at five levels. Sutanto et al. [7] also have studied the responses of a continuous devulcanization process by using an experimental design. They investigated the effect of different process parameters such as temperature, screw speed, and feed rate on the degree of devulcanization of the devulcanized rubber.

In the previous chapter, we established a continuous, high throughput, and stable devulcanization process using an industrial twin screw extruder. The effect of the extruder set up on process stability was studied. We also studied the effect of process parameters such as temperature, feed rate, and screw speed on the torque value of the extruder motor. Finally, some rheological, physical and mechanical properties of devulcanized rubber, obtained from the devulcanization process, were evaluated.

In this chapter we have studied the effect of different process parameters such as temperature, screw speed, and feed rate on the properties of the devulcanized rubber. A statistical design was used to study the effect of process variables on the crosslink structure, gel and sol fractions and degree of devulcanization of devulcanized rubber. We also measured rheological, physical and mechanical properties to evaluate how changing the process variables can affect these important properties. Temperature, screw speed, and feed rate were selected as the process variables, since they directly affect the values of other operating parameters such as shear rate, residence time, and torque. A fractional factorial design in three levels was used to study the effects of process variables. The main objectives for this research effort were:

5- Develop an experimental design to study the effect of main process variables on the properties of the devulcanized rubber.
6- Analyze the experiment results using statistical methods to investigate how significantly these parameters and their interactions affect the output properties.

7- Derive a mathematical model using response surface methodology to optimize the process.

8- Find out the optimum values for the process parameters to optimize the devulcanized rubber properties within the range of experiments.

5.2 Experimental

5.2.1 Material and equipment

The starting material that we used was buffing rubber from Rubber Venture retreading company. The material was obtained from retreading process by abrading the tread of the used tires into a small particle size (mesh -20) rubber buffing. Zinc oxide, stearic acid, and sulfur were supplied by Sigma Aldrich and Fisher Scientific. TBBS was supplied by Airboss Co. in Kitchener, ON. A 50 mm twin screw extruder (Leistritz, NJ) was used for the devulcanization process. The experimental set up for the twin screw extruder was the one described in the previous chapter. Supercritical carbon dioxide was fed into the extruder barrel using a gas injection system from Thar Inc.

Rubber crumb was fed into the extruder barrel using a gravimetric feeder. Devulcanized rubber extrudate was immersed into a water bath right after coming out of the die in order to cool it down and it was subsequently dried by air on a conveyor belt prior to collection.

5.2.2 Experimental design

A fractional factorial design in three levels was used to study the effect of three different input variables, i.e. screw speed, temperature, and feed rate on the devulcanized rubber properties. We chose three levels for the independent variables, because we wanted to make sure that we are testing both linear and quadratic effects (and interactions) of those variables on the dependent variables of interest.

A high value, a low value, and a center value were set for each input variable. The high value was coded as 1, center value as 0, and the low value as -1. A total number of 9 experiments were needed to complete a $3^{(3-1)}$ fractional factorial design. Table 5.1 shows the variables and their high, low and center values. In order to evaluate the maximum and minimum levels for all three variables we conducted screening tests before the set up of the experimental design. The temperature levels were selected based on process stability and torque limitations. Due to the capacity limitation of the twin screw extruder we were not able to run more than 300 lb/hr with this specific screw design and machine size (50 mm). Therefore, the lowest value for the screw speed was determined to be 300 rpm in order to maintain a Q/N value smaller than the critical value which shuts the machine down due to the torque limitation. The highest value for screw speed (600 rpm) was set in a way that the extruder can perform at the lowest feed rate (100 lb/hr) without causing screw starvation and damage to the machine.

Table 5.1: Experimental levels

Factor	factor name	low value	center value	high value
T	Temperature (°C)	100	140	180
N	Screw speed (rpm)	300	450	600
Q	Feed rate (lb/hr)	100	200	300

Nine devulcanization experiments were conducted using the set values for the process variables according to Table 5.2.

Table 5.2: $3^{(3-1)}$ fractional factorial design matrix

Run	Coded level for Temperature	Process Temperature (°C)	Coded level for Screw speed	Screw speed (rpm)	Coded level for Feed rate	Feed rate (lb/hr)
1	-1	100	-1	300	-1	100
2	-1	100	0	450	1	300
3	-1	100	1	600	0	200
4	0	140	-1	300	1	300
5	0	140	0	450	0	200
6	0	140	1	600	-1	100
7	1	180	-1	300	0	200
8	1	180	0	450	-1	100
9	1	180	1	600	1	300

Using the quantitative design factors we can build a model for each dependent variable:

$$\text{dependent variable} = C_1T + C_2T^2 + C_3N + C_4N^2 + C_5Q+C_6Q^2 + \text{Intercept} \pm \text{Error} \quad (5.1)$$

C_1 - C_6 are regression coefficients for the linear and quadratic forms of each factor. T, N, and F are temperature, screw speed and feed rate respectively. Dependent variables (responses) that are studied in this design are: sol fraction, crosslink density, Mooney viscosity, tensile strength, and elongation at break of the devulcanized rubber.

5.2.3 Characterization techniques

Crosslink network analysis

In order to analyze the crosslink structure, the devulcanized rubber specimens were continuously extracted by acetone for 16 hr (according to ASTM D-297) [8]. After drying to constant weight, specimens were swelled in toluene for 72 hr to measure the total crosslink density of the rubber sample. Using the Flory-Rehner equation crosslink density of devulcanized samples was measured [9]:

$$\vartheta_e = \frac{-[\ln(1-V_r)+V_r+\chi_1 V_r^2]}{[V_1(V_r^{\frac{1}{3}}-V_r)/2]} \quad (5.2)$$

where V_r, χ_1 , V_1, and ϑ_e are the rubber volume fraction in the swollen sample, rubber-solvent interaction parameter, molar volume of solvent and the crosslink density of devulcanized sample and crumb rubber respectively.

ϑ_e = effective number of chains in a real network per unit volume

V_r= volume fraction of polymer in a swollen network in equilibrium with pure solvent

In order to calculate V_r we should use the following relation:

$$V_r = \frac{(\text{weight of the dry rubber})/(\text{density of dry rubber})}{\frac{\text{weight of the dry rubber}}{\text{density of dry rubber}} + \frac{\text{weight of the solvent absorbed by sample}}{\text{density of solvent}}} \quad (5.3)$$

The calculation below was used to determine the devulcanization degree:

$$\%\ Devulcanization = [1 - \left(\frac{Crosslink\ density\ of\ devulcanized\ rubber)}{Crosslink\ density\ of\ control\ crumb\ rubber)}\right)] \times 100)] \quad (5.4)$$

Sol and gel fraction measurement

After acetone extraction, all samples were immersed in toluene for 72 hr and the toluene was refreshed every 24. Before swelling, the weight of each specimen was measured precisely. Samples then dried in an air ventilated oven at 72°C overnight until a constant weight was reached. The difference between the weight measurement taken before swelling the samples and after drying them gave us the sol content of the devulcanized rubber. The sol and gel fractions can be calculated using the following equations [10]:

$$Sole\ fraction(\%) = \frac{weight\ before\ swelling - weight\ of\ dried\ sample}{weight\ before\ swelling} \times 100 \quad (5.5)$$

$$Gel\ fraction\ (\%) = 100 - Sol\ fraction\ (\%) \quad (5.6)$$

Mooney viscosity

A Mooney viscometer was used in order to measure the Mooney viscosity of devulcanized samples. Using a large rotor, Mooney viscosity measurement is conducted at 100°C and MU (ML 1+4 @100°C) is reported for each sample in compliance with ASTM D 1646 [11].

Curing behavior

The curing behavior of the devulcanized rubber compounds was evaluated using a MDR Rheometer. M_L (minimum torque), M_H (maximum torque) and ts_2 (scorch time) were measured according to ASTM D2084 [12].

Physical and mechanical properties measurements

A Haake mixer was used to mix the sulfur and curing chemicals with the devulcanized rubber. The curing recipe is shown in table 5.3. Devulcanized samples were milled later to achieve a more uniform sample using a lab scale two roll mill. After milling, a slab pre-form was cut for each sample and then all samples were pressed and cured at 160 °C for 10 minutes, using a hydraulic hot press. Using a standard die cut, dumbbell shape specimens were cut from the cured standard slabs and the tensile strength and elongation at break were measured using an Instron tensiometer according to ASTM D 412-98a. For each sample the average of three replicates was reported [13].

Table 5.3: Ingredients for re-vulcanization of devulcanized sample

Ingredients	***phr***
Devulcanized Rubber	100
Zinc oxide	3
Stearic Acid	1
OBTS	1.5
Sulfur	1.5

5.3 Results and Discussion

5.3.1. Network analysis

Table 5.4 shows the crosslink density, acetone soluble fraction, sol fraction, and gel fraction measurement results.

Table 5.4: Network analysis results

Sample #	Feed rate	Screw speed	Melt temp	Total CRD $*10^{-4}$	Acetone soluble%	Gel fraction (%)	Sol fraction (%)
1	100	300	100	1.17	10	74	16
2	300	450	100	1.33	9.1	78.9	12
3	200	600	100	1.14	10.1	71.6	18.3
4	300	300	140	1.25	9.4	80	10.6
5	200	450	140	1.17	9.8	74.4	15.8
6	100	600	140	1.07	11.4	66.3	22.3
7	200	300	180	1.1	9.5	74.9	15.6
8	100	450	180	1.1	10	70.7	19.3
9	300	600	180	1.25	9.4	77.5	13.1

The ANOVA table for the sol fraction of devulcanized rubber is created by Statistica software (table 5.5):

Table 5.5: ANOVA table for sol fraction of devulcanized rubber.

ANOVA; Var.:Sol%; R-sqr=.96066; 1 Blocks, 9 Runs;					
	SS	**df**	**MS**	**F**	**p**
(1)Temp (L)	0.4817	1	0.48167	0.22357	0.682912
Temp (Q)	0.5339	1	0.53389	0.24781	0.667969
(2)Screw speed (L)	22.0417	1	22.04167	10.23079	0.085408
Screw speed (Q)	0.1606	1	0.16056	0.07452	0.810467
(3)Feed rate (L)	79.9350	1	79.93500	37.10237	0.025910
Feed rate (Q)	2.0672	1	2.06722	0.95952	0.430602
Error	4.3089	2	2.15444		
Total SS	109.5289	8			

From the data provided in the ANOVA table (p-values), we can see that only the feed rate has a significant effect on the sol fraction. Figure 5.1 shows the Pareto chart which is drawn by Statistica®. Pareto chart is a helpful tool to identify which process parameter has significant effect on our dependent variable. From figure 5.1 it is clear that only the linear effect of feed rate is significant for the sole fraction of the devulcanized rubber and screw speed and temperature are not significantly affecting the sol fraction of the devulcanized rubber. The calculated regression coefficients for sol fraction are presented in table 5.6.

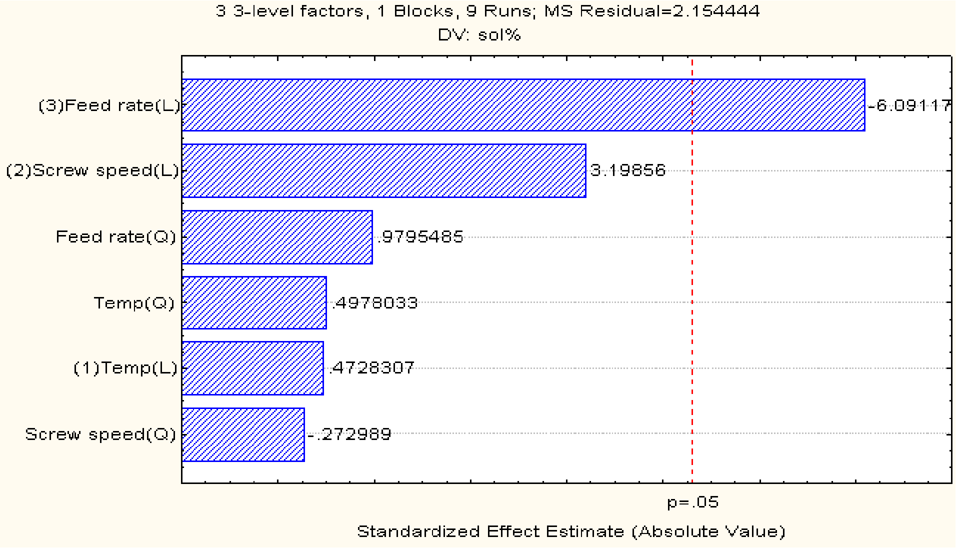

Figure 5.1: Pareto chart of standardized effects for sol fraction

Table 5.6: Regression coefficients for sol fraction

Regr. Coefficients; Var.:sol%; R-sqr=.96066; Adj:.84264
(Spreadsheet7) 3 3-level factors, 1 Blocks, 9 Runs

	Regressn - Coeff.
Mean/Interc.	9.434722
Temp (L)/C_1	0.097500
Temp (Q)/C_2	-0.000323
Screw speed(L)/C_3	0.001444
Screw speed(Q)/C_4	0.000013
Feed rate(L)/C_5	0.004167
Feed rate(Q)/C_6	-0.000102

Figure 5.2 shows predicted values of sol fraction versus observed values. A nice agreement between the calculated values by the statistical model and the measured data is shown by the graph. A regression model can be built using equation 5.1 and the regression coefficients. A 3D surface plot can be drawn, using the regression model (figures 5.4 and 5.5).

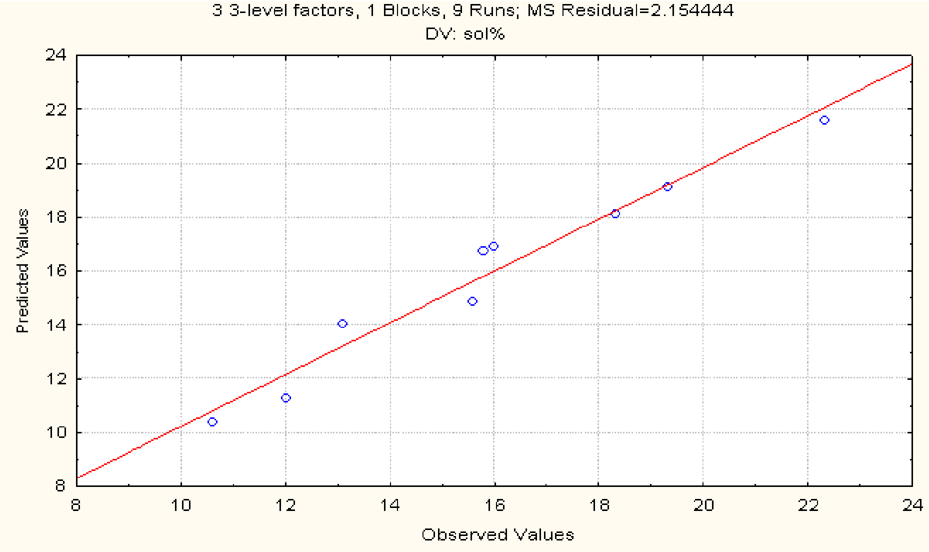

Figure 5.2: Predicted values versus observed values (Sol fraction)

Figure 5.3 shows a 3D surface plot of sol fraction versus the feed rate and the temperature when the screw speed is 450 rpm. It can be seen that in the range of our experiments, temperature shows almost no effect on the sol fraction of devulcanized rubber. On the other hand, feed rate has a significant effect on the sol fraction of the devulcanized rubber. Sol fraction increases when feed rate decreases. Decreasing the feed rate at constant rpm increases the residence time. Results show that within the range of our experiment set up, the feed rate is the most significant process variable which affects the sol fraction value of devulcanized rubber.

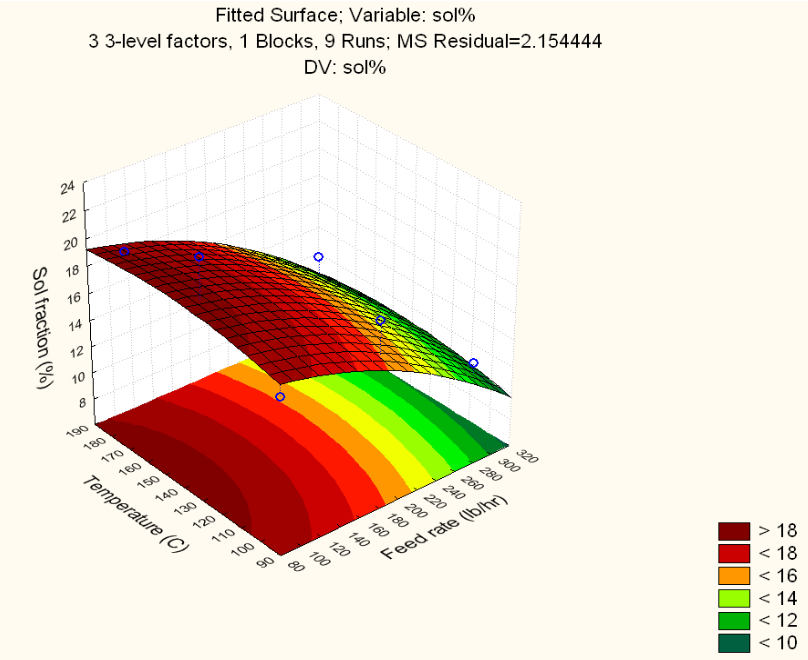

Figure 5.3: Sol fraction as a function of screw speed and temperature

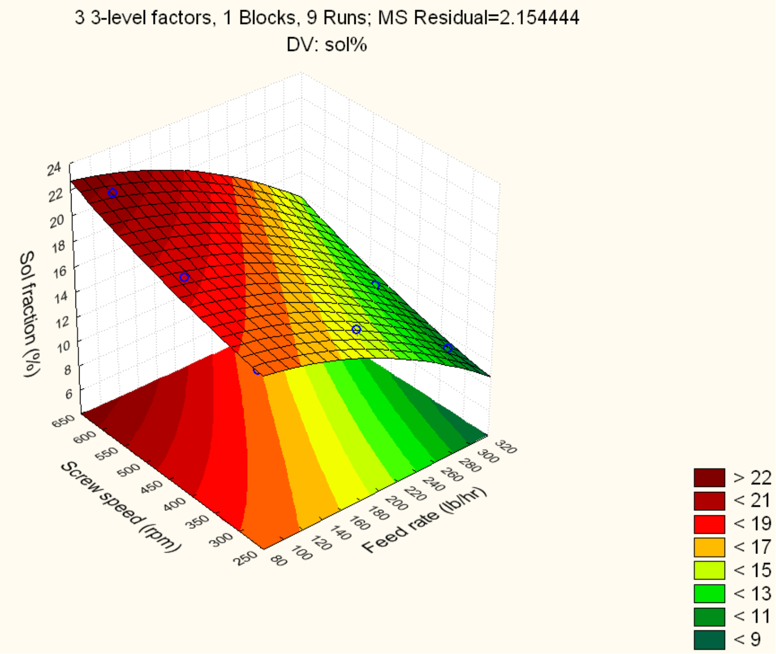

Figure 5.4: Sol fraction as a function of screw speed and feed rate

Figure 5.4 shows another surface plot of sol fraction this time as a function of screw speed and feed rate. Increasing the screw speed and decreasing the feed rate have similar effect on the sol fraction of devulcanized rubber and they both increase this value. The effect of feed rate is more significant compared to screw speed.

