MODIFIED SOYBEAN OIL-EXTENDED SBR COMPOUNDS AND VULCANIZATES

A Thesis
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

Jiaxi Li
May, 2014
MODIFIED SOYBEAN OIL-EXTENDED SBR COMPOUNDS AND VULCANIZATES

Jiaxi Li

Thesis

Approved:  
Advisor  
Dr. Avraam I. Isayev

Accepted:  
Department Chair  
Dr. Robert Weiss

Committee Member  
Dr. Thein Kyu

Dean of the College  
Dr. Stephen Cheng

Committee Member  
Dr. Younjin Min

Dean of the Graduate School  
Dr. George Newkome

Date
ABSTRACT

Petroleum oils are widely used as plasticizers in rubber products, however, they are nonrenewable and in some cases harmful to the environment. Renewable soybean oil (SO) was studied to replace the petroleum oils in rubber products, but their performance properties are inferior. Therefore, the present study is an attempt to improve mechanical properties of the SO extended rubber through modification of SO. In this study, SBR compound and 60 phr of carbon black (CB) filled SBR compounds and vulcanizates containing 30 phr of SO, modified soybean oil (MSO) and naphthenic oil (NO) were prepared. The MSO is norbornylized SO prepared through the reaction of SO and dicyclopentadiene of different ratios at a pressure of 0.14-0.21 MPa and 240°C. The power consumption and discharge temperature during compounding, curing behavior, thermal properties, gel fraction, crosslink density, bound rubber fraction, mechanical properties, dynamic properties and the reaction between the SO, MSO and the curatives were evaluated. It was found that SBR/MSO compounds and vulcanizates showed a lower T_g than those of SBR/NO leading to a better low temperature performance, and better thermal stability. SBR/MSO compounds also indicated a shorter curing time and a lower maximum torque compared to those of the SBR/NO compounds. The bound rubber fraction of the CB-filled SBR/MSO compounds decreased with an increase of the modification level. Swelling test indicated that with an increase of the modification level, the gel fraction of the SBR/MSO vulcanizates slightly increased and the crosslink density decreased. Unfilled
and CB-filled SBR/MSO vulcanizates exhibited lower modulus and higher tensile properties in comparison with unfilled and CB-filled SBR/NO vulcanizates. After adjusting the curative recipe, SBR/MSO vulcanizates indicated an increased modulus and showed a similar strength and an increase of the elongation at break by more than 100% compared to the SBR without any oil. The SBR/MSO vulcanizates also had similar abrasion resistance and a lower hardness than the SBR/NO vulcanizate. The performance predictors from the dynamic analysis of CB-filled SBR/MSO vulcanizates indicated better traction but higher rolling resistance compared to the CB-filled SBR/NO vulcanizate. After adjusting the recipe, CB-filled SBR/MSO vulcanizates exhibited similar traction and lower rolling resistance than the CB-filled SBR/NO vulcanizate. The addition of MSO to SBR showed improved thermal and mechanical properties and had a promising possibility to replace petroleum oils in the rubber.
ACKNOWLEDGEMENTS

The author would like to express sincere gratitude to his advisor, Dr. Avraam I. Isayev, for his excellent instructions on research and courses. The author would like to express his thanks to his parents for their support. The author is also grateful to Mr. Keyuan Huang, Mr. Jing Zhong, Mr. Tian Liang, Mr. Xiang Gao and Mr. Ivan Mangili for their selfless and patient help.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>x</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>xiii</td>
</tr>
</tbody>
</table>

## CHAPTER

### I. INTRODUCTION

1

### II. LITERATURE SURVEY

4

2.1 Vegetable oils

4

2.1.1 Culinary uses

4

2.1.2 Hydrogenated oils

6

2.1.3 Industrial uses

6

2.1.4 Vegetable oil-based fuel

7

2.2 Soybean oil

8

2.2.1 Polymers from unmodified soybean oil

9

2.2.2 Epoxidized soybean oil

11

2.2.3 Polyols and polyurethanes

13

2.3 Bio-based oils in rubber

13

### III. EXPERIMENTAL

19

3.1 Materials

19

3.2 Compounding

23
3.3 Vulcanization ................................................................................................................. 25

3.4 Characterization ........................................................................................................... 26
  3.4.1 Rheological Properties .............................................................................................. 26
  3.4.2 Measurement of thermal properties .......................................................................... 27
  3.4.3 Measurement of mechanical properties ................................................................... 28
  3.4.4 Measurement of dynamic mechanical properties ...................................................... 29
  3.5.5 Swelling test ............................................................................................................ 30

IV. RESULTS AND DISCUSSION ......................................................................................... 33

  4.1 Processing Characteristics ............................................................................................ 33

  4.2 Rheological Properties ................................................................................................ 35
    4.2.1 Rheological properties of various SBR gums ......................................................... 35
    4.2.2 Rheological properties of various CB-filled SBR compounds ......................... 38
    4.2.3 Rheological properties of various unfilled SBR vulcanizates ......................... 41
    4.2.4 Rheological properties of various CB-filled SBR vulcanizates ...................... 45

  4.3 Thermal Properties ...................................................................................................... 49
    4.3.1 TGA analysis ............................................................................................................ 49
    4.3.2 DSC analysis .......................................................................................................... 55

  4.4 Curing behaviors .......................................................................................................... 62
    4.4.1 Unfilled SBR ............................................................................................................ 62
    4.4.1 CB-filled SBR ......................................................................................................... 65

  4.5 Swelling test .................................................................................................................. 67
    4.5.1 Gel Fraction ............................................................................................................ 67
    4.5.2 Crosslink density ................................................................................................... 69
4.5.3 Bound rubber fraction................................................................. 71

4.6 Reaction of MSO ............................................................................ 73

4.7 Mechanical properties................................................................. 78

4.7.1 Tensile properties ........................................................................ 78

4.7.2 Hardness and abrasion ............................................................... 84

4.8 DMA test and performance predictors ........................................ 87

V. SUMMARY ......................................................................................... 101

REFERENCES ....................................................................................... 104
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Fatty acid chemical structures of vegetable oils</td>
<td>5</td>
</tr>
<tr>
<td>2.2 Chemical structure of soybean oil</td>
<td>9</td>
</tr>
<tr>
<td>3.1 Preparation of MSO</td>
<td>20</td>
</tr>
<tr>
<td>3.2 $^1$H NMR spectra of soybean oil (a), 30MSO (b), and 45MSO (c)</td>
<td>22</td>
</tr>
<tr>
<td>4.1 Storage (a) and loss (b) modulus as a function of frequency of various SBR gums at 90°C</td>
<td>36</td>
</tr>
<tr>
<td>4.2 Tan $\delta$ (a) and complex viscosity (b) as a function of frequency of various SBR gums at 90°C</td>
<td>37</td>
</tr>
<tr>
<td>4.3 Storage (a) and loss (b) modulus as a function of frequency of various CB-filled SBR compounds at 90°C</td>
<td>39</td>
</tr>
<tr>
<td>4.4 Tan $\delta$ (a) and complex viscosity (b) as a function of frequency of various CB-filled SBR compounds at 90°C</td>
<td>40</td>
</tr>
<tr>
<td>4.5 Storage (a) and loss (b) modulus as a function of frequency of various unfilled SBR vulcanizates at 90°C</td>
<td>42</td>
</tr>
<tr>
<td>4.6 Tan $\delta$ (a) and complex viscosity (b) as a function of frequency of various unfilled SBR vulcanizates at 90°C</td>
<td>44</td>
</tr>
<tr>
<td>4.7 Storage (a) and loss (b) modulus as a function of frequency of various CB-filled SBR vulcanizates at 90°C</td>
<td>48</td>
</tr>
<tr>
<td>4.8 Tan $\delta$ (a) and complex viscosity (b) as a function of frequency of various CB-filled SBR vulcanizates at 90°C</td>
<td>48</td>
</tr>
<tr>
<td>4.9 Storage modulus as a function of strain amplitude of various CB-filled SBR compounds (a) and vulcanizates (b)</td>
<td>50</td>
</tr>
<tr>
<td>4.10 TGA curves of various extender oils</td>
<td>51</td>
</tr>
</tbody>
</table>
4.11 TGA curves of various SBR gums (a) and various CB-filled SBR compounds (b) .............................................................................................................. 53
4.12 TGA curves of various unfilled SBR vulcanizates (a) and various CB-filled SBR vulcanizates (b) .............................................................................................................. 54
4.13 DSC curves of various extender oils (a) and NO and SO at lower temperature (b) ................................................................................................................................. 56
4.14 DSC curves of various SBR gums (a) and CB-filled SBR compounds (b) .... 57
4.15 DSC curves of various unfilled SBR vulcanizates (a) and various CB-filled SBR vulcanizates (b) ................................................................................................................... 58
4.16 Curing curves of various unfilled SBR compounds at 160°C ................. 63
4.17 Curing curves of various CB-filled SBR compounds at 160°C .............. 64
4.18 Gel fraction of various unfilled and CB-filled SBR vulcanizates ............ 68
4.19 Crosslink densities of various unfilled and CB-filled SBR vulcanizates. .... 70
4.20 Bound rubber fraction of various CB-filled SBR compounds .................. 72
4.21 DSC curves for SO, 10MSO and 30MSO at 160°C (a), and SO/Curatives, 10MSO/Curatives and 30MSO/Curatives at 160°C (b) .................................................. 74
4.22 Viscosity as a function of shear rate of SO, 10MSO and 30MSO, SO/Curatives, 10MSO/Curatives and 30MSO/Curatives at 35°C. ..................................................... 76
4.23 Schematic picture of possible crosslinks between rubber chains ............ 77
4.24 Strain-stress curves of unfilled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates ............................................................................................................. 79
4.25 M100 (a), M300 (b), elongation at break (c) and strength (d) of the unfilled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates ............................................................................................................. 80
4.26 Strain-stress curves of the CB-filled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates ............................................................................................................. 82
4.27 M100 (a), M300 (b), elongation (c) and strength (d) of CB-filled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates .................................................. 83