Analysis of variance results for crosslink density of the gel network are shown in table 5.7. From p- values, one can see that similarly to the sol fraction, the feed rate is the only independent variable which has a significant effect on the cross link density value of the devulcanized rubber.

Table 5.7: ANOVA table for crosslink density of devulcanized rubber.

ANOVA; Var.:CRD; R-sqr=.96562; 3 3-level factors, 1 Blocks, 9 Runs;					
	SS	**df**	**MS**	**F**	**p**
(1)Temp (L)	0.006017	1	0.006017	5.95055	0.134873
Temp (Q)	0.000672	1	0.000672	0.66484	0.500516
(2)Screw speed (L)	0.000600	1	0.000600	0.59341	0.521655
Screw speed (Q)	0.002689	1	0.002689	2.65934	0.244517
(3)Feed rate (L)	0.040017	1	0.040017	39.57692	0.024348
Feed rate (Q)	0.006806	1	0.006806	6.73077	0.121977
Error	0.002022	2	0.001011		
Total SS	0.058822	8			

The regression coefficients for the crosslink density of devulcanized rubber are calculated and shown in table 5.8. A model was created using formula 5.1 and the regression coefficients and two 3D surface plots (figure 5.6 and 5.7) were drawn. Predicted crosslink density values by the statistical model versus experimental results are shown in figure 5.5. One can see that the predicted values are in a good agreement with measured crosslink density values.

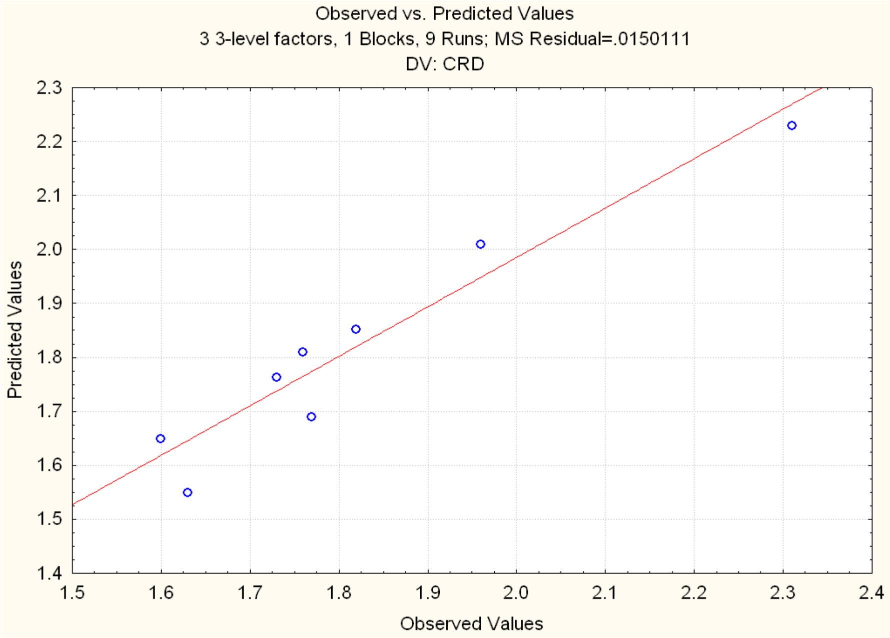

Figure 5.5: Predicted values versus observed values (Sol fraction)

Table 5.8: Regression coefficients for crosslink density

Regr. Coefficients; Var.:CRD; R-sqr=.96562 3 3-level factors, 1 Blocks, 9 Runs	
	Regressn - Coeff.
Mean/Interc.	1.254306
Temp (L)/C_1	-0.004000
Temp (Q)/C_2	0.000011
Screw speed(L)/C_3	0.001400
Screw speed(Q)/C_4	-0.000002
Feed rate(L)/C_5	1.254306
Feed rate(Q)/C_6	-0.004000

Figure 5.6 shows the crosslink density as a function of screw speed and feed rate when the temperature was set at 140 °C. The effect of screw speed on crosslink density is very small and almost negligible but feed rate has a significant effect on the crosslink density value of the devulcanized rubber.

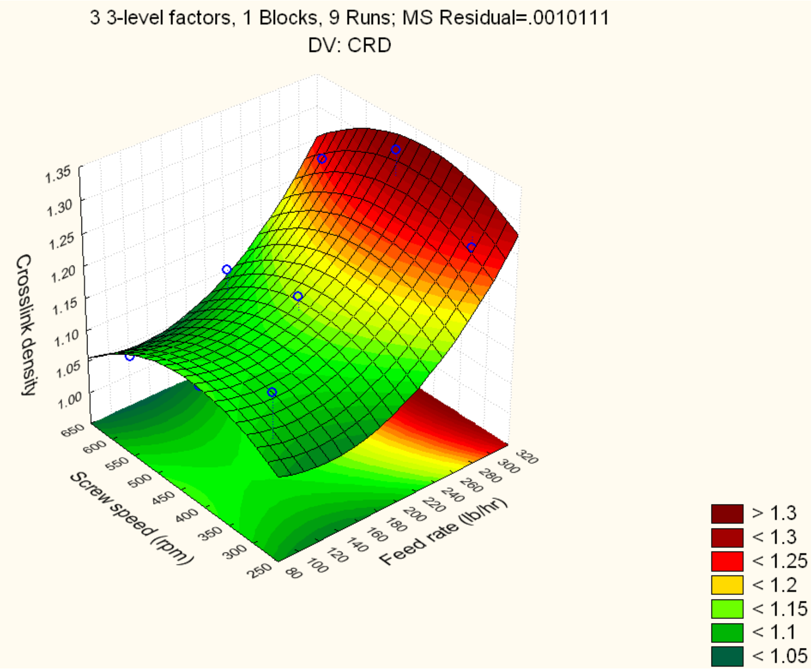

Figure 5.6: Crosslink density as a function of screw speed and feed rate (Temperature= 140 °C)

As the feed rate value decreases the crosslink density value of devulcanized rubber decreases too.

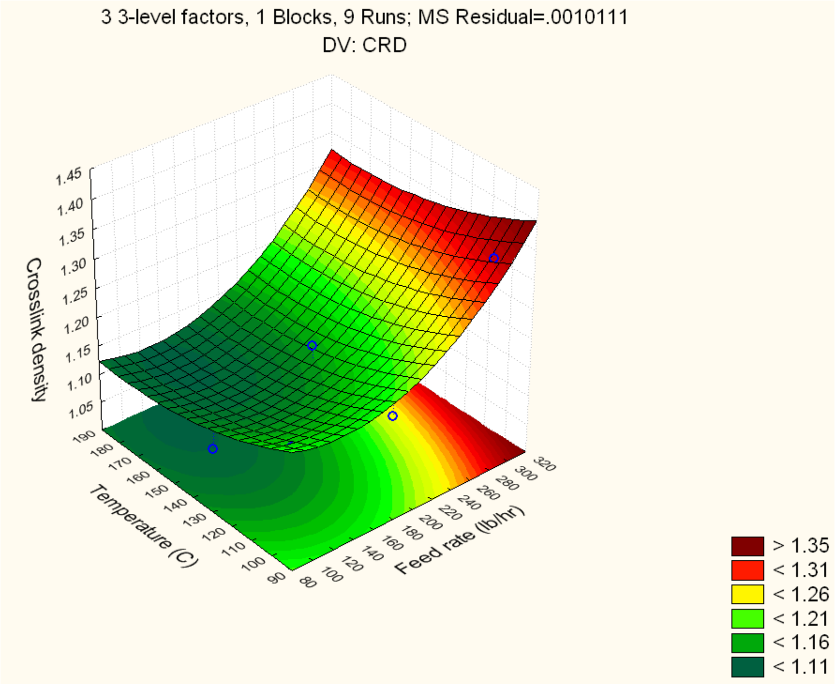

Figure 5.7: Crosslink density as a function of temperature and feed rate (screw speed=450 rpm)

Crosslink density as a function of feed rate and temperature when the screw speed was set at 450 rpm is shown in figure 5.7. The effect of temperature on the crosslink density value of the devulcanized rubber is very small and insignificant, but again we can see that the feed rate has a significant positive effect and by increasing the feed rate the crosslink density value of the devulcanized rubber increases.

Horikx's theory [14] was applied to determine how selectively the sulfur bonds are broken in our devulcanization experiments. This theory considers a relation between the degree of devulcanzation of the gel part and sol fraction content of the devulcanized rubber after devulcanization process. Selective cleavage of sulfur bonds is expressed by equation (5.7) while random chain scission is expressed by equation (5.9). Equation (5.8) is used to calculate γ_1 and γ_2.

$$1-\frac{v_{e2}}{v_{e1}}=1-\frac{\gamma_2\left(1-s_2^{1/2}\right)^2}{\gamma_1\left(1-s_1^{1/2}\right)^2} \qquad (5.7)$$

$$s=1/(1+\gamma-\gamma s)^2 \qquad (5.8)$$

$$1-\frac{v_{e2}}{v_{e1}}=1-\frac{\left(1-s_2^{1/2}\right)^2}{\left(1-s_1^{1/2}\right)^2} \qquad (5.9)$$

In which [14]:

v_e= Crosslink density of the gel fraction

S= sol fraction content

γ= crosslinking index

1= index used for the values before devulcanization

2= index used for the values after devulcanization

Using the Horikx theory, measured and theoretical values for sol fraction as a function of degree of devulcanization are plotted in figure 5.8. The solid line curve represents the theoretical data for the random chain scission, the dashed line shows the theoretical curve for selective crosslink cleavage, and the small circles are measured values for our devulcanized samples. All the experimental data are close to the selective sulfur cleavage theoretical line. From these results, it can be concluded that the dominant de-crosslinking mechanism for all our devulcanized samples is the selective sulfur bond cleavage rather than random chain scission.

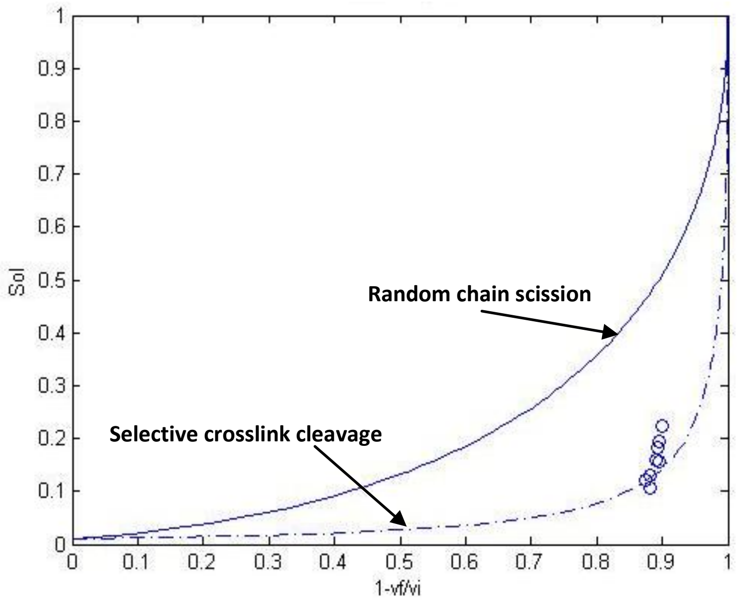

Figure 5.8: Sol fraction content versus degree of devulcanization of devulcanized rubber

5.3.2 Mooney viscosity and curing characteristics

Mooney viscosity and curing characteristics measurement results are shown in table 5.9.

Table 5.9: Mooney viscosity and curing characteristics results

Sample #	**Feed rate (lb/hr)**	**Screw speed (rpm)**	**Melt Temp (°C)**	**Mooney viscosity**	**M_L (lb.in)**	**M_H (lb.in)**	**TS_2 (min)**
1	100	300	100	48.2	1.20	11.28	0.45
2	300	450	100	97	1.44	12.22	0.40
3	200	600	100	43	1.11	11.02	0.43
4	300	300	140	119.8	1.87	12.76	0.40
5	200	450	140	60.2	1.37	12.04	0.45
6	100	600	140	19.4	0.75	8.513	0.45
7	200	300	180	51.4	1.28	11.73	0.42
8	100	450	180	25.6	0.87	9.933	0.44
9	300	600	180	78.1	1.42	12.02	0.40

Analysis of variance results for Mooney viscosity of the devulcanized rubber are shown in table 5.10. P-values show that among all three process variables, linear effect of feed rate and linear effect of screw speed have are significant factors for Mooney viscosity value of the devulcanized rubber. All regression coefficients are calculated and shown in table 5.11.

Table 5.10: ANOVA table for Mooney viscosity of devulcanized rubber.

ANOVA; Var.:,Mooney viscosity R-sqr=.98996; 3 3-level factors, 1 Blocks, 9 Runs;

	SS	**df**	**MS**	**F**	**p**
(1)Temp (L)	182.602	1	182.602	4.2266	0.176109
Temp (Q)	171.125	1	171.125	3.9609	0.184843
(2)Screw speed (L)	1037.535	1	1037.535	24.0152	0.039208
Screw speed (Q)	1.805	1	1.805	0.0418	0.856954
(3)Feed rate (L)	6780.482	1	6780.482	156.9435	0.006311
Feed rate (Q)	345.845	1	345.845	8.0051	0.105516
Error	86.407	2	43.203		
Total SS	8605.800	8			

A model was developed using this data and equation 5.1. Figure 5.9 shows predicted values versus observed values for Mooney viscosity. This graph shows that there is a very good correlation between calculated Mooney viscosity values by model and measured data. Using the regression model, 3D response surface plots were drawn in Statistica for Mooney viscosity (figures 5.10 & 5.11).

Table 5.11: Regression coefficients for Mooney viscosity

Regr. Coefficients; Var.:CRD; R-sqr=.96562 3 3-level factors, 1 Blocks, 9 Runs	
	Regressn - Coeff.
Mean/Interc.	1.254306
Temp (L)/C_1	-0.004000
Temp (Q)/C_2	0.000011
Screw speed(L)/C_3	0.001400
Screw speed(Q)/C_4	-0.000002
Feed rate(L)/C_5	1.254306
Feed rate(Q)/C_6	-0.004000

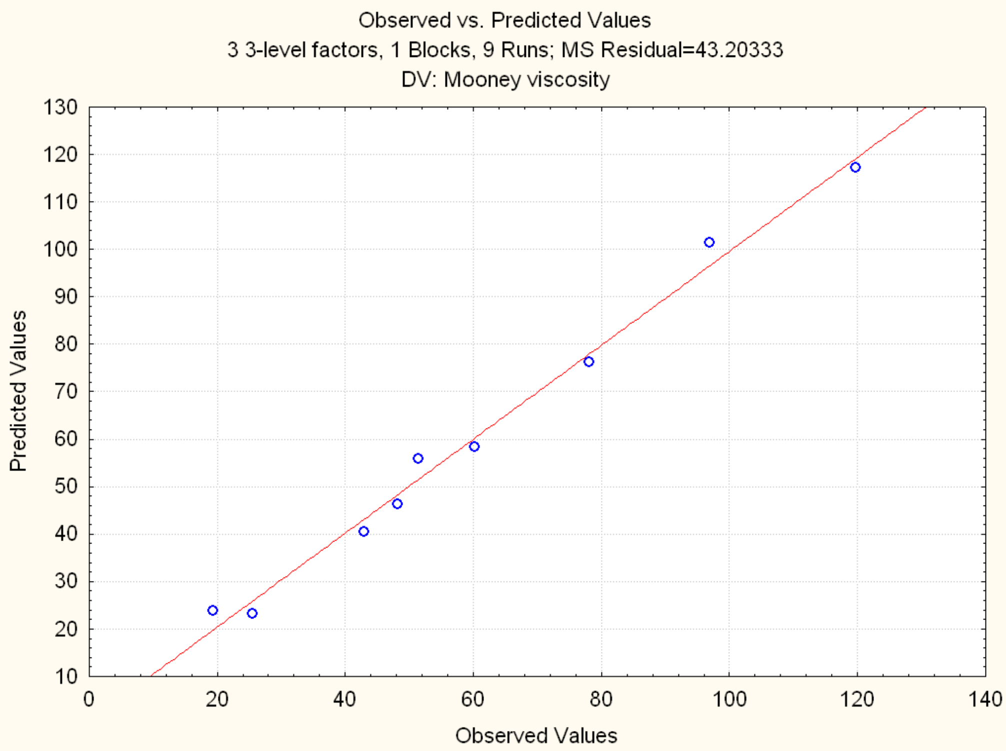

Figure 5.9: Predicted values versus observed values (Sol fraction)

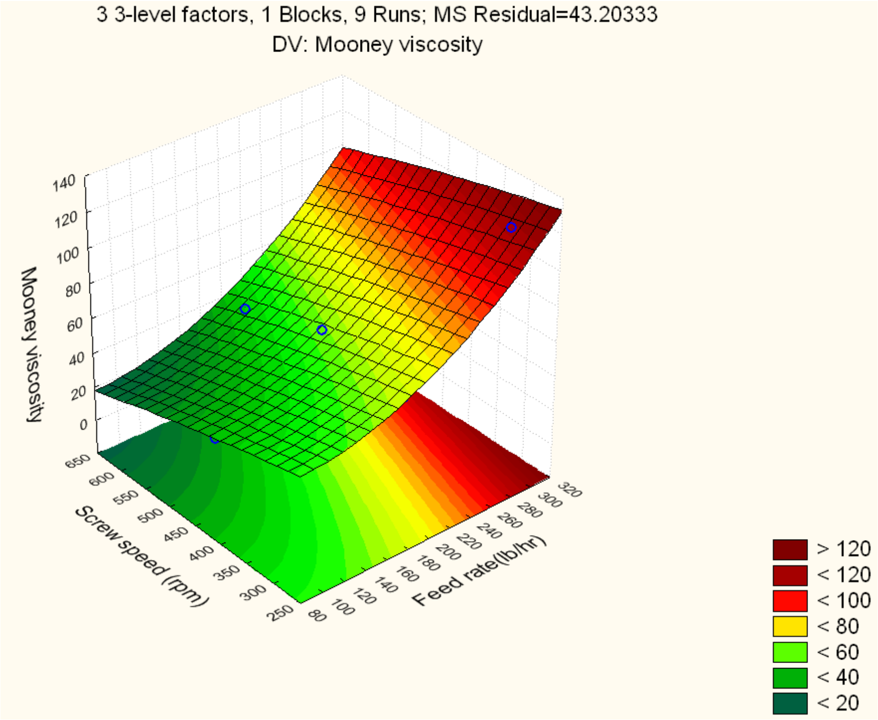

Figure 5.10: Mooney viscosity as a function of screw speed and feed rate (Temperature=140 °C)

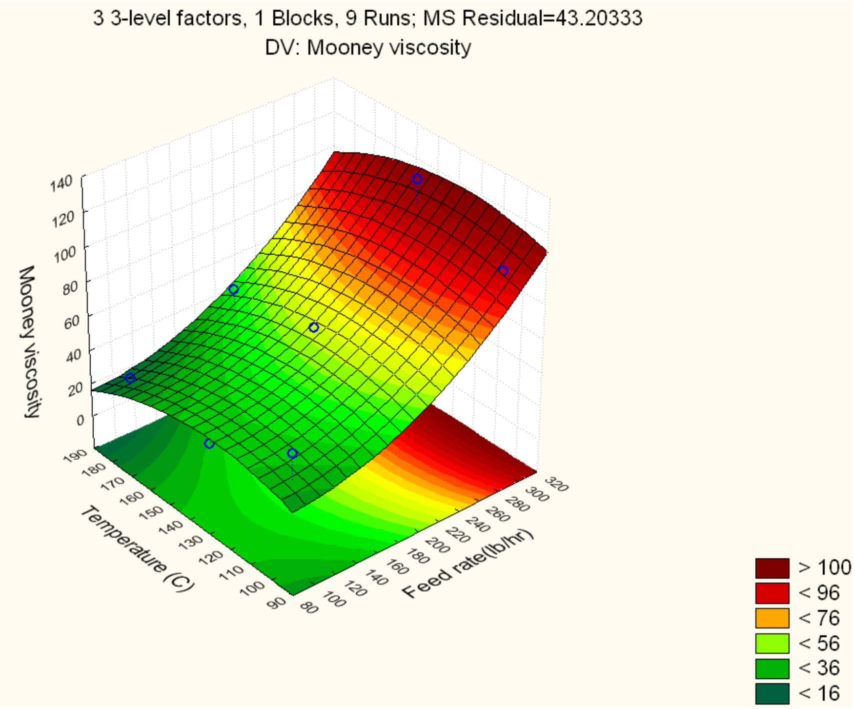

Figure 5.11: Mooney viscosity as a function of temperature and feed rate (screw speed=450 rpm)

Figure 5.10 shows the Mooney viscosity of the devulcanized rubber as a function of screw speed and feed rate when the process temperature is 140 °C. Mooney viscosity of devulcanized rubber decreases as screw speed increases. Feed rate has more significant effect on Mooney viscosity of devulcanized rubber and increasing the feed rate increases the value of Mooney viscosity. The minimum Mooney viscosity was obtained at highest screw speed and lowest feed rate. These results show that the Mooney viscosity of the devulcanized rubber can be easily manipulated by screw speed and feed rate adjustments. In figure 5.11 we can see the effect of temperature and feed rate on the Mooney viscosity of the devulcanized rubber when screw speed was set at 450 rpm. The lowest values for Mooney viscosity were obtained either at the maximum or the minimum temperatures, although the process temperature does not show a significant effect on the Mooney viscosity of the devulcanized rubber for the range of our experiments. Like the previous plot (figure 5.10) feed rate shows a significant positive effect on the Mooney viscosity of the devulcanized rubber, i.e., increasing the feed rate increases the Mooney viscosity of the devulcanized rubber. We were expecting that screw speed and process temperature would show a more significant effect on Mooney viscosity value because higher screw speed increases mechanical shear, which should plasticize the rubber more significantly, and also higher temperature should have shown the same effect. But in the range of our selected independent process variables, it seems that the feed rate plays a more important role and has a higher effect on the Mooney viscosity value of the devulcanized rubber than the other independent variables. ML is plotted against Mooney viscosity in figure 5.12. Mooney viscosity represents the viscosity of rubber at process temperatures whereas ML is a measure of the rubber viscosity at curing temperatures.