4.28 Abrasion loss of the CB-filled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates ........................................................................................................................................................................................................................................... 86

4.29 Storage modulus as a function of temperature of various unfilled SBR vulcanizates ........................................................................................................................................................................................................................................... 89

4.30 Loss modulus as a function of temperature of various unfilled SBR vulcanizates ........................................................................................................................................................................................................................................... 90

4.31 Tan δ as a function of temperature of various unfilled SBR vulcanizates ...... 91

4.32 Storage modulus as a function of temperature of various CB-filled SBR vulcanizates ........................................................................................................................................................................................................................................... 92

4.33 Loss modulus as a function of temperature of various CB-filled SBR vulcanizates ........................................................................................................................................................................................................................................... 93

4.34 Tan δ as a function of temperature of various CB-filled SBR vulcanizates .... 94

4.35 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of various CB-filled SBR vulcanizates ........................................................................................................................................................................................................................................... 95

4.36 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of CB-filled SBR/NO, SBR/SO, SBR/5MSO and SBR/5MSO-2 vulcanizates ........................................................................................................................................................................................................................................... 96

4.37 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of CB-filled SBR/NO, SBR/SO, SBR/10MSO and SBR/10MSO-2 vulcanizates ........................................................................................................................................................................................................................................... 97

4.38 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of CB-filled SBR/NO, SBR/SO and SBR/30MSO vulcanizates .... 98

4.39 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of CB-filled SBR/NO, SBR/SO and SBR/45MSO vulcanizates .... 99
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Compounding Recipes of SBR Vulcanizates</td>
<td>24</td>
</tr>
<tr>
<td>4.1 Discharge temperature and power consumption from Banbury Mixer at an initial temperature of 50ºC</td>
<td>34</td>
</tr>
<tr>
<td>4.2 T&lt;sub&gt;g&lt;/sub&gt; of SBR Gums, Unfilled and CB-filled SBR Vulcanizates</td>
<td>59</td>
</tr>
<tr>
<td>4.3 T&lt;sub&gt;95&lt;/sub&gt; of unfilled and CB filled SBR</td>
<td>66</td>
</tr>
<tr>
<td>4.4 Hardness of the unfilled and CB-filled SBR vulcanizates</td>
<td>85</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

Styrene-butadiene rubber also known as SBR, is a synthetic rubber being a copolymer of styrene and butadiene\(^1\). SBR has good wear resistance and traction performance, it is the primary rubber for passenger car tire tread compounds. These compounds typically contain an extender oil that works as a plasticizer. Various types of oil can be added into the rubber compound in order to reduce its viscosity, get better processing properties, increase low temperature flexibilities and decrease cost. Producing of oil-extended rubbers has been industrialized since 1950s in the United States using petroleum based extender oils such as aromatic oil, naphthenic oil and paraffinic oil. Aromatic oil is the most widely used extender oil in modern tire manufacturing due to its good compatibility with tire rubbers, such as SBR and natural rubber\(^2\). However, in 1994 a report by Swedish National Chemicals Inspectorate showed that polycyclic aromatic hydrocarbon (PAH), which is the main constituent of aromatic oil, is highly carcinogenic\(^3\). According to European Union’s REACH Regulation (EC No. 1907/2009, Annex XVII), extender oil used in tires must contain PAH below 3.0 wt% with the sum of individual PAH must be below 10 mg/kg and Benzo(a)pyrene lower than 1 mg/kg \(^4\).

In tire industry, each tire requires approximately seven gallons of oil, about five gallons are used to synthesize the rubber and about two gallons are used as energy supply\(^5\). In 2013, around 161.9 million of tires were produced in the US according to
Rubber Manufacturers Association’s 2013 Tire Industry Factbook, and each year the US generates around 250 million of scrap tires\(^5\). Each tire on average contains about 2 lbs of petroleum plasticizer, therefore large amount of petroleum plasticizer is consumed by tire industry each year. These resources will probably be depleted in the 22nd century\(^6\). Accordingly, polymer industry is facing a challenge of the oil resources.

Researchers have been looking for sustainable replacement of conventional petroleum oils in rubber industry. Vegetable oil such as soybean oil is a renewable and inexpensive oil resource, and efforts of replacing the conventional petroleum oils with vegetable oils were made by many researchers. Soybean comprises about 90% of U.S. oilseed production, and in 2012 around 2.2 billion pounds of soybean oil was produced in the United States\(^7\). Thus soybean oil could be an excellent resource to replace petroleum oils in various fields. Soybean oil can be used as a plasticizer in rubber matrix. Previous studies\(^3,8\) already reported that the rubber product containing soybean oil could have similar properties compared to the rubber product containing conventional petroleum oil. However, it is still necessary to further investigate the usage of soybean oil in the rubber product to get improved properties than the rubber product using petroleum oils.

In this study instead of using the virgin soybean oil directly, the soybean oil is modified and compounded into SBR matrix. The double bonds on the fatty acids of the soybean oil are modified into norbornyl groups. The norbornyl groups have more reactive double bonds than the unmodified double bonds on the fatty acid chains\(^9\), thus it is anticipated that the modified soybean oil is more reactive than the unmodified soybean oil. The reactive double bonds can play an important role during the curing of the rubber compound. Soybean oils of various levels of modification are used as extender oils in the
SBR to replace the naphthenic oil. Rheological, thermal, mechanical properties and swelling tests of the SBR compounds and vulcanizates are studied, and the unique effect of the modified soybean oil on the rubber product is evaluated and compared with conventional naphthenic oil. The reaction of the modified soybean oil during the curing of the rubber is also studied.

In this study, Chapter II provides literature survey including the previous study on vegetable oils, different applications of soybean oil, and bio-based plasticizers. Chapter III presents the experimental methods including materials, sample preparations and characterization methods. Chapter IV discusses the results of comparative analysis of properties of SBR compounds and vulcanizates containing various oils. Chapter V provides a summary of this thesis.
CHAPTER II
LITERATURE SURVEY

2.1 Vegetable oils

Vegetable oils are mostly extracted from the seeds of various plants, including soybean oil, sunflower oil, olive oil, peanut oil, corn oil, palm oil, rapeseed oil, etc.. These vegetable oils have been used by human for thousands of years. Most vegetable oils are triglyceride-based esters of glycerol and three fatty acid chains, the oils can be classified by their fatty acid distributions. The primary composition of the fatty acid chains are shown in Figure 2.1, including palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid. The relative level of unsaturation of the oil can be determined from the fatty acid composition, and the distribution varies upon the oilseed source and processing methods. Vegetable oils have a wide variety of applications, such as foods, fuels (biofuels), paints, lubricants, pharmaceuticals, cosmetics, plasticizers, and construction materials.

2.1.1 Culinary uses

Vegetable oils such as soybean oil, olive oil and corn oil can be consumed directly as food to give a better texture and flavor. Common food such as baked breads, crackers, cakes, cookies, salad dressing and mayonnaises are all produced with vegetable oil.
Figure 2.1 Fatty acid chemical structures of vegetable oils
Also, vegetable oils can be heated to cook other foods. Santos et al.\textsuperscript{11} studied the effect of heating and cooling on rheological properties of edible vegetable oils. In this work, the temperature-dependent rheological behavior of un-used and used vegetable cooking oils such as soybean oil, sunflower oil, olive oil, rapeseed oil, corn oil, rice oil and oil mixtures was evaluated. Saturation of the oils increased after the frying, also generated dark, viscous and smelly oils. The results indicated that deep frying of the oil could change the properties of the edible oils.

2.1.2 Hydrogenated oils

The hydrogenation of vegetable oils was discovered in 1897, by using catalyst such as powdered nickel compound. The carbon-carbon double bonds in the fatty acids are converted into carbon-carbon single bonds. As the degree of saturation increases, the viscosity and melting points increase, therefore the liquid oils are converted into semisolid fats\textsuperscript{12}.

2.1.3 Industrial uses

Vegetable oil can be used in many industry fields such as cosmetic product, electronics, coatings, inks, lubricants and animal food industry. Vegetable oils are non-toxic, renewable, biodegradable, and have high flash and fire points, therefore vegetable oils are widely used to replace part of the conventional petroleum oils.

Vegetable oils are being used as biodegradable hydraulic fluids. Wan et al.\textsuperscript{13} evaluated the temperature and shear rate dependence of rheological properties of palm, coconut, canola, corn and sunflower oils. Various empirical rheological models including
Ostwald de-Waele, Cross, Carreau, Herschel–Bulkley and Arrhenius-type relationship were used to evaluate the properties of the oils. Results showed that these oils were stable in terms of shear rate and temperature effects and could be a potential replacement of conventional hydraulic oils.

2.1.4 Vegetable oil-based fuel

Vegetable oils can be used as fuels for diesel engines. The inventor of the diesel engine Rudolph Diesel first used peanut oil as fuel on his first diesel engine\textsuperscript{14}. Later on the vegetable oil-based fuels were used as emergency fuel supplies in the 1930s and 1940s\textsuperscript{15}. Since 1970s, with the eruption of the petroleum crises and a growing concern of the environmental problems, more and more researchers focused on the vegetable oils-based fuels as a substitute of petroleum fuels. In the late 1990s, biodiesel started to be widely used by the European Union in order to deal with the energy demand and pollution problems\textsuperscript{16}.

Biodiesel have several advantages. First, the sources of the fuels are easy to obtain and renewable. Second, the biodiesel contains much less sulfur compared to conventional diesel, therefore the biodiesel is “greener”\textsuperscript{17}. The disadvantages of the biodiesel are its higher viscosity, lower volatility and polyunsaturated character, also the engines need modification\textsuperscript{18}.

To produce biodiesel, the viscosity of vegetable oil needs to be reduced. Four different techniques can be used, dilution with hydrocarbons, emulsification, pyrolysis, and transesterification to monoalkyl esters \textsuperscript{19}. 
Biodiesel can also be used in other fields. Angelini\textsuperscript{20} studied biodiesel as a plasticizer in tire rubbers. Biodiesel was compounded with SBR and the properties were compared with SBR compounded with aromatic oil. The solubility parameter of the major components of the biodiesel was calculated and compared with rubber such as EPDM, BR, IR, butyl rubber, SBR and NBR. Results showed that the biodiesel was compatible with those rubbers except NBR, and could work as an internal lubricant in diene rubber matrix similar to aromatic oils. Biodiesel could react with sulfur and thus lower the modulus, tensile, hardness of the vulcanizates and increase elongation compared to rubber compound with aromatic oil.

2.2 Soybean oil

Soybean oil is extracted from the seed of soybean. The soybeans are cracked, heated to 60-88°C, then rolled into flakes and extracted using solvent such as hexanes. Soybean oil contains around 23.4% of oleic, 53.3% of linoleic, 7.8% of linolenic, and around 15% of palmitic and stearic acids. The distribution of the fatty acids may vary from different soybeans and processing methods\textsuperscript{21}.

To deal with the dependence on petroleum oil and pollution problems, renewable naturally occurring oils such as soybean oil have been studied to replace the petroleum oils. Soybean oil is one of the most widely used vegetable oils in the world. According to the report from the United States Department of Agriculture, in 2014 the estimate soybean production in United States will be 3.46 billion bushels, and 287.7 million tons in the global market\textsuperscript{22}. Each year 2.2 billion pounds of soybean oil is produced in the U.S. and more than 30 million tons in the world\textsuperscript{7}. Abundant supply of the soybean leads to a
low price of soybean oil about $870/ton (CME Group, Feb. 2014). It is sustainable, environment friendly and inexpensive compared to petroleum oils. As a drying oil, which means it can be crosslinked due to autoxidation, soybean oils can be used in various fields such as coatings, lubricants, plastics, and elastomers\textsuperscript{21, 23}. Soybean oil and other bio-based oils products have shown great environmental impact and evaluated by earlier reports\textsuperscript{24}.

As shown in Figure 2.2, soybean oil is triglyceride-based esters of glycerol and three fatty acid chains. Soybean oil has several function groups available for further reaction, such as carbon-carbon double bonds and ester bonds. Epoxidation and hydroformylation can be applied for carbon-carbon double bonds, and ester bonds can be used to prepare alkyd resins by transesterification and reaction with phthalic anhydride\textsuperscript{23}. Thus, soybean oil can be polymerized and various kinds of polymers can be derived\textsuperscript{25}.

![Figure 2.2 Chemical structure of soybean oil](image)

2.2.1 Polymers from unmodified soybean oil

Soybean oil can be thermally polymerized by heating to 300°C with the Diels-Alder addition. However, the loss of the oil due to the thermal degradation is tremendous. Soybean oil can also be polymerized through sulfur vulcanization to prepare factice.
Erhan and Kleiman\textsuperscript{26} investigated the preparation of factice using vegetable oils. Meadowfoam and rapeseed oils could be used to produce high quality brown factice. Soybean oil could be used to produce low quality but less expensive factice. Erhan and Kleiman found that a 1:1 mixture of soybean oil and meadowfoam or rapeseed oil could produce a similar quality factice as the 100\% meadowfoam or rapeseed oil did. The low cost factice could benefit the rubber industry.

Cowan et al.\textsuperscript{27} used heat polymerized soybean oil and ethylene glycol to prepare polyester, and then cured with sulfur and other conventional reagents to obtain a rubber like materials. The resulting material had improved properties such as oxygen and zone resistance compared with factice.

Soybean oil has unsaturated groups and it can be copolymerized with other monomers using cationic polymerization and yield various polymers. Li and Larock\textsuperscript{28} studied the copolymerization of soybean oil, styrene and divinylbenzene. The copolymers were characterized by dynamic mechanical analysis (DMA), and dynamic mechanical properties and glass transition temperatures of the copolymers were studied. The tensile test and SEM were applied to the copolymer to investigate the mechanical properties and fracture surfaces\textsuperscript{29}. The copolymer had a good damping property and the shape memory effect, time-temperature-transformation cure diagrams were studied\textsuperscript{30-31}. Larock et al.\textsuperscript{32} also found that the copolymer made from soybean oil with styrene and dicyclopentadiene had good mechanical properties and thermal stability.

Kammann Jr. and Phillips\textsuperscript{33} found that sulfurized vegetable oils including soybean oil could be used as lubricant additives. Vegetable oils were sulfurized in the presence of methyl lardate, high-sulfur products were made using a 50:50 ratio of soybean oil to
methyl lardate, and low-sulfur products were made using a 70:30 ratio. Extreme pressure, friction and wear performances were tested and the vegetable oils showed promising results to replace the conventional products.

Xia et al.\textsuperscript{34} studied a bio-based thermosets synthesized by the ring-opening metathesis polymerization (ROMP) of norbornenyl-functionalized fatty alcohols derived from soybean oil, Dilulin, ML189 and castor oil. The thermal and mechanical properties of the new bio-based thermosets were investigated using Soxhlet extraction, DMA, TGA and tensile tests. Results showed that the final properties were influenced by the structures and the viscosities of the monomers.

Valverde et al.\textsuperscript{35} studied bio-based rubbery thermosets. The thermosets were synthesized by the cationic copolymerization of various amount of conjugated soybean oil, styrene, and 1,5-hexadiene or isoprene as flexible crosslinkers. The molecular structures were studied, also the thermal, mechanical properties, and the abrasion resistance of these new bio-rubbers were evaluated. Wang et al.\textsuperscript{21} studied a novel soybean-oil-based elastomer. Poly(epoxidized soybean oil-co-decamethylene diamine) (PESD) was synthesized by ring-opening polymerization from epoxidized soybean oil and decamethylene diamine in different ratios. The reaction and product structure was characterized by TGA, FTIR and NMR. The bio-elastomer exhibited good damping property, low water absorption, and low degradation rate in phosphate buffer solution.

2.2.2 Epoxidized soybean oil

Epoxidized soybean oil is widely used as a plasticizer and a HCl scavenger in PVC plastics\textsuperscript{36}. The epoxidized soybean oil is produced by the epoxidation of soybean oil. The
The epoxide group is more reactive compared with carbon-carbon double bond on the fatty acid chain. It is a good HCl scavenger that can react with the HCl released by the PVC at high temperature, and also a plasticizer in the PVC plastic. The epoxidation process can be achieved by using peroxide or peroxycetic acid to convert the carbon-carbon double bonds into epoxide groups. The epoxidized soybean oil can also be used as replacement for conventional polyols, and to prepare PU foams, elastomers and coatings.

Yang et al.\textsuperscript{37} studied the structure and properties of epoxidized soybean oil. In the study, various levels of epoxidized soybean oils were prepared. The epoxidation level was characterized by FTIR, viscosity, activation energy and thermodynamic properties. Molecular mass was also investigated. Results showed that with the increase of the epoxidation level of the soybean oil the thermal stability decreased first but increased at higher levels. The melting point increased after the epoxidation. GPC test showed that the molecular mass increased at lower epoxidation extent, then decreased at higher epoxidation extent.

Epoxidized soybean oil can also be used in crumb rubber filled asphalt. Yin et al.\textsuperscript{38} investigated the anti-aging performance of asphalt modified by crumb rubber impregnated in epoxidized soybean oil. The crumb rubber was radiated by microwave and then impregnated in the epoxidized soybean oil. The penetration, softening point, ductility, mass loss, viscosity and anti-aging mechanism of the modified asphalt were discussed. The results showed that the asphalt modified by crumb rubber impregnated in epoxidized soybean oil had an edge over the microwave radiated crumb rubber modified asphalt in terms of high temperature stability, low temperature ductility and anti-aging performance.
2.2.3 Polyols and polyurethanes

Soybean oil and its derivatives can be converted into polyols and copolymerized with various isocyanates such as toluenediisocyanate (TDI) and methylene-4,4’-diphenyl-diisocyanate (MDI)\(^{39}\).

Guo et al.\(^{40}\) studied the polyurethanes derived from soybean oil via hydroformylation. The double bonds of soybean oil are first converted to aldehydes through hydroformylation using either rhodium or cobalt as the catalyst. The aldehydes are hydrogenated by Raney nickel to alcohols, forming a triglyceride polyol. The latter is reacted with polymeric MDI to yield the polyurethane. A hard rubber like and a rigid plastic like PU were obtained and the physical and mechanical properties were compared.

2.3 Bio-based oils in rubber

Bio-based oils can be used as plasticizer in the rubber or plastic matrix. Compare to conventional petroleum plasticizer, the bio-based oils are more environmental friendly and renewable.

Researchers have studied various bio-based oils in different polymer systems. Flanigan et al.\(^{8}\) evaluated various bio-based oils including palm, flaxseed, cashew nut shell liquid and soybean oil replacing part of the petroleum oil in the silica-based, 80/20 blends of SBR/NR formulations, as well as blends with an alternative bio-derived rubber, guayule. The study indicated that the product containing bio-based oils exhibited similar mechanical properties compared to the product with conventional petroleum oils. Also the alternative bio-derived rubber product had similar properties as the standard natural rubber.
Wang et al.\textsuperscript{41} compared the properties of EPDM with various amount of transgenic soybean oil (TSO) and paraffin oil (PO). The results showed that the TSO reacted with the curing agent and the plasticization effect was higher than that of PO. When the amount of the plasticizer was under 15 phr, the TSO-plasticized EPDM vulcanizate had higher tensile and tear strength, elongation at break, extraction resistance, and thermal stability, but lower Shore A hardness compared to the PO-plasticized EPDM vulcanizate. When the plasticizer amount was over 15 phr, the mechanical properties of the TSO-plasticized EPDM dropped.