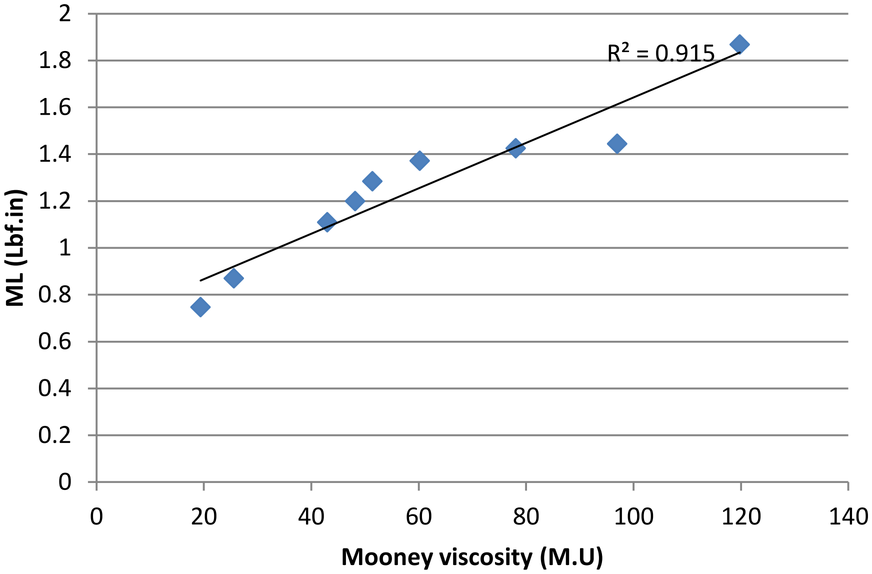

Figure 5.12: Mooney viscosity vs. Crosslink density

Figure 5.13 shows that there is a very good correlation (R^2=0.91) between the Mooney viscosity and the ML value of the devulcanized rubber samples. Therefore, we can conclude that the effects of the different process variables on the ML value must be exactly the same as their effects on the Mooney viscosity of the devulcanized rubber.

Figure 5.13 shows the Mooney viscosity values versus the crosslink density values of all devulcanized samples. As was reported previously by Mouri et al. [15-17], there is a correlation between the Mooney viscosity and crosslink density of devulcanized rubber. The Mooney viscosity is plotted against sol fraction in figure 5.14, in which we can see a very good correlation (R^2=0.91) between the Mooney viscosity and the sol fraction of the devulcanized rubber.

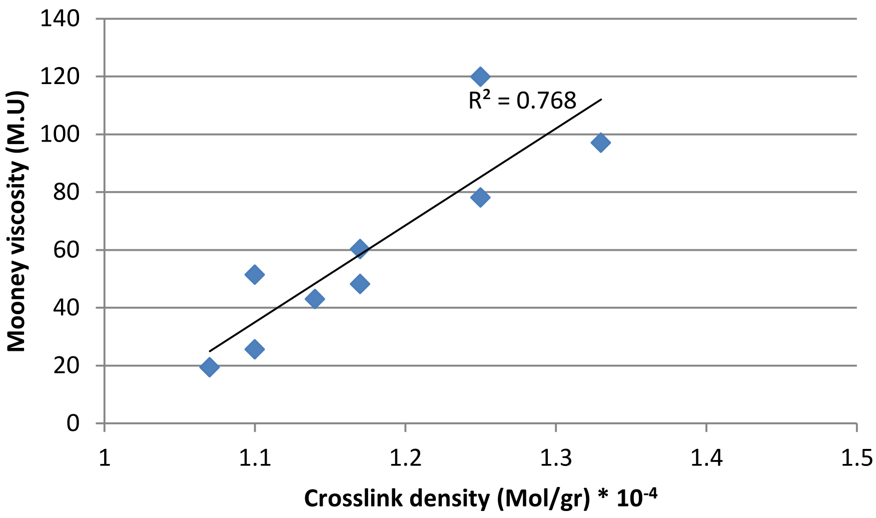

Figure 5.13: Mooney viscosity vs. Crosslink density

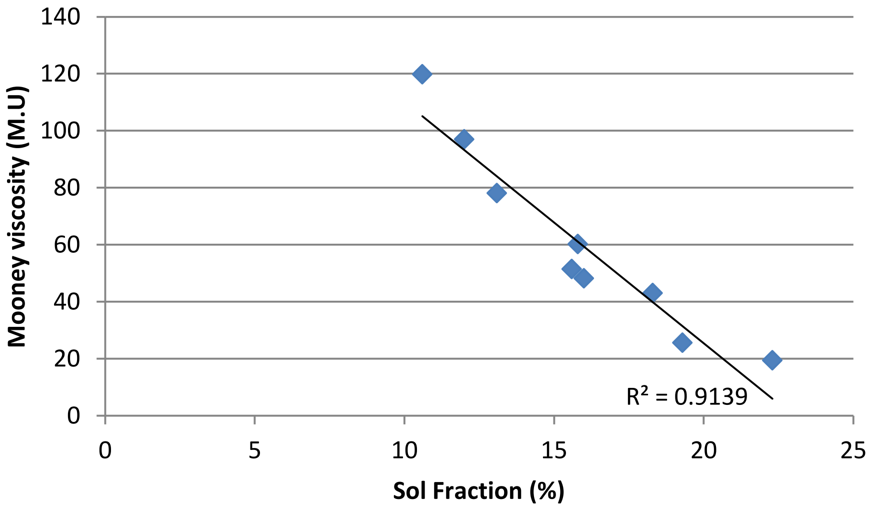

Figure 5.14: Mooney viscosity vs. sol fraction

5.3.3 Tensile properties

Tensile properties measurement results are shown in table 5.12. Pareto charts for tensile strength and elongation at break of the devulcanized rubber are shown in figures 5.15 and 5.16.

One can see that none of the process variables show any significant effect on tensile strength and elongation at break values of the devulcanized rubber.

Table 5.12: Tensile strength, elongation at break, and tensile modulus measurement results

Sample #	Feed rate (lb/hr)	Screw speed (rpm)	Melt Temp (°C)	Tensile strength (Mpa)	Elongation at break (%)	Modulus @100% (psi)
1	100	300	100	10.07	220	455
2	300	450	100	10.54	214	487
3	200	600	100	10.65	225	458
4	300	300	140	10.98	209	521
5	200	450	140	11.23	223	487
6	100	600	140	9.44	223	422
7	200	300	180	10.20	213	482
8	100	450	180	9.56	217	450
9	300	600	180	11.42	225	502

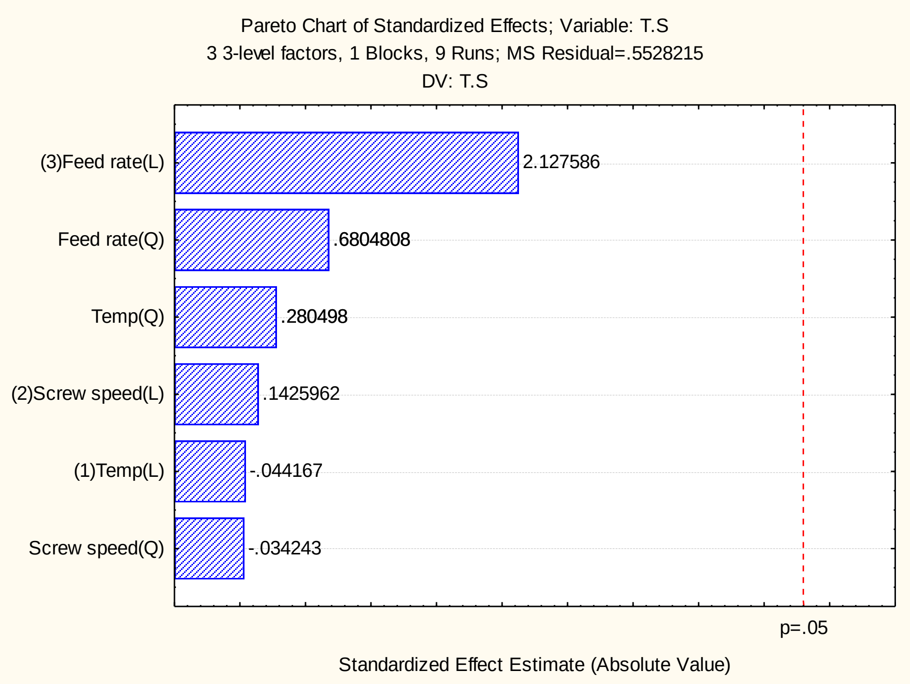

Figure 5.15: Pareto chart of standardized effects for tensile strength

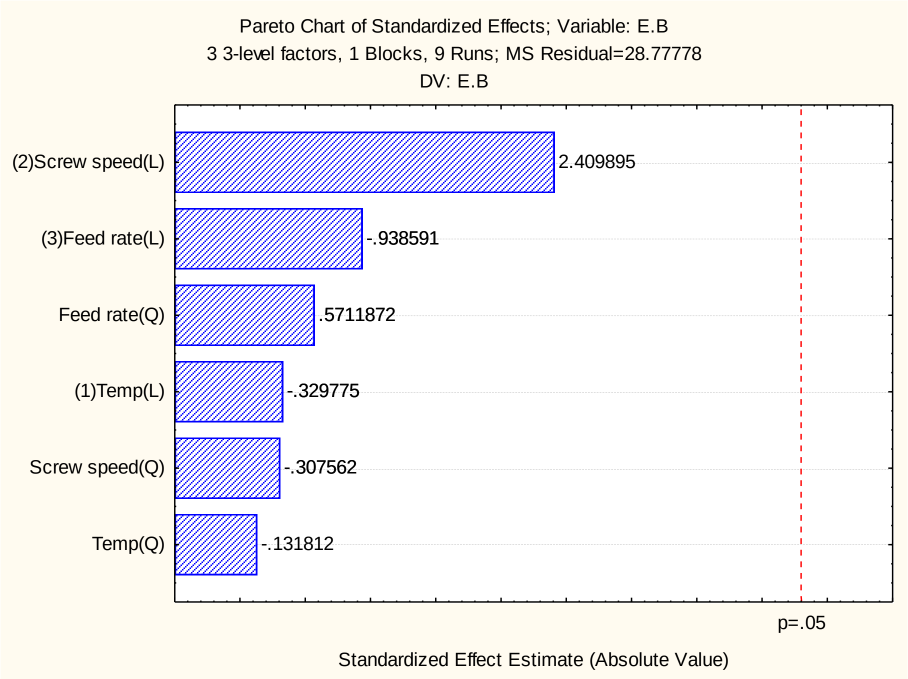

Figure 5.16: Pareto chart of standardized effects for elongation at break

5.4 Concluding remarks:

1) Surface response methodology was used to study and optimize the process variable effects including screw speed, feed rate and process temperature on the final properties of the devulcanized scrap tire rubber.

2) Nine different samples were collected in order to fulfill a three level fractional factorial design (3^{3-1}=9) and crosslink density, sol fraction, Mooney viscosity, curing characteristics, and tensile properties of devulcanized rubber were measured and analyzed.

3) The results obtained for crosslink density analysis show that only feed rate has a significant effect on the sol fraction value and crosslink density of the devulcanized

rubber (in the range of our experiments). As feed rate increases, sol fraction decreases and crosslink density increases.

4) Mooney viscosity measurement results show that feed rate and screw speed are significant variables for the Mooney viscosity value of the devulcanized rubber (in the range of our process variables). Mooney viscosity value decreases as the feed rate decreases and screw speed increases.
5) It was shown that there are correlations between Mooney viscosity and sol fraction and also between Mooney viscosity and crosslink density of devulcanized rubber.
6) In the range of our experiments, none of the independent process variables including screw speed, feed rate, and process temperature, show any significant effect on the tensile properties of devulcanized rubber.

5.5 References

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CHAPTER 6 INCORPORATION OF DEVULCANIZED RUBBER INTO A VIRGIN TIRE TREAD RUBBER COMPOUND

6.1 Introduction

Rapid development and economic growth, have increased the amount of waste polymer material in past decades. One of the most important issues in waste management is recycling the scrap tires. A great amount of rubber waste materials are produced annually and most of it comes from scrap tires. Statistics in 2005 shows that about 299 million scrap tires were generated in the U.S. [1]. Only a small percentage of the waste rubber materials is recycled and made into new products. More recent statistics show that the percentage of consuming of scrap tires in the end use market has increased and for an instance this percentage in 2007 was 89.3% compared to 87% in 2005 [2,3]. Recycling of waste rubber has a certain problem: the crosslinked structure of thermoset rubber. Due to the presence of three dimensional crosslink structures in the rubber products, they cannot be reprocessed by application of heat, as done for thermoplastic materials.

In order to recycle and reuse the vulcanized rubber we need to break down the crosslink bonds. Devulcanization refers to a process in which the crosslink bonds in the vulcanized rubber are cleaved preferentially. Different devulcanization processes are utilizing heat, chemicals, ultrasound, and mechanical stresses in order to break down the crosslink structure of vulcanized rubber and convert the insoluble thermoset rubber into a soft and sticky material which can be processed and vulcanized again.

In the thermo-mechanical devulcanization process, shear and elongational stresses are used to break down the crosslink bonds. Extruders and open mills are common equipment which are suitable for this purpose. The process usually involves heating to increase the cleavage performance of crosslink chemical bonds. However, shear and elongational stresses alongside high temperature can easily break down the main chains of polymer, thus resulting in a significant decrease in molecular mass and poor physical properties. In order to cleave the crosslink bonds selectively, the characteristics of equipment and the processing parameters are very important [4]. Even in the most optimum devulcanization process still some of the main polymer chains are breaking and therefore the physical and mechanical properties of the devulcanized rubber are inferior compared to a virgin rubber compound. Depending on the desired application, devulcanized rubber can be used either by its own or mixed with a new rubber compound. For high demanding applications such as tire tread, the devulcanized rubber must be blended with a virgin compound to maintain the required physical and mechanical properties of the tire compound. Incorporation of the devulcanized rubber in the new tire compounds not only helps to lower the material cost for tire manufacturers but also opens up a big market for the rubber recycling industry since the tire manufacturing market is the biggest rubber consuming market.

Many researchers have studied the effect of incorporation of recycled rubber into new rubber compounds. Li et al. [5] studied the effect of using ground rubber powder and devulcanized rubber in a virgin natural rubber on different properties of the blend. They studied the cure characteristics, swelling behavior, crosslink density, and mechanical properties of the mixture of the virgin natural rubber with ground rubber powder and devulcanized rubber. They showed that the compounds containing devulcanized rubber have better properties than those with ground rubber powder. Another study was conducted by Lamminmaki et al. [6] on the feasibility of devulcanized rubber incorporation in virgin natural rubber. Their results show that the properties of the devulcanized rubber and natural rubber blend improve significantly if devulcanized rubber is used as part of rubber and not as filler. Zhang et al. [7] utilized a self designed pan-milled type mechano-chemical reactor to devulcanize ground tire rubber. Then they blended the obtained devulcanized rubber with a natural rubber compound at different ratios. The curing characteristics and physical and mechanical properties of different blends were investigated. Their results indicate that the mechanical properties of devulcanized rubber and virgin rubber compound are much higher than a ground rubber and natural rubber blend showing the advantages of the partial devulcanization.

In this chapter, a continuous thermo-mechanical devulcanization process with supercritical CO_2 was carried out in an industrial scale twin screw extruder. In order to facilitate the extrusion process supercritical carbon dioxide is used. Supercritical carbon dioxide diffuses into the rubber particles during the devulcanization process and facilitates the process by expanding and softening the rubber particles. The obtained devulcanized rubber was then incorporated in a virgin tire rubber compound and the impact of devulcanized rubber utilization on tire compound performance was studied.

6.2 Experimental

6.2.1 Material

The material used in these experiments was devulcanized rubber obtained from 60 mesh scrap tire tread crumb supplied by Edge Rubber. Retread compound was supplied by AirBoss compounding company from Kitchener, Ontario. It was a natural rubber based compound which is used for retread applications. Sulfur and all other curing chemicals are supplied by AirBoss.

6.2.2 Devulcanization process

A co-rotating and fully intermeshing twin screw extruder from Leistritz Co. model HP was used to perform the devulcanization process. The twin screw extruder had a 50 mm screw diameter and an L/D ratio of 44:1 with eleven heating zones along the extruder barrel. Crumb rubber was fed into the twin screw extruder in order to perform the devulcanization process. Supercritical CO_2 was injected in the extruder to swell the rubber crumb particles and facilitate the devulcanization process. Tire tread crumb was devulcanized under mechanical deformation induced by the rotating screws. A continuous and sticky ribbon of devulcanized rubber was cooled and collected at the die exit of the extruder. The process conditions for this devulcanized rubber are listed in table 6.1.

Table 6.1: Process conditions for devulcanized rubber

Process variable	Description
Starting material	60 mesh tire tread crumb
Screw speed	100 rpm
Feed rate	100 lb/hr
Temperature	180 °C

6.2.3 Sample preparation

Effect of incorporation of devulcanized rubber into a virgin rubber compound for tire application is studied by incorporation of different amounts (10, 20, and 30 %) of devulcanized rubber into a virgin tire compound. The virgin tire compound and devulcanized rubber were first mixed in a Banbury mixer and then curing agents were added during the milling step using a two-roll mill external mixer. A summary of virgin tire compound samples having different amounts of the devulcanized rubber is shown in table 6.2. The first sample (S-R) is the 100 % virgin tire compound or our reference. Ten percent of the reference compound is replaced by the devulcanized rubber in order to prepare the next sample (S-10). For the next two samples, i.e., S-20 and S-30, 20% and 30% of tire compound are replaced by the devulcanized rubber.

Table 6.2: Summary of sample preparation recipe

Formulation (phr)	S-R (Reference)	S-10 (10%)	S-20 (20%)	S-30 (30%)
Virgin Tire compound	100	90	80	70
Devulcanized rubber	0	10	20	30

6.2.4 Characterization of the samples

Mooney viscosity

A Mooney viscometer was used in order to measure the Mooney viscosity of the devulcanized samples. Using a large rotor, Mooney viscosity measurement is conducted at 100°C and MU (ML 1+4 @100°C) is reported for each sample in compliance with ASTM D 1646 [8].

Curing behavior

MDR rheometer was utilized to evaluate the curing behavior of the devulcanized rubber compounds. M_L (minimum torque), M_H (maximum torque), t_{s2} (scorch time), and t_{90} (optimum cure time) were measured according to ASTM D2084. The curing temperature was set at 191 °C and the test time was 3 minutes [9].

Physical and mechanical property measurements

Standard slabs were prepared later by pressing and curing the devulcanized rubber using a hot press at 240 MPa and 148 °C for 20 minutes. Dumbbell shape specimens were cut from the cured standard slabs and the tensile strength, elongation at break, and modulus at 100%, 200%, and 300% extension were measured using an Instron tensiometer according to ASTM D 412-98a. For each sample the average of three replicates was reported [10].

Tear strength was measured using an Instron tensiometer machine. Tear specimens (trousers) were cut from a standard rubber slab, using a special tear die. ASTM D624 describes the test and sample preparation procedures. By pulling the tear specimen, the force required to tear it was measured and the value of the required force per unit of the specimen thickness is reported as KN/m [11]. The hardness of each sample was measured using a shore A hardness durometer in compliance with ASTM D 2240 [12].

Heat buildup and damping

Rubber specimens were subjected to an oscillating compressive stress and the heat generation (temperature rise) by the rubber sample is measured using a Flexometer. This test measures how effectively our sample performs, in terms of heat generation, during its service life when it is subjected to a dynamic force. The test was conducted in accordance with ASTM D 623 [13].

Cut and chip test

Cutting and chipping resistance of the rubber compound was evaluated by a cut and chip tester machine. Rubber specimens in form of a disk were placed on a rotary shaft. The mass loss and diameter reduction of each specimen is measured and reported in percent. The test temperature was 148 °C and the test duration was 45 minutes [14].

6.3 Results and Discussion

6.3.1 Mooney viscosity

Table 6.3 shows the Mooney viscosity measurement results for devulcanized sample, retread compound (S-R), and the other blended samples.

Table 6.3: Mooney viscosity results

Sample	Mooney viscosity (ML 1+4 @ 100°C)
Devulcanized rubber	69.6
Retread compound (S-R)	33.2
S-10 (10%)	34.7
S-20 (20%)	38.5
S-30 (30%)	39.1

Figure 6.1 shows the Mooney viscosity as a function of devulcanized rubber content in virgin rubber compound. A slight increase for Mooney viscosity can be observed when the amount of devulcanized rubber in virgin rubber compound increases, but even when we replace 30% of the reference compound with the devulcanized rubber, the Mooney viscosity of the blend stays in an acceptable range. It should be mentioned that this test is very repeatable and standard deviation for Mooney viscosity measurement is usually below 1 percent.

The Mooney viscosity value of the devulcanized rubber is higher than that of the virgin rubber compound and when we incorporate more devulcanized rubber into the virgin rubber compound, the Mooney viscosity of the mixture increases. The devulcanized rubber is not a fully devulcanized material and there are some cross-links left in its structure. Presence of these cross-link bonds could be the reason for the higher Mooney viscosity of the devulcanized rubber. It was shown in the previous chapters that the Mooney viscosity can be adjusted over a wide range by manipulating process variables such as screw speed and feed rate.

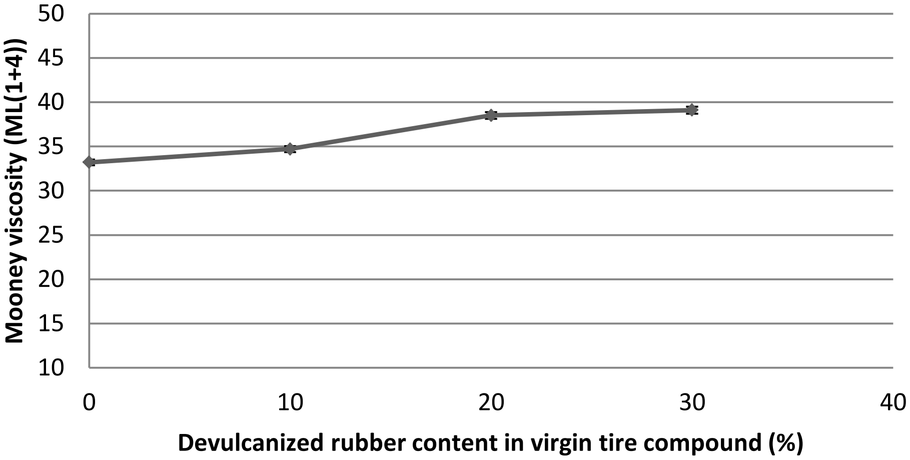

Figure 6.1: Effect of incorporation of the devulcanized rubber on the Mooney viscosity value of the compound.

6.3.2 Curing properties

Curing characteristic measured values including ML (minimum torque), Ts_2 (scorch time), Tc_{90} (optimum cure time) for different samples are shown in table 6.4.

Table 6.4: Curing properties for different samples

Curing characteristic (MDR)	S-R(Reference)	S-10(10%)	S-20(20%)	S-30(30%)
ML	0.97	1.13	1.33	1.44
Ts2	0.71	0.71	0.70	0.70
Tc90	1.15	1.16	1.15	1.13
MH	8.63	8.74	8.66	8.38

Figure 6.2 shows the effect of devulcanized rubber addition on the scorch and optimum cure time. One can see that addition of the devulcanized rubber up to 30 phr does not show any effect on the scorch and optimum cure time.

The minimum torque value (ML) is plotted versus the content of devulcanized rubber in a virgin tire compound (figure 6.3). This value is a measure of the viscosity of the compound at the curing temperature while the Mooney viscosity is the relative viscosity of the compound at mixing and processing temperature. Addition of more devulcanized rubber into virgin tire compound increases the ML value of the blend. This test also is highly repeatable and the standard deviation is usually below 1 %. Again same as Mooney viscosity this behavior can be explained by the fact that there are still some unbroken crosslink bonds left in the devulcanized rubber and due to their presence, the viscosity of the whole blend increases.

The same trend for both Mooney viscosity and ML value can be observed when one compares figures (6.1) and (6.3). This confirms that the viscosity change due to addition of the devulcanized rubber into a virgin tire compound is very similar at both processing and curing temperature. One can see a very good correlation (R^2=0.97) between Mooney viscosity and ML value (figure 6.4).

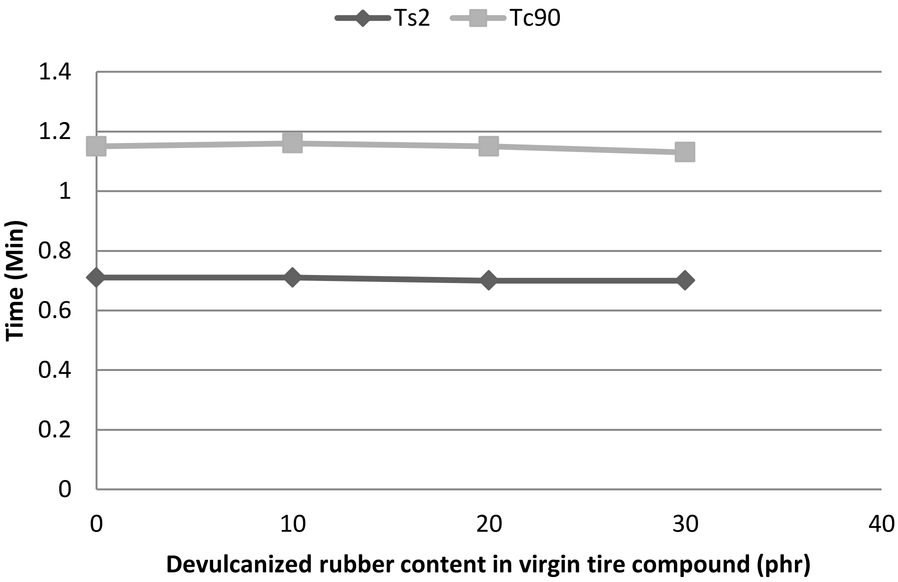

Figure 6.2: Effect of incorporation of devulcanized rubber on the scorch and optimum cure time of a virgin tire compound

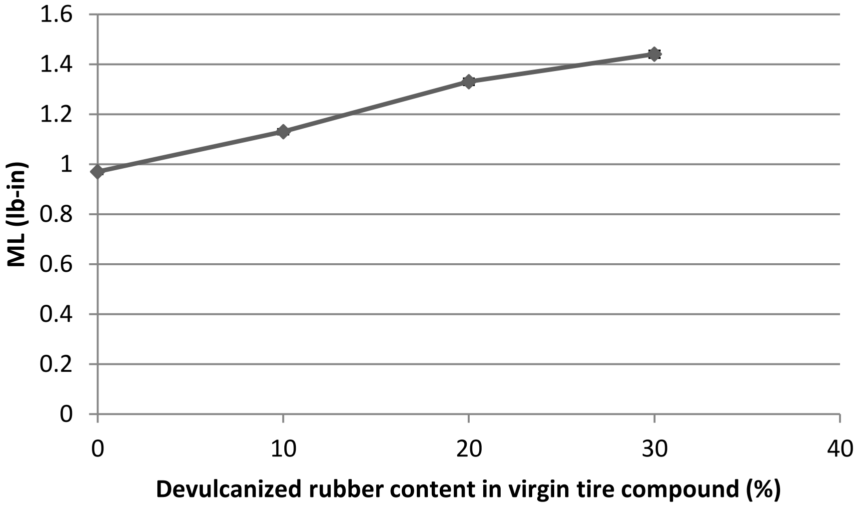

Figure 6.3: Effect of incorporation of devulcanized rubber on the ML value of a virgin tire compound (measured at 191°C).

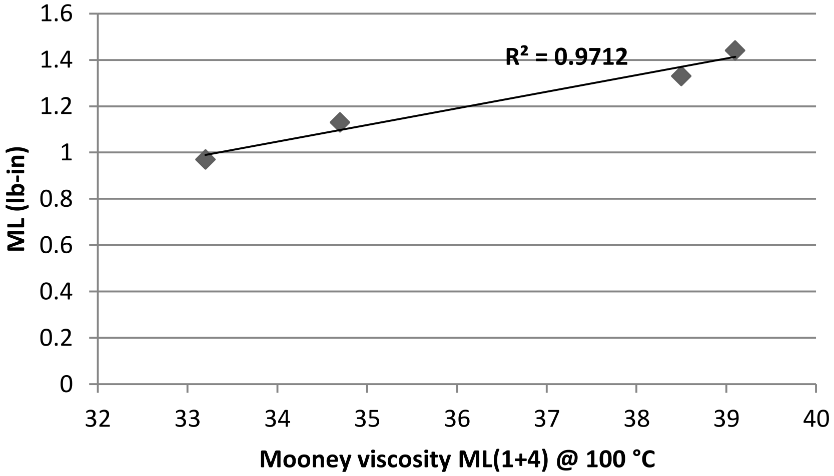

Figure 6.4: ML vs. Mooney viscosity

Maximum torque (M_H) value as a function of devulcanized rubber content is shown in figure 6.5. There is a very slight increase at the beginning (by adding 10 phr devulcanized rubber) and then M_H starts to decrease. The difference is very low so it can be concluded that the M_H value remains almost constant. M_H is a measure of material elasticity and elastic modulus.

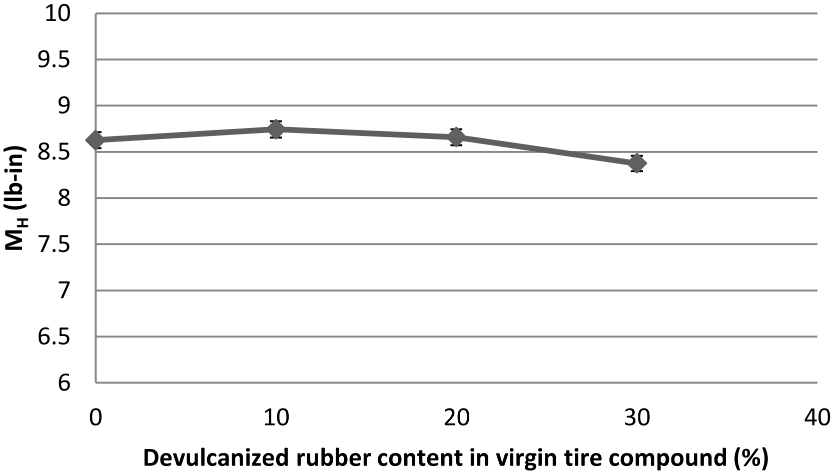

Figure 6.5: Effect of incorporation of devulcanized rubber on the M_H value of a virgin tire compound (measured at 191°C).

6.3.3 Physical and mechanical properties

Tensile properties

Tensile property measurement results are shown in table 6.5. Tensile strength, elongation at break, and modulus at 100%, 200%, and 300% extension are measured and reported.

Table 6.5: Tensile property values for different samples

Tensile property	S-R(Reference)	S-10(10%)	S-20(20%)	S-30(30%)
Tensile strength (Mpa)	20.76	19.82	17.94	17.24
Elongation at break (%)	589	555	500	473
Modulus at 100% (Mpa)	1.75	1.94	2.13	2.09
Modulus at 200% (Mpa)	4.37	4.87	5.26	5.25
Modulus at 300% (Mpa)	8.18	8.90	9.44	9.65

Retentions of tensile strength value and elongation at break percentage are shown in figure 6.6 and 6.7. As can be seen, tensile strength and elongation at break decrease by addition of devulcanized rubber into a virgin tire compound. As mentioned before, the devulcanized rubber is a partially devulcanized material and when it is blended with a virgin compound it cannot form a 100% homogeneous matrix. It was shown in chapter 4 that devulcanized rubber has active double bonds to form cross-links again but in our case apparently the vulcanization reaction does not take place between the devulcanized rubber and virgin rubber compound in a uniform manner. Except for the compatibility problem between the virgin rubber and devulcanized rubber which reduces the tensile performance, the other reason for getting lower tensile properties comes from the fact that the starting rubber material has been through ozone, mechanical and thermal degradation during its service life as a tire and also during the grinding process. Moreover, the devulcanization process is not 100% selective on only sulfur bonds and it also breaks the main chains of the polymer, which results in even more molecular weight reduction. Considering the above facts, it becomes obvious that the devulcanized rubber must have a lower molecular weight compared to a new virgin rubber and as a result it shows lower physical and mechanical properties.

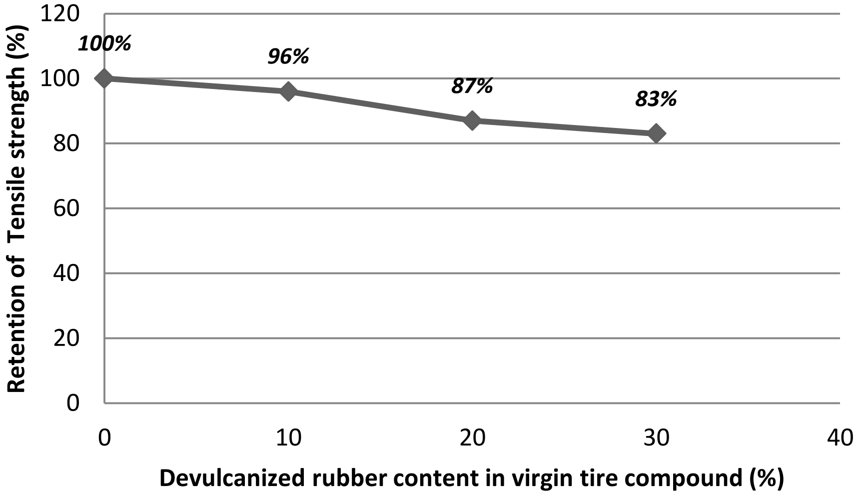

Figure 6.6: Effect of increasing devulcanized rubber content on retention of tensile strength value

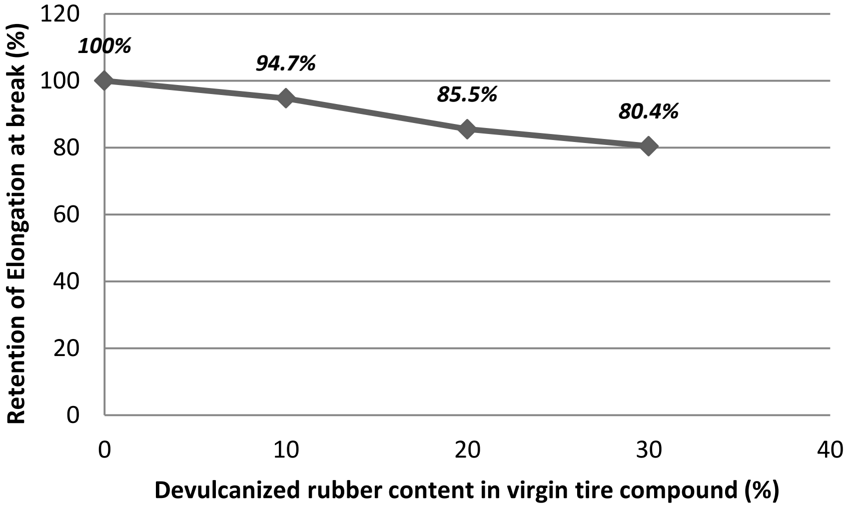

Figure 6.7: Effect of increasing devulcanized rubber content on retention of elongation at break value

Figure 6.8 shows the results for tensile modulus at 100%, 200%, and 300% elongation. By increasing the devulcanized rubber content up to 30 phr all the modulus values show 20% increase. This shows that the presence of devulcanized rubber makes the rubber matrix tougher.