Kundu et al.\textsuperscript{42,43,44} studied the coupling effect of vegetable oil between carbon black and rubber. The carbon black was first pretreated with vegetable oil or paraffinic oil, and then mixed with rubber and compared. The physical and mechanical properties of the vegetable oil treated filled rubber were improved compared to the paraffinic oil treated sample when the amount of the vegetable oil was under 3 phr. The monolayers of the oil on carbon black had microplasticization effect and could work as a coupling agent, therefore increase the interaction between carbon black and rubber. However, when the oil content was beyond 3 phr, the macroplasticization was predominant and the properties had the opposite trend.

Dasgupta et al.\textsuperscript{3} compared various physico-chemical properties of various naturally occurring processing oils and conventional petroleum processing oils. The naturally occurring and petroleum processing oils were compounded with a natural rubber based truck tire tread formula. The processing properties including Mooney viscosity, rheology properties and filler dispersion were compared. The results showed that these naturally occurring oils were more environmental friendly and could act as the best alternative processing oils of the conventional petroleum oils. Dasgupta et al. also studied naturally
occurring oils including neem oil and kurunj oil in different tire formulations, the results showed that the naturally occurring oils could give better filler dispersion and tread life compared to conventional aromatic oils.

Nandanan et al. studied bio-based oils such as rubber seed oils and coconut oils in SBR and NR systems. Rubber with bio-based oils showed better mechanical properties such as tensile and abrasion compared to the rubber with aromatic oil. The research showed a possibility to replace petroleum oils by these bio-based oils.

Petrović et al. studied the polymerized soybean oils of different molecular weights used as plasticizers in NR/SBR compositions. The research focused on the polymerized soybean oils of different molecular weights used as plasticizers in NR/SBR compositions. Elastomers were extended with naphthenic oil, pure soybean oil and polymerized soybean oils of different molecular weights, then the properties were compared. It was found that the polymerized soybean oil-extended rubber gave minimal differences in mechanical and dynamic properties compared to those of the naphthenic process oil-extended rubber.

Joseph et al. investigated epoxidized rubber seed oil in rubber compounds. Acrylonitrile butadiene rubber (NBR) was compounded with rubber seed oil (RSO), various level of epoxidized RSO (ERSO) and dioctyl phthalate (DOP) as plasticizer, the properties were compared. Results indicated that ERSO in NBR gave better abrasion resistance whereas the tensile strength and tear strength were comparable to vulcanizates containing DOP as a plasticizer. The ERSO could be used as a less leachable and low volatility plasticizer for NBR.

Bio-based plasticizers were also studied by rubber producers, numbers of patents on bio-based plasticizers such as soybean oil were filed. US patent 8034859 claimed a
rubber composition comprised a rubber, an oil blend of a petroleum oil and a bio-based oil (soy oil), and a filler, wherein the soy oil is 10 to 50 percent by weight of the total weight of the petroleum oil. The soy oil could be non-hydroxyl-functionalized, hydroxyl-functionalized, or combinations of both. Most samples exhibited acceptable properties.

Recker et al. claimed a rubber mixture for vehicle air-inflated tires, seat belts, belts and hoses. The rubber mixture comprised a rubber, a filler and a softener, wherein the softener is free of polycyclic aromatics according to Directive 76/769/EEC, and the carbon source for the softener comes from non-fossil sources. The examples indicated that the replacement of aromatic processing oil by environmentally friendly bio-based processing oil didn’t affect the properties of the rubber mixtures. Wilson claimed a rubber composition with non-petroleum based oils. The non-petroleum based oil could replace traditional process oils and could be used in rubber compositions in general and specifically in footwear applications. The moldable rubber composition comprised a rubber resin consisting of natural rubber, synthetic rubber, a curing agent, a silica filler, and a non-petroleum oil present at a level of 5 phr or less. The examples demonstrated that the vegetable oils could replace conventional petroleum processing oils in the silica filled rubber compositions.

Thompson and Saintigny claimed a tire tread composition consisting butadiene rubber and styrene-butadiene rubber. The rubber composition also included a high Tg plasticizing resin and a vegetable oil. The test result showed that the tire rubber with various amount of sunflower oil had a significant increase in rolling resistance and improved wet, dry, and snow grip properties compared to the control sample. US patent
7335692\textsuperscript{54} claimed a cross-linkable or cross-linked rubber composition usable for constituting a tire tread. The composition based on one or more diene elastomers and a plasticizer. The plasticizer comprised petroleum oils and natural oils such as sunflower oil. The sample that contained natural oils had a better grip on dry or damp ground compared to the control sample.

Vegetable oil such as soybean oil can be mixed with other bio-materials and used as an environmental friendly plasticizer in rubber. Herberger et al.\textsuperscript{55} claimed a tire component and tires that contained a rubber composition (100 phr), 3 to 20 phr of soybean oil, 3 to 20 phr of starch/plasticizer composite with a starch/plasticizer weight ratio being from 0.5/1 to 5/1, coupling agents and fillers. The example showed that the sample containing the combination of soybean oil and starch/plasticizer composite exhibited a similar physical property compared to the control sample containing petroleum processing oil.

The vegetable oil derived plasticizer can also be used in thermoplastics such as PVC. Benecke et al.\textsuperscript{56} claimed a plasticized vinyl chloride (PVC) composition comprising 100 parts by weight PVC resin, and 10 to 230 parts by weight of plasticizers. The plasticizer plasticizer comprised a fatty acid product derived from a vegetable oil and the unsaturated fatty acids were substantially fully esterified with a monool or a polyol and then fully epoxidized.

Previous studies showed that the polymer matrices containing bio-based plasticizers could give similar mechanical properties compared to the polymer matrices with petroleum plasticizers. However, most researches directly used the virgin vegetable oils without any modification, and the content of vegetable oils in the rubber product is
usually lower than 20 phr. Also, there was no report on the application of norbornylized soybean oil in rubber. The reaction between the oils and curatives during the curing of the rubber were not systematically studied. Although the previous studies claimed some improvement in properties of tire rubbers such as the elongation at break. A tremendous increase in both the tensile strength and elongation at break is not reported. Therefore, it is necessary to study the usage of the norbornylized soybean oil in the SBR matrix to replace the conventional petroleum plasticizers. The study will give a deeper understanding of the modified soybean oil for future use with aim in tire rubber.
CHAPTER III
EXPERIMENTAL

3.1. Materials

A solution polymerized SBR named EB091/HX739 manufactured by Firestone Polymers (Akron, OH) was used. It is tin coupled, and has 20 % bound styrene, 60 % vinyl, and a non-staining antioxidant stabilizer system\(^{57}\). Carbon black N330 by Sid Richardson (Fort Worth, TX) was used as a filler. Its Brunauer-Emmet-Teller (BET) surface area was 78 m\(^2\)/g and dibutyl-phthalate absorption was 102 mL/100 g. Naphthenic oil under the trade name Plasticizer LN by Akrochem Corporation (Akron, OH) was used as a petroleum extender oil. It is a hydro-treated naphthenic rubber process oil. A technical grade RBD soybean oil by Cargill Industrial Oils & Lubricants (Minneapolis, MN) was used.

Various extents of modified soybean oil (MSO) were used. The MSOs were prepared with stoichiometric mol ratios of dicyclopentadiene (DCPD) to C=C bonds of soybean oil at 13%, 25%, 150%, and 450%. About 5%, 10%, 30% and 45% of the C=C bonds in the modified soybean oil were converted into norbornyl groups and named as 5MSO, 10MSO, 30MSO and 45MSO, respectively. The double bonds in the norbornyl groups are more reactive compared to those in the unmodified fatty acid chains\(^9\). The strategy of the preparation of MSO is shown in Figure 3.1. The oil modification was carried out by Dr. Xiaofeng Ren in Dr. Soucek’s group.
Figure 3.1 Preparation of MSO
Soybean oil (300 g), dicyclopentadiene (14, 26, 155, or 466 g), and 4% BHT (based on the weight of DCPD) were charged into a flask and stirred until all the BHT dissolved. The mixture were then transferred to a 1000 ml Parr reactor and heated to 240°C. The pressure increased with the increasing temperature and reached a stable value between 20 to 30 psi. The temperature was maintained until the pressure dropped to atmosphere pressure, and then the reaction mixture was slowly cooled to room temperature. Hexane was used to dilute the mixture, and the mixture was stirred for 0.5 h. This solution was filtered, and the solvent was removed with a rotary evaporator at 55-60 °C. 5MSO, 10MSO and 30MSO were obtained as light yellow liquid, and 45MSO was a highly viscous soft solid.

Figure 3.2 compares the ^1H NMR spectra of SO (Figure 3.2(a)), 30MSO (Figure 3.2(b)), and 45MSO (Figure 3.2(c)). In Figure 3.2(a), the resonance at δ=5.34 ppm (H_9 and H_{10}) were observed. In 30MSO and 45MSO, the intensity of this resonance decreased and new resonances at δ=6.08-5.95 ppm (H_2 and H_3), δ=2.50 ppm (H_1 and H_4), δ=1.82 ppm (H_5 and H_6), and δ=1.05-1.20 ppm (H_{syn} and H_{anti}) were observed. The intensity of the new resonances for 45MSO was much stronger than those of 30MSO. It indicated that with an increase of the modification level, more carbon double bonds on the fatty acid chains were converted into norbornyl groups.

Rubber compounding ingredients were zinc oxide (ZnO) under the trade name of Zinc Oxide RGT-M, N-octadecanoic acid (stearic acid) under the trade name of Stearic Acid Rubber Grade, sulfur under the trade name of Rubber Maker (RM) Sulfur, and accelerator N-cyclohexyl-2-benzothiazole sulfenamide (CBTS). These ingredients were provided by Akrochem Corporation (Akron, OH).
Figure 3.2 $^1$H NMR spectra of soybean oil (a), 30MSO (b), and 45MSO (c).
3.2 Compounding

Different recipes of SBR compounds were made, as listed in Table 3.1. SBR was mixed with 30 phr of naphthenic oil (NO), soybean oil (SO), 5MSO, 10MSO, 30MSO and 45MSO using a Banbury mixer (1.2 L Model 86EM9804, Banbury USM Corp., Ansonia, CT). A rotor speed of 60 rpm, a fill factor of 0.7, and setup temperature with cooling water of 50°C were used. First, SBR gum was placed in the Banbury mixer for 120 s, 1/2 of extender oil was added, and mixed for another 120 s. Then the other 1/2 of oil was added, and mixed for 180 s, with total time of mixing being 420 s. SBR without any extender oils was also mixed at the same condition for 420 s.

For unfilled rubber compounds, SBR, naphthenic oil-extended SBR (SBR/NO), soybean oil-extended SBR (SBR/SO), various modified soybean oil-extended SBR (SBR/MSO) and SBR from the Banbury mixer were mixed with curatives including 5 phr of ZnO, 1 phr of stearic acid, 2 phr of sulfur and 1.3 phr of CBTS using a two roll mill (Dependable Rubber Machinery Co., Cleveland, OH) for about 7-8 minutes with a gap size of 5 mm. A rotor speed of 20 rpm and a cooling water temperature of 40°C were used.

For filled rubber compounds, SBR gums and various oil-extended SBR gums from the Banbury mixer were mixed with 60 phr of carbon black (CB), 5 phr of ZnO and 1 phr of stearic acid using a Brabender mixer manufactured by C.W Brabender Instruments, Inc. (80 mL, Model Plasti-corder, So. Hackensack, NJ). A rotor speed of 55 rpm, a gap size of 6 mm and a setup temperature of 80°C for SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO and SBR/45MSO compounds were used. For SBR compounds, a set up temperature was 95°C was used due to its higher viscosity compared to oil-extended SBR compounds. First, the rubber was mixed for 90 s, 5 phr of ZnO and 1 phr of stearic acid
Table 3.1 Compounding Recipes of SBR Vulcanizates

<table>
<thead>
<tr>
<th></th>
<th>SBR</th>
<th>SBR/NO</th>
<th>SBR/SO</th>
<th>SBR/5MSO</th>
<th>SBR/10MSO</th>
<th>SBR/30MSO</th>
<th>SBR/45MSO</th>
<th>SBR/5MSO-2</th>
<th>SBR/10MSO-2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(phr)</td>
<td>(phr)</td>
<td>(phr)</td>
<td>(phr)</td>
<td>(phr)</td>
<td>(phr)</td>
<td>(phr)</td>
<td>(phr)</td>
<td>(phr)</td>
</tr>
<tr>
<td>SBR</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>NO</td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO</td>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5MSO</td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10MSO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30MSO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45MSO</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Accelerator (CBTS)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.95</td>
<td>1.95</td>
</tr>
<tr>
<td>CB</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>Total</td>
<td>169.3</td>
<td>199.3</td>
<td>199.3</td>
<td>199.3</td>
<td>199.3</td>
<td>199.3</td>
<td>199.3</td>
<td>200.95</td>
<td>200.95</td>
</tr>
</tbody>
</table>
was added. At 120 s, 60 phr of carbon black was added, and then mixed for 240 s, with total mixing time being 360 s. 2 phr of Sulfur and 1.3 phr of accelerator CBTS were then mixed with rubber on a two roll mill (Dependable Rubber Machinery Co., Cleveland, OH) for about 5-6 minutes. A rotor speed of 20 rpm and a cooling water temperature of 40°C were used.

For both unfilled and CB-filled SBR/5MSO and SBR/10MSO, samples with 3 phr of sulfur and 1.95 phr of accelerator (SBR/5MSO-2, SBR/10MSO-2) were also prepared. Compounding procedures and parameters were kept the same.

3.3 Vulcanization

The curing curves of unfilled and CB-filled SBR compounds were measured by the Advanced Polymer Analyzer (APA2000, Alpha Technologies, Akron, OH) at a temperature of 160°C, a frequency of 1.67 Hz, and a strain amplitude of 4.2%. A curing time \( T_{95} \) (time for 95% of curing torque) was calculated based on curing curves. The specific torque \( S'_{95} \) at \( T_{95} \) was calculated using the equation:

\[
S'_{95} = (S'_{\text{max}} - S'_{\text{min}}) \times 0.95 + S'_{\text{min}}
\]

\( S'_{\text{max}} \) and \( S'_{\text{min}} \) are the maximum and minimum torque during the curing, the \( T_{95} \) was the corresponding time of the \( S'_{95} \). The vulcanizate slabs with a dimension of 150 mm × 150 mm and a thickness range of 1.7–2.2 mm for tensile test, and abrasion test samples with a diameter of 16 mm and a length of 12 mm were prepared using an electrically heated compression-molding press (Carver, Wabash, IN) under the temperature of 160°C and a pressure of 15 MPa.
To study the reaction between SO and MSO with curatives, SO, 10MSO and 30MSO were mixed with curatives and heated at 160°C to simulate the condition in rubber matrix. First, 10g of oils were mixed with 0.667g sulfur, 0.433g CBTS, 1.667g ZnO and 0.333g stearic acid in an aluminum pan, then the mixtures were placed in vacuum oven preheated to 160°C and vacuumed to avoid thermal degradation. After heating at 160°C for 60 min, the mixtures were taken out and cooled down at room temperature for 24 hours.

3.4 Characterization

3.4.1 Rheological Properties

Rheological properties of various SBR gums and CB-filled SBR compounds were measured by the Advanced Polymer Analyzer (APA2000, Alpha Technologies, Akron, OH). A frequency sweep test was applied, in a frequency range from 0.02-200 rad/s (logarithmic mode) at a strain amplitude of 4.2% and a temperature being 90°C. The storage modulus, loss modulus, complex viscosity and tan δ of SBR gums and CB-filled SBR compounds were measured.

A strain sweep was applied to various CB-filled SBR compounds using APA2000. The strain amplitude ranged from 0.3% to 200% (logarithmic mode) at a frequency of 0.6 rad/s and a temperature of 90°C. The storage modulus, loss modulus, complex viscosity and tan δ of the CB-filled SBR compounds were obtained.

Rheological properties of unfilled and CB-filled SBR vulcanizates were measured by the APA2000. The samples were first cured at 160°C using the T₉₅ in the APA2000, then a frequency sweep test and a strain sweep test were performed, respectively. The frequency
sweep test ranged from 0.02-200 rad/s (logarithmic mode) at a strain amplitude of 4.2% at a temperature of 90°C. The storage modulus, loss modulus, complex viscosity and tan δ of unfilled and CB-filled SBR vulcanizates were measured. The strain sweep test ranged from 0.3% to 50% (logarithmic mode) at a frequency of 0.6 rad/s and a temperature of 90°C. The storage modulus, loss modulus, complex viscosity and tan δ of the CB-filled SBR vulcanizates were obtained.

Viscosities of SO, 10MSO, 30MSO and SO/curatives, 10MSO/curatives and 30MSO/curatives after the reaction were measured by a Discovery Hybrid Rheometer (DHR, TA Instruments, New Castle, DE). The mixture of oils and curatives were first centrifuged at 3500 rpm for 5 min and then the upper liquid oils were placed in DHR. Simple shear mode was used and shear rate ranged from 5 s⁻¹ to 100 s⁻¹. The test was performed at 35°C.

3.4.2 Measurement of thermal properties

Thermal properties were measured by TA Instruments Differential Scanning Calorimeter Q200 (DSC), and TA Instruments Thermogravimetric Analysis Q50 (TGA).

DSC curves of various extender oils, various SBR gums, CB-filled SBR compounds, unfilled and CB-filled SBR vulcanizates were obtained under N2 atmosphere. The experiments were in a temperature range from -90°C to 50°C for all the samples. The sample weight used was from 3 to 8 mg. The sample was heated up to 80°C to erase the thermal history. Then it was cooled down to -90°C at a cooling rate of 10 °C/min, and heated up to 50°C at a heating rate of 10 °C/min. The second heating curves were selected to report the thermal properties.
In addition, the DSC curves of NO and SO at lower temperature were obtained using TA Instruments Differential Scanning Calorimeter 2920 (DSC). DSC curves of NO and SO were obtained under N2 atmosphere. The samples were first heated up to 80°C to erase the thermal history, and then quenched to -150°C using liquid nitrogen and heated up to 40°C at a heating rate of 10 °C/min. The second heating curves were selected to report the thermal properties of the NO and SO.

To study the reaction of SO, MSO with curatives, the mixture was placed in DSC2920 and heated up to 160°C and kept for 10 min. The data in the isothermal step were used to characterize the reaction.

TGA curves of various extender oils, various SBR gums, CB-filled SBR compounds, unfilled and CB-filled SBR vulcanizates were obtained under N2 atmosphere. The temperature was increased from room temperature to 600°C at a heating rate of 20 °C/min.

3.4.3 Measurement of mechanical properties

For tensile tests, the unfilled and CB-filled SBR compounds were compression molded with their curing time T95 at a temperature of 160°C and a pressure of 15 MPa, and vulcanized into slabs of dimension of 150 mm × 150 mm and a thickness range of 1.7–1.9 mm which due to the different properties of various samples. Dumb-bell shape specimens (ASTM D412, ISO type 1) used in the stress-strain tests were cut from the vulcanized slabs. The tests were done at room temperature using an Instron tensile tester (Model 5567, Instron, Canton, MA) at a crosshead speed of 500 mm /min. An extensometer was used. At least five specimens were used for each type of vulcanizate.
Hardness tests for various unfilled and CB-filled SBR vulcanizates were done at room temperature using a Durometer type A according to ASTM 2240.

CB-filled SBR compounds were compression molded with their curing time $T_{95}$ at a temperature of 160°C and a pressure of 15 MPa, and vulcanized into cylinder samples for the abrasion tests. Samples of a diameter of 16 mm and a length of 12 mm were prepared. At least four specimens of each vulcanize were used in the test. The abrasion test was done using a Deutsches Institut für Normung Abrader (Zwick Abrasion Tester 6102) according to DIN 53516. A load of 10 N was given to the specimens without specimen rotation. A pathway of 40 m was applied to various CB-filled SBR vulcanizates. The weight loss of the sample was used to characterize the abrasion resistance.