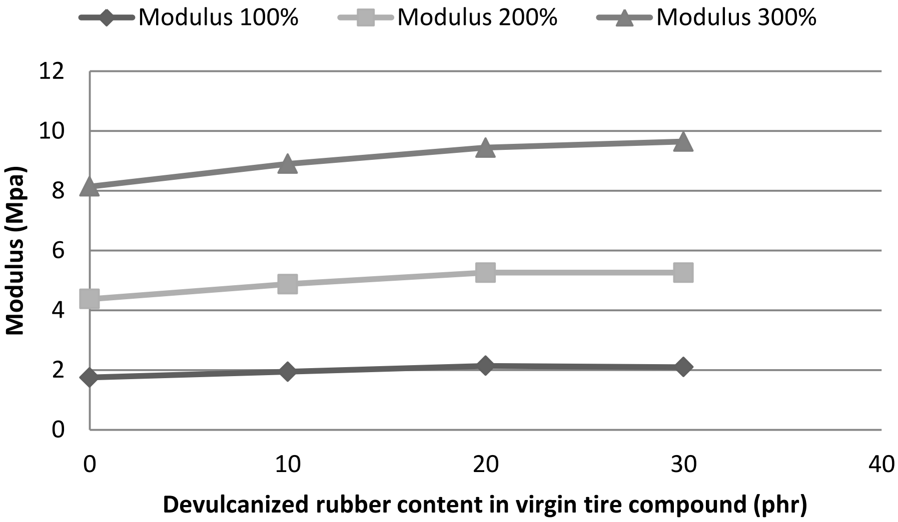

Figure 6.8: Effect of increasing devulcanized rubber content on tensile modulus at 100%, 200%, and 300% extension.

Tear strength

Tear strength measurement results are shown in table 6.6. Retention of tear strength values are shown in Figure 6.9. Tear strength shows a very slight increase at the beginning (when 10 phr devulcanized rubber is added) and then starts to decrease showing around 95 % retention when it comes to 30 phr devulcanized rubber.

Table 6.6: Tear strength measurement results for different samples

Property	S-R(Reference)	S-10(10%)	S-20(20%)	S-30(30%)
Tear strength (KN/m)	90.5	100.96	93.5	86.25

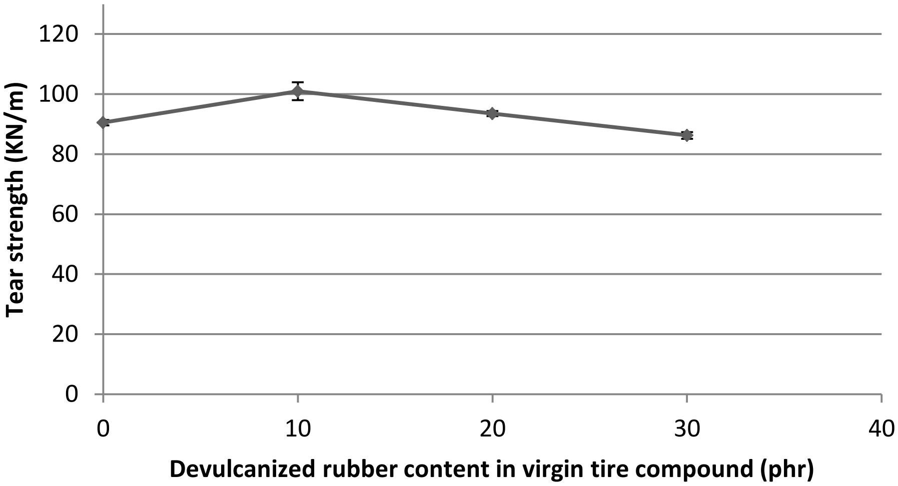

Figure 6.9: Effect of increasing devulcanized rubber content on retention of tear strength

Hardness

Hardness measurement results are shown in Figure 6.10. The hardness values are remaining stable when the amount of devulcanized rubber increases.

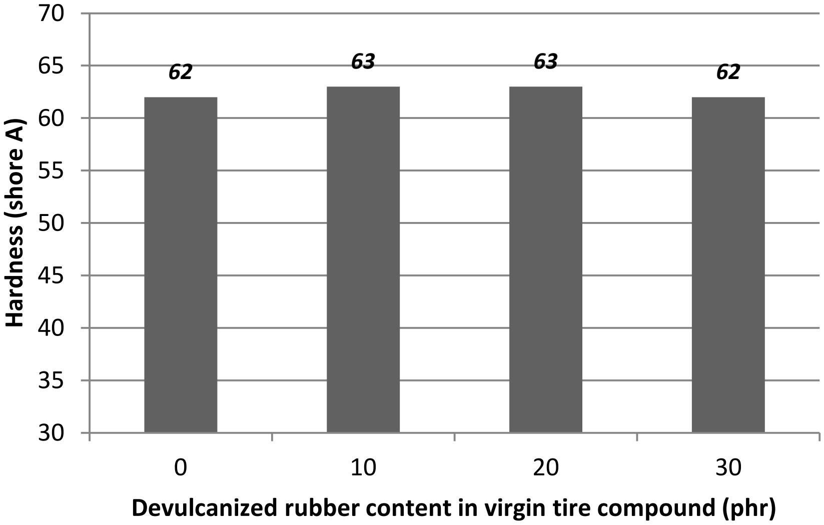

Figure 6.10: Hardness versus devulcanized rubber content

Heat buildup and damping

The flexometer test results are demonstrated in figure 6.11. This figure shows how increasing the devulcanized rubber content in devulcanized rubber and virgin rubber blend affects the damping factor and hysteresis (heat buildup under dynamic stress) of the compound.

Hysteresis is a very important viscoelastic characteristic of a tire compound. “It is the ratio of the rate-dependent or viscous component of rheological behavior to the elastic component of deformation resistance”[13]. During the cyclic deformation and recovery, when tire is rolling under the vehicle, the tire compound exhibits hysteresis. This happens when the energy of recovery is lower than the energy of deformation. This energy dissipates as heat and results in heat buildup in the tire. This is more important for big tires such as truck and off-road tires because the thickness of rubber is higher in the structure of those tires and it is harder to dissipate the generated heat to the surrounding atmosphere. This heat buildup can damage the tire rubber and reduce its service life [14].

As one can see in figure 6.11, hysteresis decreases as content of devulcanized rubber increases in tire tread compound. Since the devulcanized rubber is not 100% devulcanized, presence of the left over crosslink bonds increases the crosslink density of the compound. Increasing the crosslink density increases the elasticity of the rubber compound. Therefore, higher crosslink density results in lower hysteresis or heat buildup in a rubber compound [13].

Tan δ (damping) does not show a distinguishable trend and fluctuates from 0.332 to 0.408.

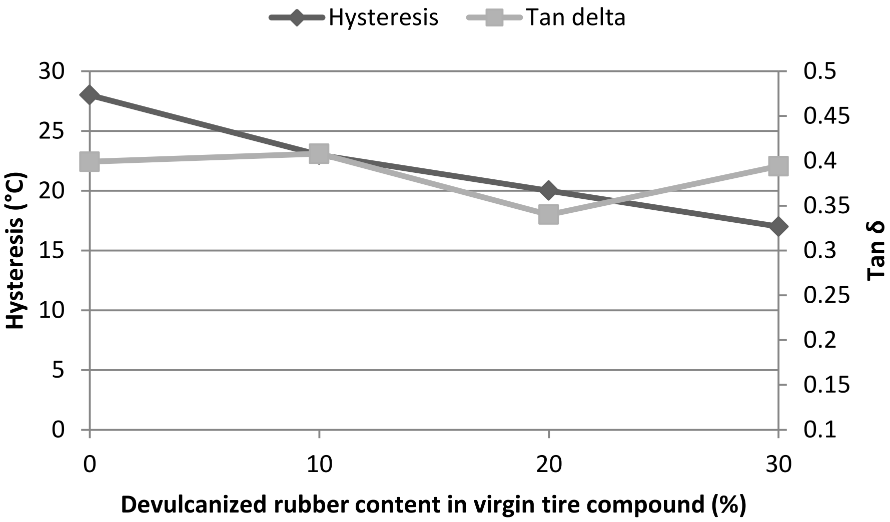

Figure 6.11: Effect of increasing the devulcanized rubber content on hysteresis and damping factor of the tire compound.

Cut and chip test

The cut and chip test results are demonstrated in figure 6.12. This is a special test for tire tread and shows the service performance of a tire tread compound when subjected to sharp objects during its service life.

Percent of mass loss in a cut and chip test increases as the percent of devulcanized rubber increases in a tire tread compound. The mass loss value for the virgin compound is 11%. Adding 10% of the devulcanized rubber into a tire tread compound increases the mass loss of the tread compound by only 0.7%. At 20% loading of devulcanized rubber the mass loss value increases by 2% (compared to the reference compound) and finally when the devulcanized rubber content reaches to 30 % the mass loss value increases by 3.2 %. The effect of incorporation of devulcanized rubber (up to 30%) into a virgin tread compound is not significant and is still in an acceptable range.

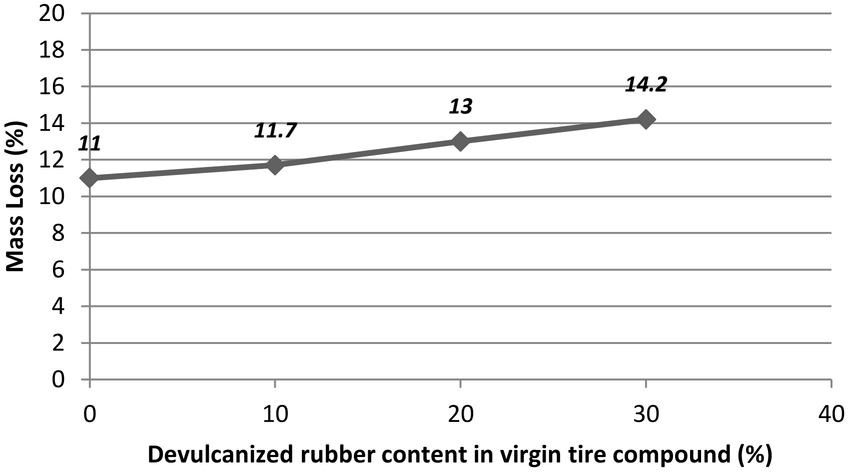

Figure 6.12: Effect of increasing the devulcanized rubber content on the mass loss percentage in a cut and chip test.

6.4 Concluding remarks:

1) Devulcanized rubber obtained from our devulcanization process was incorporated in a virgin tire tread compound and the results show that by addition up to 30 % of devulcanized rubber the Mooney viscosity, hardness, tear strength, curing properties, and mass loss % in a cut and chip test do not change significantly. Tensile strength and elongation at break decrease up to 15 % and 20%, respectively, and heat buildup improves.

2) These results show that devulcanized rubber can be incorporated in a tire compound in order to lower the price without significant deterioration of compound properties.

6.5 References

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CHAPTER 7 DEVULCANIZATION OF EPDM RUBBER: EFFECT OF PROCESS PARAMETERS ON THE DEVULCANIZED SCRAP EPDM RUBBER PROPERTIES

7.1 Introduction

One of the mostly used synthetic elastomers in the automotive industry is EPDM rubber. EPDM stands for ethylene-propylene-diene rubber. Letter M refers to a class of rubber materials in which the polymer backbone is saturated. The common dienes that are used for EPDM manufacturing are: dicyclopentadiene (DCPD), ethylidene norbornene (ENB), and vinyl norbornene (VNB) [1].

Due to the saturated nature of the EPDM backbone, it shows an outstanding ozone resistance. It also has an excellent heat and weather resistance. In addition, EPDM has a very low conductivity which makes it a perfect material for insulation applications. In contrast to other elastomers, EPDM can be filled with a high level of fillers and plasticizers, and still maintain its processability and final properties [2].

EPDM is mostly used in the automotive industry to make seals, radiator hoses, weather strips, and different rubber profiles. Another main application is cable industry for cable insulations. It is also used in the construction industry for roof sheets, membranes, and seals. Moreover, it blends with thermoplastics to make thermoplastic elastomers (TPEs) and thermoplastic vulcanizates (TPVs) [3].

As it was explained in previous chapters, rubber recycling and rubber waste management is a very serious issue for humankind. EPDM rubber, as it is widely used in different industries (ranked second after tire rubber), is one of the major sources of scrap rubbers. In many different studies many researchers have tried to devulcanize EPDM rubber. Mouri et al. published a number of papers [4- 7] regarding the thermo-mechanical devulcanization of EPDM rubber crumb. A new continuous devulcanization technique, based on a shear flow reaction control technology, is utilized to break down the EPDM crosslink bonds selectively. The process is carried out in a twin screw extruder and effects of various parameters, like screw geometry, screw speed and processing temperature were investigated.

Another study was done by Fukumori et al. [8]. They further developed the same technology which was presented by Mouri et al. previously. They utilized a 30 mm twin screw extruder and optimized the devulcanization process by adjusting different parameters like shear stress, temperature and internal pressure. They tried three different screw configurations, three different temperatures and two different screw speeds. Jalilvand and co-workers [9] studied the devulcanization of EPDM in the presence of diphenyl disulfide as a devulcanization agent by using a twin screw extruder. Percent devulcanization, sol fraction, Mooney viscosity and curing behavior of devulcanized EPDM were evaluated. They reported that the Mooney viscosity and sol fraction strongly depended on the barrel temperature and that shear stress has an important role on devulcanization percent.

Sutanto and co-workers [10] performed a series of studies on devulcanization of EPDM rubber in both batch and continuous processes using an amine as the devulcanizing agent. They modeled the kinetics of EPDM devulcanization in a batch mixer using hexadecylamine (HDA) as a devulcanizing agent. The effect of the process parameters such as temperature, shear rate, concentration of devulcanization agent, and devulcanization time on the degree of de-crosslinking was studied. The derived model was verified against experimental results and it was shown that the model can predict the de-crosslinking degree quite adequately.

In previous chapters, we established a continuous, high throughput, and stable devulcanization process using an industrial twin screw extruder. We also studied the effect of different process parameters such as temperature, screw speed, and feed rate on the properties of the devulcanized tire rubber. In this chapter a statistical design is used to investigate the effect of independent process variables on the properties of the devulcanized EPDM rubber. The crosslink structure, gel and sol fractions and degree of devulcanization of the devulcanized EPDM rubber was evaluated. We also measured rheological, physical and mechanical properties to study how changing the process variables can affect these important properties. Screw speed, and feed rate were selected as the process variables, since they directly affect the values of other operating parameters such as shear rate, residence time, and torque. In this design, temperature was kept at a constant value. A central composite experimental design was used to study the effects of process variables. The main objectives for this research were:

9- Establish a high throughput devulcanization process for devulcanization of EPDM rubber.
10- Develop an experimental design to study the effects of main process variables on the properties of the devulcanized EPDM rubber.
11- Analyze the experimental results using statistical methods to investigate how significantly these parameters and their interactions can affect the output properties.
12- Derive a mathematical model using response surface methodology in order to optimize the process.

13- Find out the optimum values for the process parameters to optimize the devulcanized EPDM rubber properties within the range of experiments.

7.2 Experimental

7.2.1 Material and equipment

The starting material that we used was 8-10 mesh rubber crumb obtained from scrap automotive weather strip profiles. These scrap weather strip profiles were supplied by Cooper Standard Automotive from their rejected manufacturing line products. All curing chemicals were supplied by Cooper Standard Automotive from Stratford, ON.

A 50 mm twin screw extruder (Leistritz, NJ) was used for the devulcanization process. Supercritical carbon dioxide was fed into the extruder barrel using a gas injection system from Thar Inc. Rubber crumb was fed into the extruder barrel using a gravimetric feeder. Devulcanized rubber extrudate was immersed into a water bath right after coming out of the die in order to cool it down and it was subsequently dried by air on a conveyor belt prior to collection.

7.2.2 Experimental design

A central composite design with two factors, one block and 10 runs were selected to study the effect of two different input variables, screw speed and feed rate, on the devulcanized rubber properties.

A high value, a low value, and a center value were set for each input variable. The high value was coded as 1, center value as 0, and the low value as -1. A total number of 10 experiments were needed to complete a 2/1/10 central composite design including one replicate for the center point. Table 7.1 shows the variables and their high, low and center values. In order to evaluate the maximum and minimum levels for both variables we conducted screening tests before the set up of the experimental design. The maximum allowable screw speed of the extruder gearbox was 800 rpm. In screening experiments, we found out that the highest throughput which can be obtained for this particular crumb size, extruder size, and screw configuration was 200 lb/hr. The minimum screw speed was determined to be 400 rpm, that the minimum rpm value at which we could process a continuous and stable extrudate at the highest throughput. Using the quantitative design factors we can build a model to calculate each dependent variable:

$$\text{Dependent variable} = C_a A + C_b B + C_{ab} AB + C_{a2} A^2 + C_{b2} B^2 + \text{Intercept} \pm \text{Error} \quad (7.1)$$

where C_a, C_b, and … are regression coefficients for the linear and quadratic forms of each factor and their interactions. A and B are screw speed and feed rate respectively.

Table 7.1: Experimental levels

factor	factor name	low value	center value	high Value
A	Screw speed (rpm)	400	600	800
B	Feed rate (lb/hr)	100	150	200

Ten devulcanization experiments were conducted using the set values for the process variables according to table 7.2. The last run (#10) was a replicate for the centre point (150 lb/hr and 600 rpm).

Table 7.2: Central composite design Matrix

Run	Coded level for Feed rate	Feed rate (lb/hr)	Coded level for Screw speed	Screw speed (rpm)
1	-1	100	-1	400
2	-1	100	0	600
3	-1	100	+1	800
4	0	150	-1	400
5	0	150	0	600
6	0	150	+1	800
7	+1	200	+1	800
8	+1	200	0	600
9	+1	200	-1	400
10	0	150	0	600

7.2.3 Characterization techniques

Crosslink network analysis

In order to analyze the crosslink structures; three different specimens were prepared (~2 grams each) for each devulcanized sample. They were continuously extracted by acetone for 16 hours [11]. After drying to a constant weight they were divided into three different groups. First group of specimens were swelled in toluene for 72 hr to measure the total crosslink density of the rubber sample. Using the Flory-Rehner equation, crosslink density for each devulcanized sample was measured [12]:

$$\vartheta_e = \frac{-[\ln(1-V_r)+V_r+\chi_1 V_r^2]}{[V_1(V_r^{\frac{1}{3}}-V_r)/2]} \qquad (7.2)$$

where V_r, χ_1 , V_1, and ϑ_e are the rubber volume fraction in the swollen sample, rubber-solvent interaction parameter, molar volume of solvent and the crosslink density of devulcanized sample and crumb rubber respectively [13].

ϑ_e = effective number of chains in a real network per unit volume

V_r= volume fraction of polymer in a swollen network in equilibrium with pure solvent

In order to calculate V_r we should use the following relation:

$$V_r=\frac{(\text{weight of the dry rubber})/(\text{density of dry rubber})}{\frac{\text{weight of the dry rubber}}{\text{density of dry rubber}}+\frac{\text{weight of the solvent absorbed by sample}}{\text{density of solvent}}} \qquad (7.3)$$

The calculation below was used to determine the degree of devulcanization:

$$\%\ Devulcanization = [1 - \left(\frac{Crosslink\ density\ of\ devulcanized\ rubber)}{Crosslink\ density\ of\ control\ crumb\ rubber)}\right)] \times 100)] \qquad (7.4)$$

Second group of samples were immersed in n-hexane for 16 hr and then treated by piperidine (0.4M) and propane-2-thiol (0.4M) in n-hexane. This treatment cleaves all poly sulfuric crosslink bonds in 2 hr. For the third group, another chemical reagent (n-hexanthiol (1M) in piperidine) was used to cleave both poly and di-sulfuric crosslink bonds in 48 hours. Using the swelling test and the Flory-Rehner equation, crosslink density of devulcanized samples was evaluated after each treatment. The difference between the density of crosslinks of group 2 samples and group 3 gave us the crosslink density of the di-sulfuric bonds. In a same way, subtractiing the density obtained for group 2 from group 1 gave us the densities of the poly-sulfuric crosslink bonds. The percent of the content for different types of crosslink bonds are reported [14, 15, and 16].

Acetone soluble, Sol, and gel fraction measurement

Acetone extraction is used to remove low molecular weight components such as extended oils, free sulfur, etc. Using Soxhlet apparatus the samples are extracted with acetone for 16 hours in accordance with ASTM D-297 [11]. Then the samples are dried at 70±2 °C in an air oven, for 16±1 h. After drying we need to cool down the samples to room temperature while they are kept in a dessicator. Each sample must be weighted precisely before and after extraction. The percentage of acetone soluble content of each sample can be calculated as below:

$$Acetone\ Soluble\ (\%) = \frac{weight\ before\ extraction - weight\ of\ dried\ sample}{weight\ before\ extraction} \times 100 \qquad (7.5)$$

After acetone extraction, all samples were immersed in toluene for 72 hr and the toluene was refreshed every 24. Before swelling, the weight of each specimen was measured precisely. Samples were then dried in an air ventilated oven at 72°C overnight until the constant weight was reached. The difference between the weight before swelling and after drying gave us the sol content of the devulcanized rubber. The sol and gel fractions can be calculated using the following equations [17]:

$$Sole\ fraction (\%) = \frac{weight\ before\ swelling - weight\ of\ dried\ sample}{weight\ before\ swelling} \times 100 \qquad (7.6)$$

$$Gel\ fraction\ (\%) = 100 - Sol\ fraction\ (\%) \qquad (7.7)$$

Curing behavior

The curing behavior of the devulcanized rubber compounds was evaluated using a MDR Rheometer. M_L (minimum torque), M_H (maximum torque) and t_{90} (optimum cure time) were measured according to ASTM D2084 [18].

Mooney viscosity

The Mooney viscosity of each devulcanized sample was measured by a Mooney viscometer. Using a large rotor, Mooney viscosity measurement is conducted at 100°C and MU (ML 1+4 @100°C) is reported for each sample in compliance with ASTM D 1646 [19].

Physical and mechanical properties measurements

A Haake mixer was used to mix the sulfur and curing chemicals with the devulcanized rubber. The curing recipe is shown in table 7.3. Each sample was milled later to achieve a more uniform and homogeneous mixture using a lab scale two roll mill. After milling a slab pre-form was cut for each sample and then all samples were pressed and cured at 160 °C for 10 minutes, using a hydraulic hot press. Using a standard die cut, dumbbell shape specimens were cut from the cured standard slabs and the tensile strength and elongation at break were measured using an Instron tensiometer according to ASTM D 412-98a. For each sample the average of three replicates was reported [20].

Table 7.3: Ingredients for re-vulcanization of devulcanized EPDM samples

Ingredients	***phr***
Devulcanized Rubber	100
Zinc oxide	8.05
Stearic Acid	0.93
Sulfur	1.5
MBT	0.14
TMTD	0.61
MBTS	0.82
DPTT	0.89
ZDBC	0.33

7. 3 Results and Discussion

The results for all of the experiments are shown in table 7.4.

Table 7.4: Test results for EPDM samples.

Run	Feed rate (lb/hr)	Screw speed (rpm)	Acetone soluble %	Sol Fraction %	devulcanization degree (%)	Mooney Viscosity	ML (lb-in)	MH (lb-in)	Tensile Strength (Mpa)	Elongation at Break (%)
1	100	400	21.88	6.62	59.30	82.9	1.60	10.13	9.46	177
2	100	600	18.43	9.94	80.36	51.5	0.83	7.28	10.24	197
3	100	800	17.13	15.61	87.81	40.9	0.43	5.50	8.76	175
4	150	400	20.14	8.39	50.36	97.3	1.78	9.86	9.49	183
5	150	600	17.43	11.39	68.73	80.7	1.14	9.31	9.56	185
6	150	800	14.67	15.41	86.22	55.9	0.60	7.68	10.31	195
7	200	800	19.11	10.19	70.15	76.5	0.98	9.04	9.58	186
8	200	600	21.37	8.6	44.18	87.4	1.48	9.71	9.85	187
9	200	400	20.46	8.4	35.63	91.1	2.65	10.33	8.82	177
10	150	600	19.92	8.7	54.47	73.3	1.14	9.28	9.83	187

7.3.1 Devulcanization degree

Crosslink density of the starting crumb was measured (ϑ_e = 12.63 mole/cm^3) and devulcanization degree was calculated using formula (7.3).

Analysis of variance was done in Statistica® and the ANOVA table was obtained (table 7.5).

Table 7.5: ANOVA table for degree of devulcanization.

ANOVA; Var.: Devulcanization degree; R-sqr=.92824;, 2 factors, 1 Blocks, 10 Runs;					
Factors	**SS**	**df**	**MS**	**F**	**p**
(1)Feed rate (lb/hr)(L)	1001.400	1	1001.400	19.35234	0.011699
Feed rate (lb/hr)(Q)	15.860	1	15.860	0.30651	0.609319
(2)Screw speed (rpm)(L)	1629.922	1	1629.922	31.49872	0.004952
Screw speed (rpm)(Q)	27.136	1	27.136	0.52441	0.509052
1L by 2L	9.052	1	9.052	0.17494	0.697238
Error	206.983	4	51.746		
Total SS	2884.469	9			

Figure 7.1 shows the Pareto chart for devulcanization degree. Pareto chart is a very helpful tool to identify which process parameter has significant effect on our dependent variable. From figure 7.1 it is clear that only linear effects of screw speed and feed rate have significant effect on the degree of devulcanization. Quadratic effects and interactions show no significant effect on the degree of devulcanization. One also can see from the ANOVA table that only screw speed (linear) and feed rate (linear) have p-values smaller than 0.05, which shows that these factors have a significant effect.

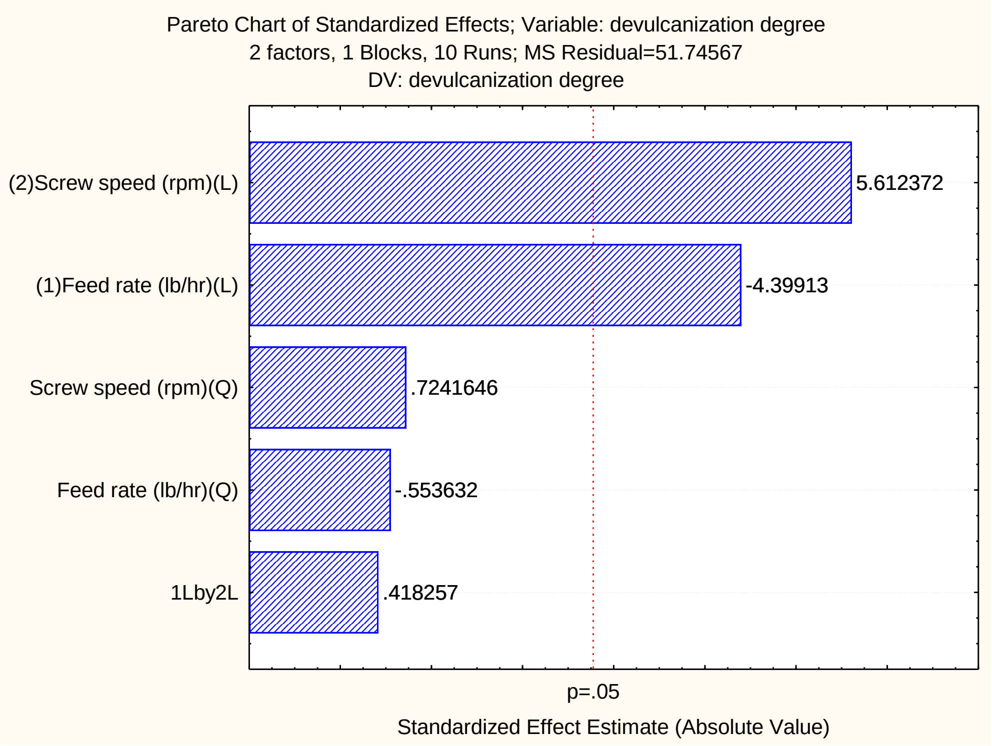

Figure 7.1: Pareto chart for devulcanization degree

Regression coefficients for degree of devulcanization are shown in table 7.6. Using the regression coefficients from table 7.6 and equation (1), a regression model can be built for degree of devulcanization.

Table 7.6: Regression coefficients for degree of devulcanization

Factors	Regressn - Coeff.
Mean/Interc.	**73.31750**
(C_b)Feed rate (lb/hr)(L)	**-0.03578**
(C_{b2})Feed rate (lb/hr)(Q)	**-0.00104**
(C_a)Screw speed (rpm)(L)	**-0.04246**
(C_{a2})Screw speed (rpm)(Q)	**0.00009**
(C_{ab})1L by 2L	**0.00015**

By plotting the predicted values for degree of devulcanization obtained from the regression model versus the observed values from the experimental data, we can validate our model. Figure 7.2 shows that the regression model for the devulcanization degree fits the experimental data very well.

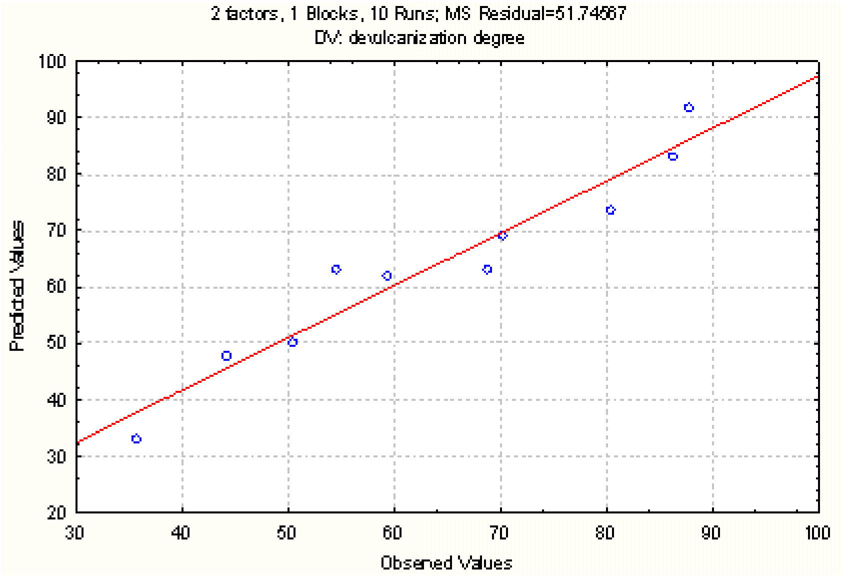

Figure 7.2: Predicted values against observed values (dependent variable: Degree of devulcanization)

A contour plot and a response surface plot were prepared in Statistica® using the regression model for degree of devulcanization.

The response surface of the regression model is presented in figure 7.3. The effect of screw speed and feed rate on degree of devulcanization is shown in this 3D plot.

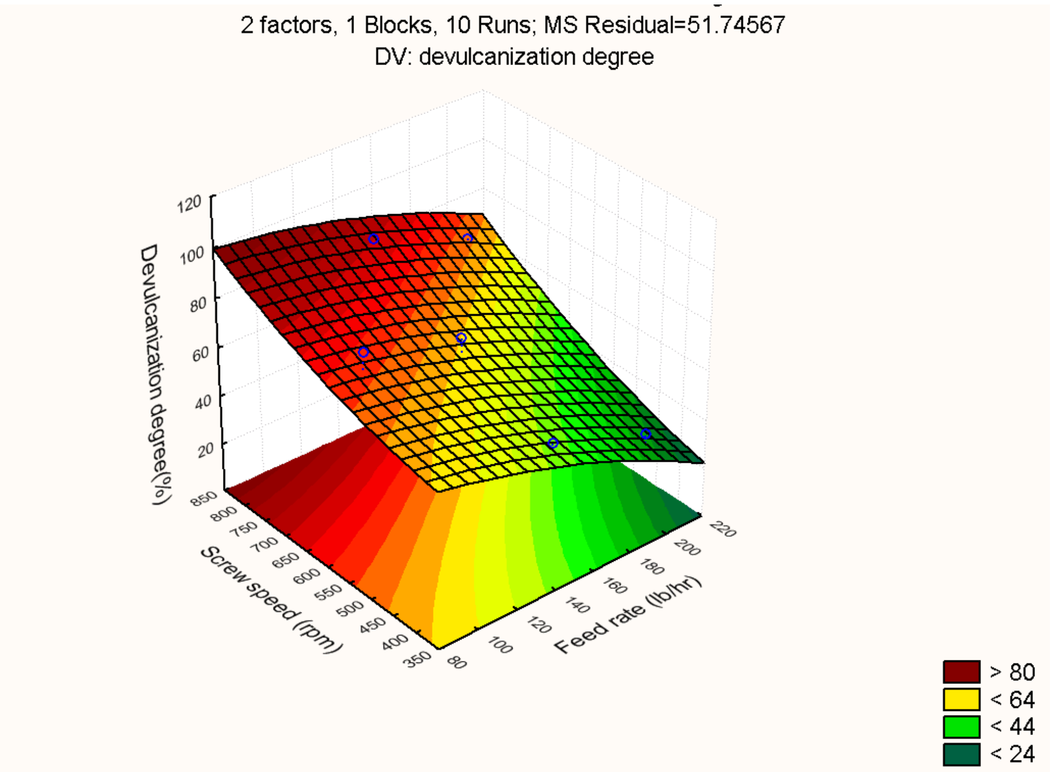

Figure 7.3: Response surface plot (fitted response) for degree of devulcanization as a function of screw speed and feed rate.

The maximum value for devulcanization degree can be obtained at the highest screw speed and lowest feed rate and vice versa. The effect of the screw speed is more significant than that of the feed rate. Increasing the screw speed increases the shear rate in the extrusion process, which increases the cleavage of the rubber crosslink bonds. Therefore, the crosslink density of the rubber decreases and the percent of devulcanization increases. On the other hand, higher feed rate results in lower residence time in the extrusion process. As a matter of fact, when the feed rate increases, the devulcanized rubber experiences a shorter residence time and as a consequence, the percent of devulcanization decreases.

A contour plot (figure 7.4) is a useful tool to determine the operational conditions to achieve the desired devulcanization degree. For a more convenient and practical evaluation of the required screw speed and feed rate values to obtain a certain devulcanization degree, one can choose a certain color which corresponds to a certain value for degree of devulcanization and then read the required screw speed and feed rate for that certain degree of devulcanization.

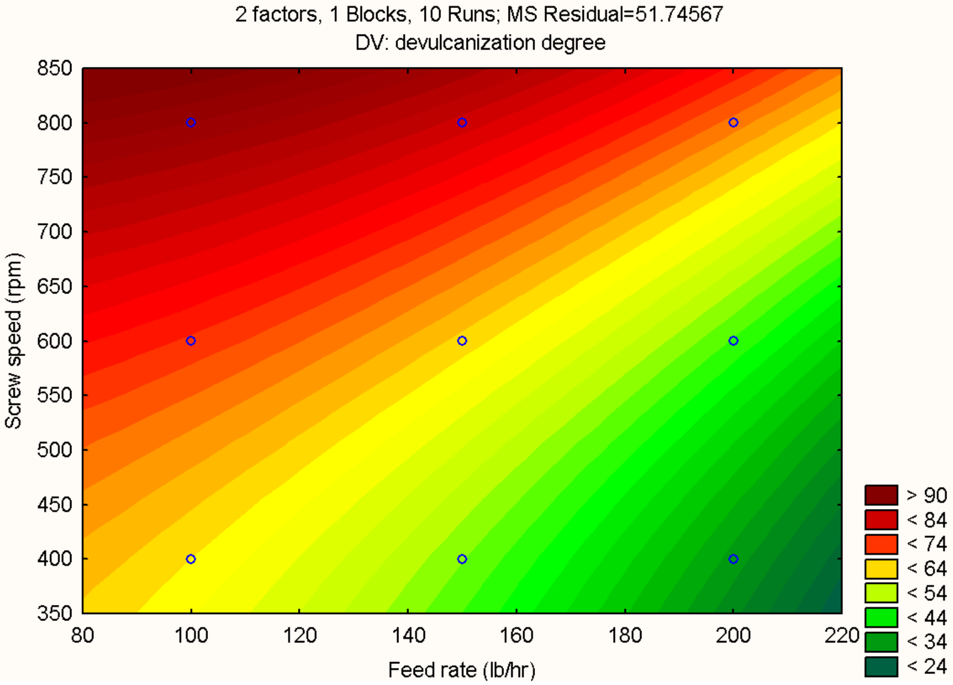

Figure 7.4: Contour plot (fitted response) for degree of devulcanization as a function of screw speed and feed rate.

7.3.2 Acetone soluble and sol fractions

Acetone soluble fraction

Analysis of variance for acetone soluble fraction is shown in table 7.7. It can be seen that only screw speed has a significant effect on the acetone soluble fraction of the devulcanized EPDM rubber since its p-value is less than 0.05.

Table 7.7: ANOVA table for acetone soluble fraction.

ANOVA; Var.: Acetone soluble %; R-sqr=.81486;, 2 factors, 1 Blocks, 10 Runs;

Factors	**SS**	**df**	**MS**	**F**	**p**
(1)Feed rate (lb/hr)(L)	2.04167	1	2.04167	1.02091	0.369459
Feed rate (lb/hr)(Q)	7.60206	1	7.60206	3.80131	0.123000
(2)Screw speed (rpm)(L)	22.31082	1	22.31082	11.15622	0.028833
Screw speed (rpm)(Q)	1.11090	1	1.11090	0.55549	0.497495
1L by 2L	2.89000	1	2.89000	1.44511	0.295613
Error	7.99942	4	1.99985		
Total SS	43.20744	9			

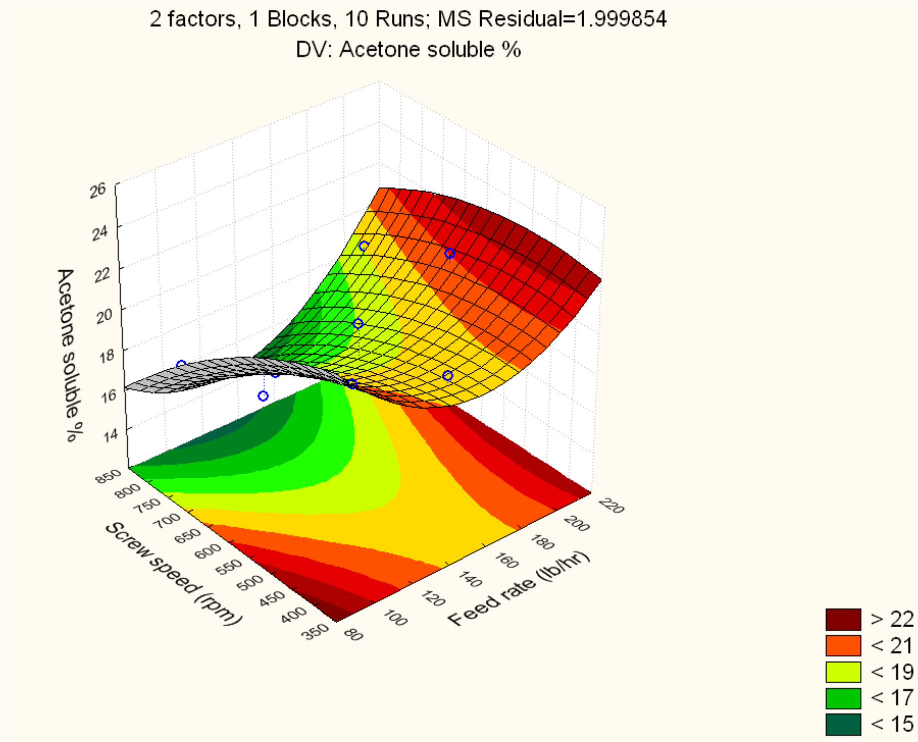

Figure 7.5: Response surface plot (fitted response) for acetone soluble fraction as a function of screw speed and feed rate.