3.4.4 Measurement of dynamic mechanical properties

The dynamic mechanical properties were evaluated using a TA Instruments Dynamic Mechanical Analysis Q800 (DMA), at a frequency of 1 Hz, a strain of 0.5% and in tensile mode. Rectangular specimens were cut from the vulcanized slabs, the thickness of the samples ranged from 1.7 to 1.9 mm, the width of the samples ranged from 4.3 to 4.7 mm and the grip distance ranged from 10 mm to 12 mm. The storage moduli ($E'$), loss moduli ($E''$) and tan $\delta$ of various unfilled and CB-filled SBR vulcanizates were obtained at temperature sweep from -90°C to 90°C, and a heating rate of 3°C/min.

The loss tangent values and storage modulus at different temperatures were used as a predictor of the performance of the rubber in tires\textsuperscript{58}. 
3.5.5 Swelling test

Gel fraction, crosslink density for unfilled and CB-filled SBR vulcanizates, and the bound rubber fraction of various CB-filled SBR compounds without curatives were measured using the swelling test.

To measure the gel fractions and crosslink densities of various unfilled and CB-filled SBR vulcanizates, the Soxhlet extraction method was employed with benzene as the solvent. A Kimax extraction set (Fisher Scientific, Hampton, NH.) was used. Samples of 0.5 to 0.8 g were put into a Whatman cellulose extraction thimble in the Soxhlet extractor, the whole apparatus was heated on a heater. After an extraction time of 24 hours, the weights of the swollen samples were measured. Then the samples were dried in a vacuum oven at 65 °C for 24 hours, the weights of dry rubber were measured. The gel fraction was determined from the following equation:

$$\text{Gel fraction} = \frac{\text{Weight of dry gel after extraction}}{\text{Weight of rubber sample before extraction}}$$

Crosslink density, \(\upsilon\), of SBR vulcanizates were calculated using the Flory-Rehner equation, and CB filled SBR were calculated with the Kraus correction factor\(^{59}\).

Flory-Rehner equation is as follows:

$$\upsilon = -\frac{\ln(1 - V_r) + V_r + \chi V_r^2}{V_1 \left( V_r^3 - \frac{V_r}{2} \right)}$$

Where \(V_r = \frac{\text{weight of dry rubber}}{\text{density of rubber}} \frac{\text{weight of dry rubber}}{\text{density of solvent}} \frac{\text{weight of solvent}}{\text{density of solvent}}\)

\(V_1\) is the molar volume of solvent. \(\chi\) is the polymer-solvent interaction parameter. Benzene has a value of \(V_1 = 88.838\) cc/mole and its density is 0.874 g/mL. The density of
the SBR is 0.93g/cm$^3$ and an interaction parameter ($\chi$) of 0.4 was used for SBR and benzene. Since the CB-filled SBR vulcanizates contained large amount of CB, a Kraus correction was applied using the following equation:

$$\frac{V_{ro}}{V_r} = 1 - \frac{\phi \left[ 3C \left( 1 - V_{ro}^{\frac{1}{3}} \right) + V_{ro} - 1 \right]}{1 - \phi}$$

Where $V_{ro}$ is the volume fraction of rubber in the unfilled swollen sample, while $V_r$ is the volume fraction of rubber in the CB-filled swollen sample. $\phi$ is the volume fraction of filler in the filled sample after drying, and $C$ is a constant depending on the type of carbon black, here $C$ was taken as 1.17 for carbon black N330$^{59}$. 

The bound rubber fraction of various CB-filled SBR compounds were also measured using Soxhlet extraction method. All the CB-filled SBR compounds were made using the Brabender mixer with the same processing parameters as discussed in section 3.2, no curatives were added, and the compounds were tested after a storage time of 8-10 days. First, cellulose extraction thimbles from Whatman were placed in a glass vacuum dryer with desiccant and put in an oven at a temperature of 80°C for 12 h in order to remove the moisture. Then the dryer was sealed and taken out from the oven and cooled down to room temperature. The dried empty thimbles were taken out and weighed within 5 seconds. Various uncured CB-filled SBR compounds of 0.7 to 0.9 g were prepared and placed in the dried thimbles and extracted in a Kimax Soxhlet extractor set. Benzene was used as the solvent and the extraction apparatus was heated on an electric heater. After an extraction time of 24 hours, the thimbles with the extracted samples inside were taken out to a vacuum oven and dried at 65°C for 24 hours to remove the solvent. Due to the long exposure time to the moisture during the repressurization, the thimbles with the extracted
samples were transferred to the glass vacuum dryer and dried at the same condition as for drying the empty thimbles. Finally, the thimbles with extracted samples were cooled down to room temperature, and weighed within 5 seconds. Then the weight of the extracted CB-filled SBR compounds was measured.

The bound rubber fraction was calculated using the following equation:

\[
\text{Bound rubber fraction} = \frac{\text{weight of bound rubber after extraction}}{\text{weight of rubber before extraction}}
\]
CHAPTER IV
RESULTS AND DISCUSSION

4.1 Processing Characteristics

The discharge temperature and power consumption of various rubber gums obtained from the Banbury mixer are shown in Table 4.1. The set up temperature for all the SBR gums were identical at 50°C. SBR gums without any extender oils had the highest discharge temperature and power consumption among all the rubber gums due to its higher viscosity. The extender oils could lower the viscosity of the rubber gums and therefore generated less heat and consumed less power. The SBR/SO gum exhibited a lower discharge temperature and power consumption compared to SBR/NO gum. The Plasticizer LN has an aniline point of 72.8°C$^{60}$, and the aniline point for soybean oil is around 29°C$^{3}$, which means the SO has higher unsaturated compounds than NO. Also according to previous study$^{48}$, the solubility parameter of SBR was around 16.6 to 16.9 (MPa)$^{1/2}$, 14.4 to 14.5 (MPa)$^{1/2}$ for NO, and 17.1 (MPa)$^{1/2}$ for SO. Thus SO has a better compatibility with SBR than NO. Also, the long fatty acid chain structure in the SO and MSO could give good plasticization effect. Therefore the SBR/SO and low level SBR/MSO gums exhibited lower discharge temperature than SBR/NO gum. With increasing level of the modification of the SO, both the discharge temperature and the power consumption increased. This is due to the increasing viscosity of the MSO at the higher modification level.
Table 4.1 Discharge temperature and power consumption from Banbury Mixer at an initial temperature of 50°C

<table>
<thead>
<tr>
<th>Material</th>
<th>Discharge Temperature (°C)</th>
<th>Power Consumption (KW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR Gum</td>
<td>100</td>
<td>17.0</td>
</tr>
<tr>
<td>SBR/NO Gum</td>
<td>83</td>
<td>10.0</td>
</tr>
<tr>
<td>SBR/SO Gum</td>
<td>78</td>
<td>9.0</td>
</tr>
<tr>
<td>SBR/5MSO Gum</td>
<td>78</td>
<td>10.0</td>
</tr>
<tr>
<td>SBR/10MSO Gum</td>
<td>79</td>
<td>11.0</td>
</tr>
<tr>
<td>SBR/30MSO Gum</td>
<td>80</td>
<td>11.0</td>
</tr>
<tr>
<td>SBR/45MSO Gum</td>
<td>85</td>
<td>11.5</td>
</tr>
</tbody>
</table>
4.2 Rheological Properties

4.2.1 Rheological properties of various SBR gums

Figure 4.1 shows the storage modulus, \( G' \) (a), loss modulus, \( G'' \) (b), and Figure 4.2 shows \( \tan \delta \) (a) and complex viscosity (b) of various SBR gums. The SBR gum without any oil exhibits the highest values of \( G' \) and \( G'' \). The oil-extended SBR gums all show lower values of \( G' \) and \( G'' \) due to the plasticization effect of oil. SBR/NO and SBR/SO have similar values of \( G' \) and \( G'' \), but the SBR/MSO gums show an increase in values of \( G' \) and \( G'' \) with an increase of the modification level. From Figure 4.1(a), it is observed that the slopes of \( G' \) vs. frequency curves of the SBR gums are lower than 2. Also, the complex viscosity of all the SBR gums shows frequency dependence at all frequencies. This indicates that the frequency range is not in the terminal region of the SBR gums. It is also observed that all the SBR gums approach the rubbery plateau at around 200 rad/s.

\( \tan \delta \) of various SBR gums (Figure 4.2(a)) shows a plateau at low frequencies for pure SBR gum, (within 0.02-0.43 rad/s) and oil-extended SBR gums (0.06-3.34 rad/s). This behavior is due to the star-shaped molecular structure of SBR. This observation is in agreement with studies of similar star-shaped rubber by other researchers\(^{61}\). The SBR gum without oils shows the lowest value of \( \tan \delta \) among various gums. The SBR/NO gum has a relatively higher value of \( \tan \delta \) than the SBR/SO gum. With an increase of the modification level, the value of \( \tan \delta \) is decreased.

The SBR gum without any oil has the highest value of complex viscosity (Figure 4.2(b)). The SBR/NO and SBR/SO gums have similar complex viscosity. The complex viscosity of the SBR/MSO gums slightly increases with an increase of the modification.
Figure 4.1 Storage (a) and loss (b) modulus as a function of frequency of various SBR gums at 90°C
Figure 4.2 Tan δ (a) and complex viscosity (b) as a function of frequency of various SBR gums at 90°C
level. The trend is similar to the effect of the modification level on values of $G'$ and $G''$. This is due to an increase of viscosity of the MSOs with the modification level. The increase of the modification level leads to an increase of the discharge temperature and power consumption of the SBR gums in the Banbury mixer.