In figure 7.5 the response surface for acetone soluble fraction as a function of screw speed and feed rate is shown. A minimum for soluble fraction percentage is observable for feed rate value between 140 lb/hr and 180 lb/hr when the screw speed is at its lowest value. At higher screw speeds, this minimum shifts to lower feed rates (100 to 140 lb/hr). Increasing the screw speed value decreases the acetone soluble fraction overall. However, a more significant effect at lower feed rates can be observed by screw speed compared to higher feed rate values. Lower acetone soluble fraction means: 1- More small molecule materials such as processing oils, and sulfur component volatiles have been removed from the rubber in form of volatiles during the devulcanization process, or 2- Less degradation of the rubber crumb in the devulcanization process.

Sol fraction

The ANOVA table for sol fraction analysis is shown in table 7.8. For this dependent variable (sol fraction) the linear effect of screw speed and also the interaction of feed rate and screw speed are significant factors.

Table 7.8: ANOVA table for sol fraction of devulcanized EPDM rubber.

ANOVA; Var.: Sol %; R-sqr=.93815;, 2 factors, 1 Blocks, 10 Runs;					
Factors	**SS**	**df**	**MS**	**F**	**p**
(1)Feed rate (lb/hr)(L)	4.13340	1	4.13340	3.26484	0.145072
Feed rate (lb/hr)(Q)	3.94767	1	3.94767	3.11813	0.152179
(2)Screw speed (rpm)(L)	52.80667	1	52.80667	41.71027	0.002960
Screw speed (rpm)(Q)	4.12300	1	4.12300	3.25662	0.145456
1L by 2L	12.96000	1	12.96000	10.23668	0.032917
Error	5.06414	4	1.26604		
Total SS	81.88225	9			

A 3D response surface plot is shown for sol fraction against screw speed and feed rate (figure 7.6). The highest sol fraction can be obtained at the highest screw speed and lowest feed rate while the lowest one can be achieved at the lowest feed rate and lowest rpm.

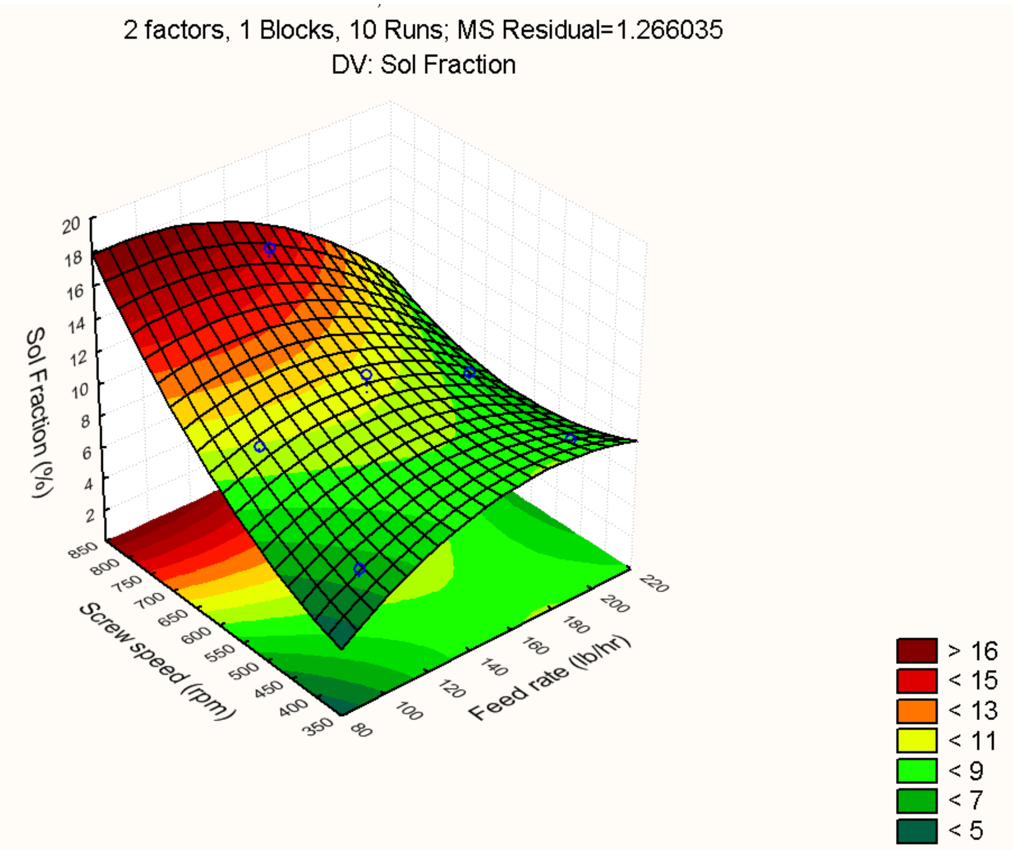

Figure 7.6: Response surface plot (fitted response) for sol fraction as a function of screw speed and feed rate

7.3.3 Analysis of crosslink structure

Using the thiol chemical probes and the method which was explained in the experimental section, the poly and di-sulfur bonds were selectively cleaved and the crosslink density values of each type of the sulfur bonds were calculated and reported individually. All measurement results are shown in table 7.9.

Table 7.9: Total, mono-sulfur, di-sulfur, and poly- sulfur crosslink density measurement results

Sample	Feed rate	screw speed	Total CRD *10-4	mono-S CRD *10-4	% of mono-S	Di-S CRD *10-4	% of Di-S	poly-S CRD *10-4	% of poly-S
1	100	400	5.14	2.05	40	2.26	44	0.825	16
2	100	600	2.48	0.818	33	0.593	24	1.07	43
3	100	800	1.54	0.923	60	0.243	16	0.372	24
4	150	400	6.27	2.17	34.5	1.45	23	2.65	42.5
5	150	600	3.95	1.3	33	1.17	30	1.48	37
6	150	800	1.74	0.691	40	0.262	15	0.784	45
7	200	800	3.77	0.942	25	1.16	31	1.67	44
8	200	600	7.05	2.1	30	3.21	45	1.75	25
9	200	400	8.13	1.21	15	5.93	73	0.995	12
10	150	600	5.75	5.75	48	2.74	24	1.64	28
EPDM Rubber crumb			12.63	0.685	5.4	0.967	7.6	10.98	87

Figures 7.7 and 7.8 show the total, mono-sulfuric, di-sulfuric, and poly-sulfuric cross link bonds as a function of screw speed. In figures 7.7 and 7.8 the feed rate is 100 lb/hr and 200 lb/hr respectively.

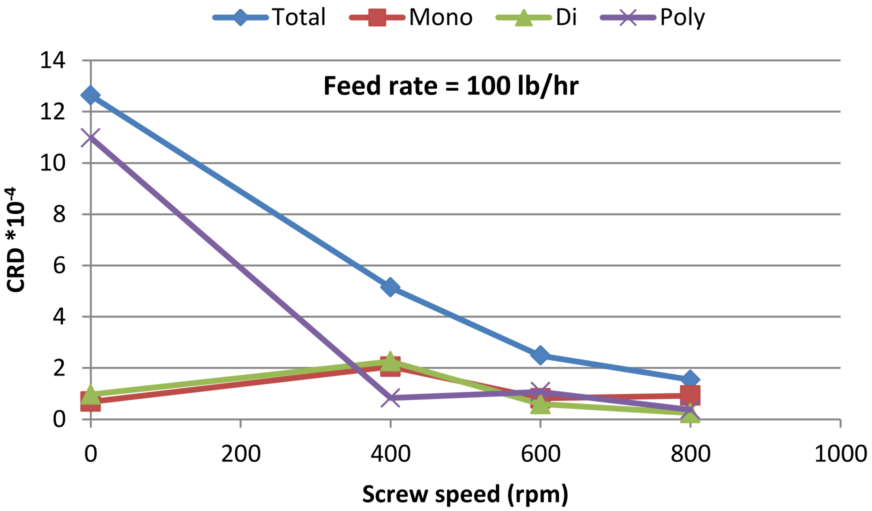

Figure 7.7: Total, Mono-sulfidic, Di-sulfidic, and Poly-sulfidic crosslink densities of the devulcanized rubber as a function of screw speed (feed rate=100 lb/hr and temperature=140°C)

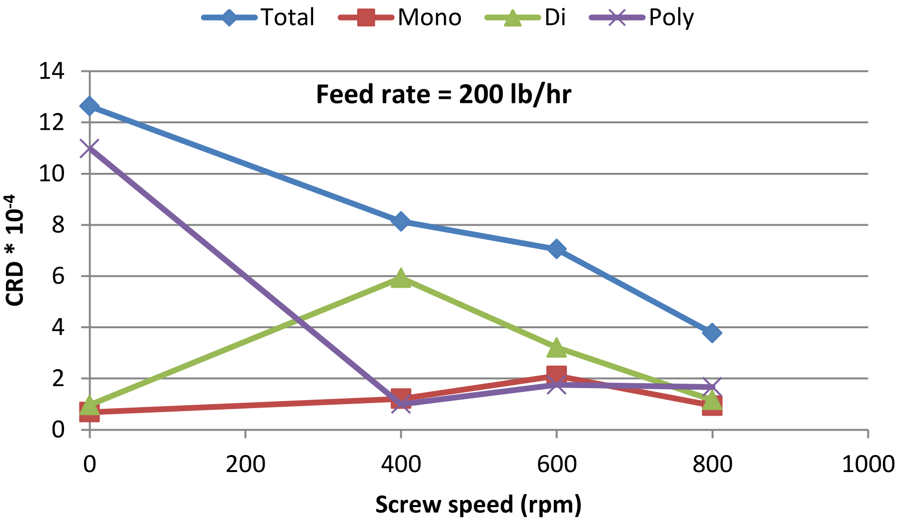

Figure 7.8: Total, Mono-sulfidic, Di-sulfidic, and Poly-sulfidic crosslink densities of the devulcanized rubber as a function of screw speed (feed rate=200 lb/hr and temperature=140°C)

From the presented data it can be seen that EPDM devulcanization results in a significant reduction of total crosslink density for both 100 lb/hr and 200 lb/hr feed rates, although this reduction is much higher for the lower feed rate. Also, it is observed that the cleavage of poly sulfur bonds governs the total crosslink density reduction. At 100 lb/hr (figure 7.7) the devulcanization process decreases the poly sulfur bonds dramatically, while only a very slight increase for both mono and di-sulfur bonds is observed. As the screw speed increases to 600 rpm, the crosslink density of poly sulfur bonds increases very slightly, and the crosslink density for both di – and mono sulfide bonds decreases. Finally as we increase the screw speed from 600 rpm to 800 rpm, the crosslink densities of both di and poly sulfur bonds decrease while the crosslink density of mono sulfidic bonds only slightly increases.

The effect of feed rate on the crosslink structure of the devulcanized rubber at two different screw speeds is shown in figures 7.9 and 7.10.

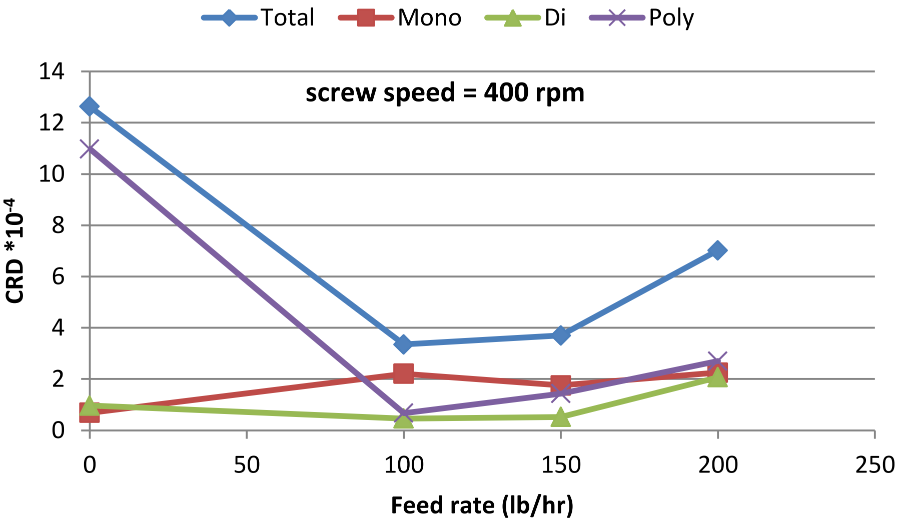

Figure 7.9: Total, Mono-sulfidic, Di-sulfidic, and Poly-sulfidic crosslink densities of the devulcanized rubber as a function of feed rate (screw speed =400 rpm and temperature=140°C)

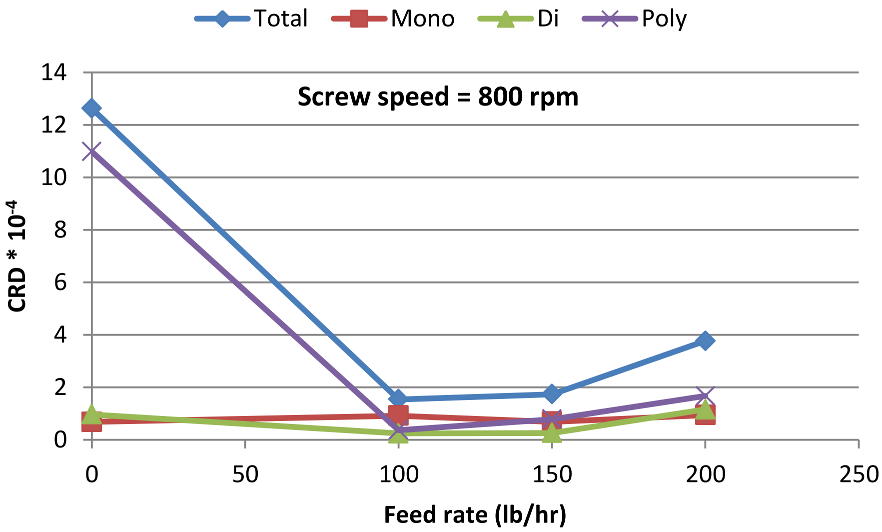

Figure 7.10: Total, Mono-sulfidic, Di-sulfidic, and Poly-sulfidic crosslink densities of the devulcanized rubber as a function of feed rate (screw speed =800 rpm and temperature=140°C)

Again a significant decrease for total crosslink density can be observed at the minimum feed rate (100 lb/hr) due to the devulcanization process which is mostly governed by cleavage of poly sulfur bonds. As we increase the feed rate from 100 lb/hr to 200 lb/hr (for both rpms) the total crosslink density increases. As it was explained before, higher values for screw speed impose higher shear rate and mechanical force on the rubber material during the extrusion process which results in more crosslink cleavage and higher degree of devulcanization. On the contrary, higher feed rates result in shorter residence time, which can affect the crosslink cleavage in a negative manner and decrease the degree of devulcanization.

Mouri et al. [4-7] have shown that thermo-mechanical devulcanization of EPDM rubber decreases the crosslink density and the gel fraction of the rubber in a significant manner. They have also shown that during the devulcanization reaction, the effect of the heat first converts the polysulfide and di-sulfide crosslinks into mono sulfide crosslinks and finally the mechanical forces breaks the monosulfidic bonds. Another study has shown that the amount of polysulfidic bonds decreases in a significant manner by only heat treatment while the proportion of monosulfidic bonds increases significantly [21].

The strength of the different crosslink bonds has been shown that increases as following: poly-sulfidic (-Sx-), di-sulfidic(-S-S-), and mono-sulfidic(C-S) [22]. Based on this fact it can be argued, that during the extrusion process heat and mechanical shear forces can preferentially cleave the weaker polysulfidic bonds. For example, in figure 7.7, at 100 lb/hr and 400 rpm, the content of polysulfidic bonds decreases significantly while the contents of both di and mono sulfur bonds slightly increase. Increasing the screw speed from 400 rpm to 600 rpm, cleaves more di and mono sulfidic bonds and decreases the content of those crosslinks. Further screw speed increasing, results in cleaving more di and poly sulfidic bonds. In the next graph (figure 7.8), due to higher feed rate and lower residence time the reduction in total crosslink density is not as significant as in the previous figure, but still the trend and significance of poly sulfidic bond reduction is the same. At the lowest screw speed (400 rpm) some of the cleaved polysulfidic bonds convert into di sulfidic crosslinks, which increases the content of di sulfidic bonds in the rubber network. Increasing the screw speed further to 600 rpm and finally 800 rpm cleaves the created di sulfidic bonds and reduces their contents close to their original values. It must be mentioned that these reactions are very complicated and very hard to follow, because all the sulfidic bonds including poly, di, and mono type, can transform to each other or form some cyclic sulfur structures during the devulcanization process [21].

In order to determine how selectively the sulfur bonds are broken in our devulcanization experiments we applied Horikx's theory [23]. This theory considers a relation between the degree of devulcanzation of the gel part and sol fraction content of the devulcanized rubber after the devulcanization process. Selective cleavage of sulfur bonds is expressed by equation (7.8) while the random chain scission is expressed by equation (7.10). Equation (7.9) is used to calculate γ_1 and γ_2.

$$1-\frac{v_{e2}}{v_{e1}}=1-\frac{\gamma_2\left(1-s_2^{1/2}\right)^2}{\gamma_1\left(1-s_1^{1/2}\right)^2} \qquad (7.8)$$

$$s=1/(1+\gamma-\gamma s)^2 \qquad (7.9)$$

$$1-\frac{v_{e2}}{v_{e1}}=1-\frac{\left(1-s_2^{1/2}\right)^2}{\left(1-s_1^{1/2}\right)^2} \qquad (7.10)$$

In which [23]:

v_e= Crosslink density of the gel fraction

S= sol fraction content

γ= crosslinking index

1= index used for the values before devulcanization

2= index used for the values after devulcanization

Using the Horikx theory, measured and theoretical values for sol fraction as a function of degree of devulcanization are plotted in figure 7.11. The solid line curve represents the theoretical data for the random chain scission, the dashed line shows the theoretical curve for selective crosslink cleavage, and small circles are measured values for our devulcanized samples.

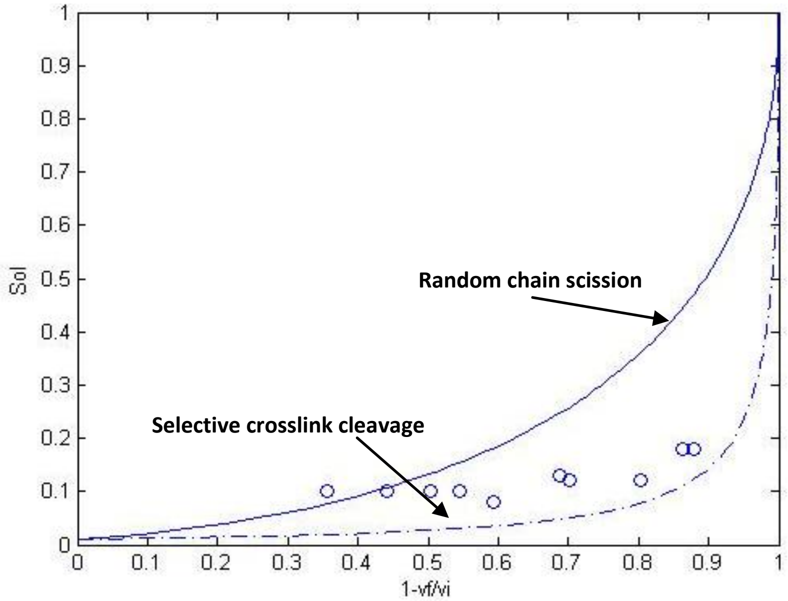

Figure 7.11: Sol fraction content versus degree of devulcanization of devulcanized rubber

From the data presented in figure 7.11, one can see that the devulcanized samples with high degree of devulcanization (more than 50%) are devulcanized through a selective crosslink cleavage mechanism while the other samples are closer to the random chain scission theoretical curve. Using the degree of devulcanization contour plot (figure 7.4) we are able to adjust the process variables in order to get the best devulcanization performance through the selective crosslink cleavage mechanism.

7.3.4 Mooney viscosity

Table 7.10 shows the Mooney viscosity measurement results for devulcanized EPDM samples.

Table 7.10: Mooney viscosity results

Sample	Feed rate	screw speed	Mooney viscosity
1	100	400	82.9
2	100	600	51.5
3	100	800	40.9
4	150	400	97.3
5	150	600	80.7
6	150	800	55.9
7	200	800	76.5
8	200	600	87.4
9	200	400	91.1
10	150	600	73.3

Analysis of variance results are shown in table 7.11. From the p-value results, one can see that only linear effects of two independent factors (feed rate & screw speed) are significant. The p-value for quadratic effects and interaction is larger than 0.005, showing that those factors have no significant effect on Mooney viscosity value of the devulcanized EPDM rubber.

Table 7.11: ANOVA table for Mooney viscosity

ANOVA; Var.: Mooney viscosity; R-sqr=.94856;, 2 factors, 1 Blocks, 10 Runs;					
Factors	**SS**	**df**	**MS**	**F**	**p**
(1)Feed rate (lb/hr)(L)	1058.682	1	1058.682	26.77358	0.006632
Feed rate (lb/hr)(Q)	67.501	1	67.501	1.70707	0.261424
(2)Screw speed (rpm)(L)	1600.667	1	1600.667	40.48014	0.003128
Screw speed (rpm)(Q)	7.322	1	7.322	0.18517	0.689140
1L by 2L	187.690	1	187.690	4.74660	0.094886
Error	158.168	4	39.542		
Total SS	3074.545	9			

Regression coefficients for Mooney viscosity results are demonstrated in table 7.12. Using equation (7.1), a model can be built to predict the Mooney viscosity value in the range of the experiment independent values. Predicted values from this model are drawn against the experimental values to evaluate the goodness of the model (figure 7.12). One can see that there is a good correlation between the predicted and experimental or measured values.

Table 7.12: Regression coefficients for Mooney viscosity of devulcanized EPDM

Factors	Regressn - Coeff.
Mean/Interc.	**114.2500**
(C_b)Feed rate (lb/hr)(L)	**0.5001**
(C_{b2})Feed rate (lb/hr)(Q)	**-0.0022**
(C_a)Screw speed (rpm)(L)	**-0.2376**
(C_{a2})Screw speed (rpm)(Q)	**0.0000**
(C_{ab})1L by 2L	**0.0007**

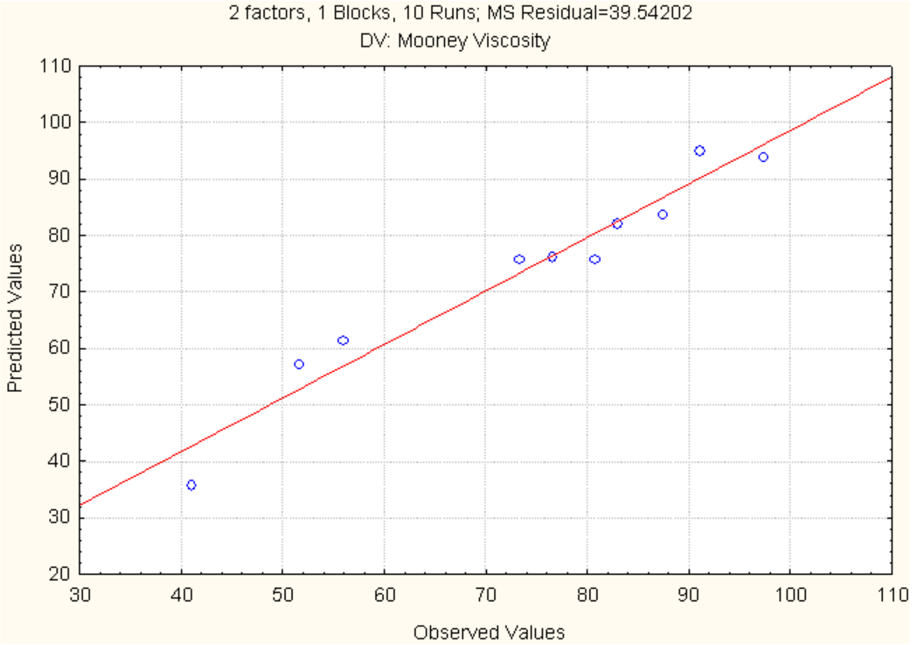

Figure 7.12: Predicted values against observed values (dependent variable: Mooney viscosity)

Using the regression model, a 3D response surface plot was prepared in Statistica® for the effect of screw speed and feed rate on the Mooney viscosity of devulcanized EPDM (figure 7.13). The surface plot shows that screw speed decreases Mooney viscosity, while the feed rate has a positive effect on Mooney viscosity. The effect of screw speed is much higher in lower feed rates and also the effect of feed rate is more significant at higher rpm. Similar to crosslink density discussion, higher screw speeds impose higher shear rate on the material, result in lower Mooney viscosity and also crosslink density values. On the other hand, at higher feed rate, residence time decreases and therefore Mooney viscosity increases.

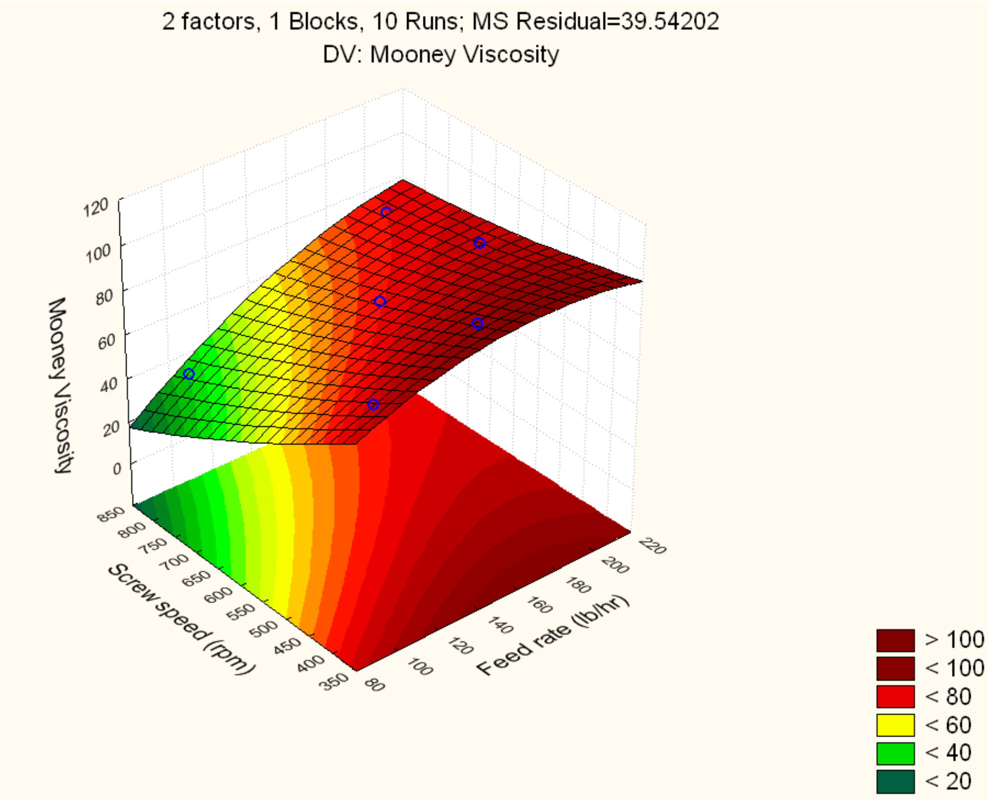

Figure 7.13: Response surface plot (fitted response) for Mooney viscosity as a function of screw speed and feed rate.

7.3.5 Tensile properties

Table 7.13 shows the tensile measurement results. For each sample, tensile strength and elongation at break were measured and reported. As it was explained in the experimental section, the tensile properties were measured using a re-cured sample. The tensile strength and elongation at break values for the original material (before devulcanization) were 7.7 Mpa and 347% respectively. Compared to the obtained results after devulcanization and re-curing (using the same curing recipe) tensile strength for all samples has increased. On the contrary, values for elongation at break have decreased compared to those of the original compound. Owing to the fact that the devulcanized EPDM is not 100% de-crosslinked and still, some leftover crosslink bonds are present in the matrix of the polymer, therefore after re-curing the devulcanized rubber, the total crosslink density value of the compound increases. Increasing the crosslink density increases the tensile strength and decreases the elongation at break [24].

Tables 7.14 and 7.15 show the analysis of variance results for both tensile strength and elongation at break, respectively. From the p-values in both ANOVA tables, it is clear that neither screw speed nor feed rate has any significant effect on the tensile strength and elongation at break of the devulcanized EPDM rubber.

Table 7.13: Tensile property measurement results

Sample	Feed rate	screw speed	Tensile strength (Mpa)	Elongation at break (%)
1	100	400	9.46	177.43
2	100	600	10.24	197.25
3	100	800	8.76	175.20
4	150	400	9.49	183.89
5	150	600	9.56	185.76
6	150	800	10.31	195.34
7	200	800	9.58	186.58
8	200	600	9.85	187.27
9	200	400	8.82	177.82
10	150	600	9.83	187.86

Table 7.14: ANOVA table for tensile strength

ANOVA; Var.: Tensile strength; R-sqr=.57664;, 2 factors, 1 Blocks, 10 Runs;					
Factors	**SS**	**df**	**MS**	**F**	**p**
(1)Feed rate (lb/hr)(L)	0.006989	1	0.006989	0.028042	0.875135
Feed rate (lb/hr)(Q)	0.174780	1	0.174780	0.701303	0.449465
(2)Screw speed (rpm)(L)	0.127722	1	0.127722	0.512484	0.513634
Screw speed (rpm)(Q)	0.405936	1	0.405936	1.628813	0.270933
1L by 2L	0.534469	1	0.534469	2.144554	0.216931
Error	0.996887	4	0.249222		
Total SS	2.354699	9			

Table 7.15: ANOVA table for elongation at break

ANOVA; Var.: Elongation at break; R-sqr=.47402;, 2 factors, 1 Blocks, 10 Runs;					
Factors	**SS**	**df**	**MS**	**F**	**p**
(1)Feed rate (lb/hr)(L)	0.5460	1	0.54602	0.008695	0.930193
Feed rate (lb/hr)(Q)	29.9806	1	29.98056	0.477402	0.527607
(2)Screw speed (rpm)(L)	53.8601	1	53.86009	0.857653	0.406813
Screw speed (rpm)(Q)	90.5011	1	90.50114	1.441115	0.296190
1L by 2L	30.1950	1	30.19503	0.480817	0.526212
Error	251.1975	4	62.79938		
Total SS	477.5818	9			

7.4 Concluding remarks

1) EPDM rubber crumb obtained from scrap automotive weather strips were devulcanized under stress in the twin screw extruder with supercritical CO_2.
2) Using an industrial scale twin screw extruder, a reasonably high throughput (up to 200 lb/hr) of devulcanized rubber was obtained and the process was continuous and totally stable.
3) The effects of process independent variables (screw speed and feed rate) at a constant temperature on different properties of devulcanized EPDM rubber were studied.
4) Feed rate and screw speed showed significant effects on the degree of devulcanization. Increasing the screw speed value increases the degree of devulcanization while increasing the feed rate value decreases the degree of devulcanization.

5) Sol fraction of the devulcanized rubber was significantly affected by screw speed and interaction of screw speed and feed rate. The effect of feed rate on sole fraction of the devulcanized EPDM is not significant.
6) Devulcanization process decreases the crosslink density of the scrap EPDM crumb significantly while this process is primarily governed by poly sulfur bond cleavage.
7) Mooney viscosity of the devulcanized EPDM was affected by both screw speed and feed rate in a significant manner. Results show that increasing the screw speed value, decreases the devulcanized rubber’s Mooney viscosity. In contrast, the effect of feed rate on the Mooney viscosity value of the devulcanized EPDM is positive and increasing the feed rate increases the Mooney viscosity of the EPDM devulcanized rubber.
8) Within the range of our experiments, screw speed and feed rate did not show any significant effect on the final tensile properties of the devulcanized EPDM rubber.

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CHAPTER 8. CONCLUDING REMARKS AND RECOMMENDATIONS

8.1 Concluding remarks

In this thesis, the devulcanization of scrap tire rubber and scrap EPDM rubber were studied. The effects of different process variables on the final properties of the devulcanized rubber were evaluated. Devulcanized scrap tire rubber was incorporated into virgin rubber compounds and the impact of its presence on different properties of the blend evaluated and discussed. Specific concluding remarks are presented at the end of each chapter. Here in this section a summary of principal conclusions is presented.

In chapter 4, ground tire rubber crumb was devulcanized under stress using a twin screw extruder with supercritical CO_2. By selecting a proper screw design, we managed to establish a high throughput devulcanization process which was totally stable. The devulcanized rubber obtained from the supercritical CO2 assisted devulcanization process, was re-vulcanized by adding curing agents, and it showed reasonable rheological, physical and mechanical properties

In chapter 5, a surface response methodology was used to study the process variables effects including screw speed, feed rate and process temperature on the final properties of the devulcanized scrap tire rubber. The results obtained for crosslink density analysis showed that only feed rate has a significant effect on the sol fraction value and crosslink density of the devulcanized rubber (within the scope of our experiments). As feed rate increases, sol fraction decreases and crosslink density increases. Mooney viscosity measurement results showed that only feed rate has a significant effect on the Mooney viscosity value of the devulcanized rubber (within the range of our process variables). Mooney viscosity value increases as the feed rate increases. Although, feed rate has positive effect on the tensile strength values and screw speed also shows the same effect on the elongation at break of the devulcanized rubber, none of these independent process variables show any significant effect on the tensile properties of devulcanized rubber. Using the Horikx theory, sol fraction as a function of degree of devulcanization was plotted. All our experimental data were close to the selective crosslink cleavage theoretical line, showing that the devulcanization mechanism for our devulcanized tire rubber is a selective crosslink cleavage.

In chapter 6, we studied the effect of incorporation of devulcanized rubber on the final properties of a virgin tire tread compound. Results showed that by addition of up to 30 % of devulcanized rubber the Mooney viscosity, hardness, tear strength, curing properties, and mass loss % in a cut and chip test do not change significantly. Tensile strength and elongation at break decrease up to 15 % and 20% respectively, and heat buildup improves. It can be concluded that devulcanized rubber can be incorporated in a tire compound in order to lower the price without significant deterioration of compound properties.

In chapter 7, EPDM rubber crumbs obtained from scrap automotive weather strips were devulcanized under stress in the twin screw extruder with supercritical CO_2. Using an industrial scale twin screw extruder, a reasonably high throughput (up to 200 lb/hr) of devulcanized EPDM rubber was obtained and the process was continuous and totally stable. At a constant temperature, The effects of screw speed and feed rate on different properties of devulcanized EPDM rubber were studied. Feed rate and screw speed showed significant effects on the degree of devulcanization in a linear manner. Increasing the screw speed value increases the degree of devulcanization while increasing the feed rate value decreases the degree of devulcanization. Sol fraction of the devulcanized rubber was significantly affected by screw speed and interaction of screw speed and feed rate. Devulcanization process decreases the crosslink density of the scrap EPDM crumb significantly while this process is mainly governed by poly sulfuric bond cleavage. Using the Horikx theory, sol fraction was plotted against the degree of devulcanization. Some of our experimental data were close to the random chain scission curve while the rest of them were close to the selective cleavage theoretical line. It was concluded that only samples with high degree of devulcanization (>60%) were devulcanized through a selective crosslink cleavage mechanism. This suggests that low feed rate and high screw speed values which can lead us to higher degree of devulcanization can also change the devulcanization mechanism from random chain scission to a selective crosslink cleavage.

Mooney viscosity of the devulcanized EPDM was affected by both screw speed and feed rate in a significant manner. Results showed that increasing the screw speed, decreases the devulcanized rubber's Mooney viscosity. In contrast, the effect of feed rate on the Mooney viscosity value of the devulcanized EPDM is positive and increasing the feed rate increases the Mooney viscosity of the EPDM devulcanized rubber. Again like what we observed for devulcanized tire rubber results, screw speed and feed rate did not show any significant effect on the final tensile properties of the devulcanized EPDM rubber, within the range of our experiment design. Compared to starting EPDM compound, the re-vulcanized rubber showed higher tensile strength and lower elongation at break. This observation can be explained by the fact that re-cured devulcanized rubber has higher crosslink density compared to the original virgin compound. Higher crosslink density increases the tensile strength and decreases the elongation at break.

8.1 Recommendations for future work

1- Study of molecular structure of the devulcanized rubber was done in this thesis. Crosslink density, sol and gel fraction of each devulcanized sample were measured and effect of different process parameters on the final value of these properties were also evaluated. For the future step the molecular weight and distribution of the sol part using a GPC machine can be evaluated. This can provide us with very valuable information about the molecular structure of devulcanized rubber.

2- In this thesis we showed how scrap tire and scrap EPDM rubber can be devulcanized and incorporated into new rubber compounds. For the next step it is recommended to try to devulcanize other types of rubbers such as Nitrile Rubber (NBR), butyl rubber, silicone rubber, etc.

3- The devulcanized rubber was incorporated into virgin tire compounds without any change in the recipe of the virgin tire compound. The recipe of the tire compound including its curing chemicals package can be adjusted in a way that incorporation of devulcanized rubber shows lower negative impacts on the final properties of the blend and in particular the physical and mechanical properties. Usage of an appropriate compatibilizer also needs to be examined.

4- Mathematical model can be established to relate different independent process variables to the devulcanized rubber properties. Theoretical data from the model can be verified with the experimental data that are provided in this thesis. Also a mathematical model can be developed to calculate the residence time and the amount of shear force for each screw design and finally those values can be related to the final properties of the devulcanized rubber.

5- For this research we used a co-rotating intermeshing twin screw machine. Different type of extruder machines such as counter rotating and non-intermeshing can be used and their performance evaluated.

6- Thermoplastic elastomer materials can be prepared by blending the devulcanized rubber with thermoplastic material such as polypropylene and polyethylene. The main objectives are lowering the final cost of these materials and also consuming more recycled rubber.

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