4.2.2 Rheological properties of various CB-filled SBR compounds

The rheological properties of CB-filled SBR compounds without curatives were measured. Figure 4.3(a) and (b) show the values of $G'$ and $G''$ of various CB-filled SBR compounds of a function of frequency. Similar to the SBR gums without CB, the CB-filled SBR without oil showed the highest values of $G'$ and $G''$ among all the samples. The CB-filled SBR/SO compounds showed the lowest values of $G'$ and $G''$. With the increase of the modification level, the CB-filled SBR/MSO compounds had increasing values of $G'$ and $G''$. The CB-filled SBR/5MSO and SBR/10MSO compounds show similar values of $G'$ and $G''$ as the CB-filled SBR/NO compounds at all frequencies. The CB-filled SBR/30MSO and SBR/45MSO compounds show similar values of $G'$ and $G''$ but higher than those of the CB-filled SBR/5MSO and SBR/10MSO.

Figure 4.4(a) shows the tan $\delta$ curves of various CB-filled SBR compounds. The CB-filled SBR compounds without oil shows the lowest value of tan $\delta$, where the CB-filled SBR/SO compound exhibits the highest value of tan $\delta$. With the increase of the modification level, tan $\delta$ of the CB-filled SBR/MSOs is decreased. The CB-filled SBR/NO compound shows a similar value as the SBR/45MSO compound. It could be observed that all the samples exhibited a plateau in the frequency range from 0.02 to 0.43.
Figure 4.3 Storage (a) and loss (b) modulus as a function of frequency of various CB-filled SBR compounds at 90°C.
Figure 4.4 Tan δ (a) and complex viscosity (b) as a function of frequency of various CB-filled SBR compounds at 90°C
rad/s. This is attributed to the star-shaped molecular structure of SBR as mentioned earlier.

The complex viscosity of various CB-filled compounds is shown in Figure 4.4(b), it is seen that the CB-filled SBR compound without oil shows the highest value of the complex viscosity. Due to the presence of the plasticizers (various oils), all the oil-extended CB-filled SBR compounds shows lower values of the complex viscosity. The CB-filled SBR/SO shows the lowest complex viscosity. While the CB-filled SBR/5MSO and SBR/10MSO compounds showed similar values. Also the CB-filled SBR/30MSO and SBR/45MSO compounds had similar values. The CB-filled SBR/NO had a close value to the CB-filled SBR/5MSO and SBR/10MSO compounds. The trend of the complex viscosities were in agreement with the $G'$ and $G''$ of the samples. At high frequency, all the oil-extended CB-filled SBR compounds had a converging complex viscosity, which was also observed in unfilled SBR gums shown in Figure 4.2(b).

4.2.3 Rheological properties of various unfilled SBR vulcanizates

Rheological properties including $G'$, $G''$, $\tan \delta$ and complex viscosities of various unfilled SBR vulcanizates are measured. The unfilled SBR compounds are first cured in APA2000 at 160°C, and then cooled down to 90°C, and a frequency sweep was performed.

Figure 4.5(a) shows the values of $G'$ of various unfilled SBR vulcanizates. The unfilled SBR vulcanizate without oil exhibited the highest values of $G'$ among all the samples, followed in decreasing order by unfilled SBR/NO, SBR/10MSO-2, SBR/5MSO-2 and SBR/SO. Those samples show the behavior of typical highly
Figure 4.5 Storage (a) and loss (b) modulus as a function of frequency of various unfilled SBR vulcanizates at 90°C
crosslinked polymer. For various unfilled SBR/MSO vulcanizates, with the increase of modification level, the values of $G'$ became more frequency dependent. Such a behavior is characteristic of a lower crosslinked polymer. It should be noted that the trend matches the decreasing crosslink densities of the unfilled SBR/MSO vulcanizates. It is observed that the values of $G'$ of the oil-extended unfilled SBR vulcanizates gradually converge at high frequencies corresponding to their rubbery plateau. According to Rosa and Winter’s theory \(^\text{62}\), the values of $G'$ are defined by the entanglement density of the rubber with the crosslink density having less effect on the $G'$.

Figure 4.5(b) shows the values of $G''$ of various unfilled SBR vulcanizates. Unfilled SBR/NO vulcanizate showed the lowest values of $G''$ at all frequencies. Unfilled SBR/5MSO-2, SBR/10MSO-2 and SBR without oil exhibit similar values of $G''$. Unfilled SBR/SO, SBO/5MSO, SBR/10MSO, SBR/30MSO and SBR/45MSO vulcanizates show increasing values of $G''$ with an increase of modification level.

Tan $\delta$ of the vulcanizates (Figure 4.6(a)) decreases with a decrease of the frequency. The unfilled SBR and SBR/NO vulcanizates exhibit similar values of tan $\delta$. Also unfilled SBR/5MSO-2 and SBR/10MSO-2 vulcanizates show similar values but higher than those of SBR and SBR/NO vulcanizates. Tan $\delta$ of unfilled SBR/SO and various SBR/MSO vulcanizates increases with an increase of the modification level. For unfilled SBR/30MSO and SBR/45MSO, the tan $\delta$ slightly decreases with an increase of frequency at high frequency.

Figure 4.6(b) shows the complex viscosity of various unfilled SBR vulcanizates. Unfilled SBR vulcanizate showed the highest complex viscosity, followed by SBR/NO, SBR/5MSO-2, SBR/10MSO-2 and SBR/SO in decreasing order. The complex viscosities
Figure 4.6 Tan \( \delta \) (a) and complex viscosity (b) as a function of frequency of various unfilled SBR vulcanizates at 90°C
of various SBR/MSO vulcanizates show similar values. It is noticed that the complex viscosity of all the oil-extended samples converged to a similar value at high frequency.

4.2.4 Rheological properties of various CB-filled SBR vulcanizates

Various CB-filled SBR compounds are first cured at 160°C in APA2000 and then cooled down to 90°C and then the frequency sweep is performed.

Figure 4.7(a) shows the storage modulus (G’) of various CB-filled SBR vulcanizates. It is observed that the CB-filled SBR vulcanizates without any oil has the highest value of G’ among all the samples. It exhibits a behavior of typical highly crosslinked polymer. The values of G’ of various oil-extended CB-filled SBR vulcanizates are decreased. The CB-filled SBR/NO vulcanizate shows a higher value of G’ than that of the CB-filled SBR/SO vulcanizate. Values of G’ of various CB-filled SBR/MSO vulcanizates decrease with the level of modification of SO and lower than that of the SBR/NO vulcanizate. The slope of the G’ vs. ω curves increases with the level of modification. This phenomenon is similar to that of the unfilled SBR/MSO vulcanizates. Due to the higher amount of curatives, the CB-filled SBR/5MSO-2 and SBR/10MSO-2 vulcanizates show values of G’ close to CB-filled SBR/NO vulcanizate. All the results indicated that the crosslink density of various CB-filled SBR vulcanizates as shown below are different. With the increase of the modification level, the crosslink density of SBR/MSO vulcanizates decrease. Similar to the unfilled SBR vulcanizates, the values of G’ for all the oil-extended SBR samples converged to a similar value at a frequency of 200 rad/s.

Figure 4.7(b) shows the loss modulus (G’’) as a function of the frequency. Similar to G’, the G” of the CB-filled SBR vulcanizate without any oil showed the highest value
Figure 4.7 Storage (a) and loss (b) modulus as a function of frequency of various CB-filled SBR vulcanizates at 90°C
among all the vulcanizates. The value of $G''$ of the CB-filled SBR/NO, SBR/SO and SBR/5MSO vulcanizates are similar. The CB-filled SBR/10MSO vulcanizate indicates a slightly higher value of $G''$ than that of the CB-filled SBR/5MSO vulcanizate. The CB-filled SBR/30MSO and SBR/45MSO vulcanizates show higher values of $G''$ than that of CB-filled SBR/10MSO vulcanizate. The CB-filled SBR/5MSO-2 shows the lowest value of $G''$ among all the vulcanizates.

From Figure 4.8(a), it is seen that the CB-filled SBR, SBR/NO, SBR/SO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates exhibit a decreased of tan $\delta$ with a decrease of the frequency at all frequency range, which is a typical behavior of a crosslinked polymer. The CB-filled SBR/5MSO to SBR/45MSO vulcanizates show a decrease in tan $\delta$ at high frequencies. Similar to the unfilled vulcanizates, the CB-filled SBR/45MSO and SBR/30MSO vulcanizates exhibit peaks in tan $\delta$ vs. frequency curves. It is possibly due to the relaxation process of the sol. The CB-filled SBR and SBR/NO vulcanizates show similar values of tan $\delta$, followed in increasing order by CB-filled SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO and SBR/45MSO vulcanizates. The CB-filled SBR/10MSO-2 vulcanizate shows slightly higher tan $\delta$ value at lower frequency and a similar tan $\delta$ at higher frequency compared to that of the CB-filled SBR/NO vulcanizate. The CB-filled SBR/5MSO-2 shows the lowest tan $\delta$ values among all the samples.

Figure 4.8(b) shows the complex viscosity of various CB-filled SBR vulcanizates. The CB-filled SBR vulcanizate without any oil exhibits the highest complex viscosity among all the samples. Due to the plasticization effect, various CB-filled oil-extended SBR vulcanizates show lower complex viscosity compared to that of the CB-filled SBR
Figure 4.8 Tan δ (a) and complex viscosity (b) as a function of frequency of various CB-filled SBR vulcanizates at 90°C
vulcanizate without any oil. The complex viscosity of various CB-filled oil-extended SBR vulcanizates followed the same order as the values of $G'$ of all the oil-extended samples at lower frequency. At higher frequency, the complex viscosity of various CB-filled oil-extended SBR vulcanizates converge to a similar value.

Figure 4.9 shows the dependence of $G'$ on the strain amplitude of uncured CB-filled SBR compounds (a) and cured CB-filled SBR vulcanizates (b). It is observed that all the CB-filled compounds show a reduction of $G'$ with the strain amplitude which is also known as Payne effect. The $G'$ curves of the various CB-filled compounds are parallel with each other indicating a similar Payne effect. Also, in Figure 4.9(b) it is seen that all the CB-filled SBR vulcanizates exhibit almost similar Payne effect. With an increase of the modification level, the CB-filled SBR/MSO vulcanizates only show a slightly increasing Payne effect. The results indicate that the presence of the plasticizers has no significant effect on the filler-filler interaction, the dispersion of filler in different compounds and vulcanizates are similar to each other.

4.3 Thermal Properties

4.3.1 TGA analysis

Figure 4.10 shows the TGA curves for various extender oils. It indicates that the SO had the best thermal stability. As the modification extent increased, the thermal stability of the MSOs decreases gradually. The NO starts to vaporize at about 100°C and completely vaporizes at about 270°C. The flash point of the NO Plasticizer LN is around 171°C, and the flash point for the SO is over 260°C. A stronger intermolecular force of SO makes its thermal stability better than NO.
Figure 4.9 Storage modulus as a function of strain amplitude of various CB-filled SBR compounds (a) and vulcanizates (b).
Figure 4.10 TGA curves of various extender oils
Figure 4.11 shows the TGA curves of various SBR gums (a) and CB-filled SBR compounds (b). In both cases, SBR without any extender oils shows the best thermal stability. For SBR gums and CB-filled compounds with various oils, the thermal stabilities follow the same order as the extender oils. SBR gums and CB-filled compounds with SO show the best thermal stability, and with the increase of the modification of the oil, the thermal stability of the SBR gums and CB-filled compounds decrease gradually. SBR gum and CB-filled compound containing NO exhibited the lowest thermal stability. For the SBR and CB-filled SBR compound without any oil, the residue is around 36.5 wt%. For various oil-extended CB-filled SBR compounds, the residue ranges from 30.5 wt% to 31.8 wt%. This residue is due to the presence of the 60 phr of CB in the SBR compound.

Figure 4.12 shows the TGA curves of various unfilled (a) and CB-filled (b) SBR vulcanizates. Both the unfilled and CB-filled SBR vulcanizates without any extender oil show the best thermal stability. Similar to the extender oils and SBR gums and CB-filled compounds containing oils, the unfilled and CB-filled SBR/SO and various SBR/MSO vulcanizates exhibit decreasing thermal stability with the increase of the modification of the SO, but they all exhibit better thermal stability than that of the unfilled or CB-filled SBR/NO vulcanizates. It can be seen from Figure 4.12(a) that the residue of pure SBR is about 4.7 wt%, and the residue of oil-extended SBRs is around 3.7 wt% for due to the presence of 5 phr of ZnO. Also from Figure 4.12(b) it is observed that the residue of CB-filled SBR vulcanizate is about 38.1 wt%, and the residue of oil-extended CB-filled SBR vulcanizates is 32.5 wt% due to the presence of 60 phr of CB and 5 phr of ZnO.
Figure 4.11 TGA curves of various SBR gums (a) and various CB-filled SBR compounds (b)
Figure 4.12 TGA curves of various unfilled SBR vulcanizates (a) and various CB-filled SBR vulcanizates (b)
4.3.2 DSC analysis

Figure 4.13 shows the DSC curves of various extender oils including NO, SO and various MSOs (a) and DSC curves of NO and SO at lower temperatures (b). NO exhibits a glass transition at -80.6°C without any additional transitions. SO has a glass transition at -105.2°C and also two melting peaks at -37.0°C and -23.4°C. In Figure 4.13(b), two crystallization peaks are observed at -86.5°C and -70.6°C. According to previous study, the two melting peaks of SO shown in Figure 4.13(a) are respectively attributed to the two main fatty acids in the SO, linoleic acid and oleic acid. It is anticipated that the two crystallization peaks of SO shown in Figure 4.13(b) are also attributed to the linoleic acid and oleic acid. These two crystallization peaks are not clearly observed due to the fact that in Figure 4.13(a), the SO sample is cooled down at a controlled cooling rate of 10°C/min, and the SO sample in the Figure 4.13(b) is quenched by the liquid nitrogen leading to a cold crystallization. At the modification level of 5%, the melting peak merges into one peak. At higher modification level, the melting peak becomes flat. This was due to the fact that the modification brings large side groups to the fatty acid chains creating hindrance and thus reducing the crystallinity.

Figure 4.14 shows the DSC curves of various SBR gums (a) and various CB-filled SBR compounds (b). Figure 4.15 shows the DSC curves of various unfilled (a) and CB-filled (b) SBR vulcanizates. Glass transition temperature, $T_g$, of rubber gums, CB-filled compounds, unfilled and CB-filled vulcanizates can be determined from the DSC curves. The results are listed in Table 4.2. It is very clear from these results that all the oil-extended SBR gums, CB-filled compounds, both unfilled and CB-filled vulcanizates have a lower $T_g$ than SBR without any oil. The extender oils could act as
Figure 4.13 DSC curves of various extender oils (a) and NO and SO at lower temperature (b)
Figure 4.14 DSC curves of various SBR gums (a) and CB-filled SBR compounds (b)
Figure 4.15 DSC curves of various unfilled SBR vulcanizates (a) and various CB-filled SBR vulcanizates (b).
<table>
<thead>
<tr>
<th></th>
<th>SBR Gums (°C)</th>
<th>CB-filled SBR Compounds (°C)</th>
<th>Unfilled SBR Vulcanizates (°C)</th>
<th>CB-filled SBR Vulcanizates (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>-31.9</td>
<td>-32.6</td>
<td>-25.4</td>
<td>-23.6</td>
</tr>
<tr>
<td>SBR/NO</td>
<td>-45.4</td>
<td>-45.8</td>
<td>-41.2</td>
<td>-38.8</td>
</tr>
<tr>
<td>SBR/SO</td>
<td>-54.1</td>
<td>-52.2</td>
<td>-46.8</td>
<td>-42.3</td>
</tr>
<tr>
<td>SBR/5MSO</td>
<td>-49.6</td>
<td>-48.8</td>
<td>-43.9</td>
<td>-41.2</td>
</tr>
<tr>
<td>SBR/10MSO</td>
<td>-47.7</td>
<td>-48.1</td>
<td>-43.5</td>
<td>-40.5</td>
</tr>
<tr>
<td>SBR/30MSO</td>
<td>-43.5</td>
<td>-42.2</td>
<td>-37.6</td>
<td>-37.7</td>
</tr>
<tr>
<td>SBR/45MSO</td>
<td>-39.0</td>
<td>-39.7</td>
<td>-34.2</td>
<td>-33.8</td>
</tr>
<tr>
<td>SBR/5MSO-2</td>
<td>-49.6</td>
<td>-48.8</td>
<td>-42.4</td>
<td>-40.4</td>
</tr>
<tr>
<td>SBR/10MSO-2</td>
<td>-47.7</td>
<td>-48.1</td>
<td>-41.6</td>
<td>-39.9</td>
</tr>
</tbody>
</table>
a plasticizer and increase the free volume of the system, subsequently decreasing its \( T_g \). A lower \( T_g \) could give a better performance for rubber at low temperatures.

Using Fox equation:

\[
\frac{1}{T_g} = \frac{\omega_1}{T_g,1} + \frac{\omega_2}{T_g,2}
\]

Where \( \omega_1 \) and \( \omega_2 \) are the weight percentages of SBR and extender oil, \( T_{g,1} \) and \( T_{g,2} \) are the glass transition temperatures of SBR and extender oil, respectively. We can acquire the theoretical \( T_g \) of SBR gums compounded with oil. It was found that \( T_g = -45.1^\circ C \) for SBR/NO gums and \(-53.9^\circ C \) for SBR/SO gums. Clearly, the results correspond to the results from DSC, demonstrating that both SO and NO are highly miscible with SBR.

SBR/SO gums has the lowest \( T_g \) of \(-54.1^\circ C \), that is by 8.7 degrees lower than that of SBR/NO gums. SBR/MSO gums exhibit a \( T_g \) vary from \(-49.6^\circ C \) to \(-39.0^\circ C \), with the increase of modification level. One can notice that the DSC curve of SBR/SO gum shows an exothermic peak at \(-38.0^\circ C \), and endothermic behavior at \(-32.1^\circ C \) to \(0^\circ C \). In SBR/5MSO and SBR/10MSO gums, these behaviors gradually disappear. This is probably due to the remnant of crystallization and melting behavior of the SO and MSOs corresponding to the behavior of the oils as shown in Figure 4.13(a).

The CB-filled SBR compounds indicate similar \( T_g \) as the SBR gums. From the DSC curves shown in Figure 4.14(b), it is noticed that all the melting peaks for CB-filled SBR/SO and SBR/MSO compounds disappear. Similar behavior is also seen in CB-filled SBR vulcanizates shown in Figure 4.15(b). For CB-filled SBR/SO and SBR/MSO
compounds, the T\textsubscript{g} increases with an increase of the modification level. The CB-filled SBR/NO compound has a T\textsubscript{g} similar to the CB-filled SBR/10MSO compound.

For unfilled SBR vulcanizates (Figure 4.15(a)), the shapes of the curves are similar to SBR gums. However, due to the presence of the crosslinks, the T\textsubscript{g} of the various SBR vulcanizates increases as shown in Table 4.2. The unfilled SBR/SO, SBR/5MSO and SBR/10MSO show a lower T\textsubscript{g} than that of SBR/NO vulcanizate. The unfilled SBR/30MSO and SBR/45MSO vulcanizate has a higher T\textsubscript{g} than that of SBR/NO vulcanizate. After increasing the amount of curatives, the T\textsubscript{g} of unfilled SBR/5MSO-2 and SBR/10MSO-2 vulcanizates increases by about 2°C compared to those of unfilled SBR/5MSO and SBR/10MSO, but it is lower than that of the unfilled SBR/NO vulcanizate.

For CB-filled SBR vulcanizates, all the samples showed a smooth DSC curve as seen in Figure 4.15(b), this is probably due to the filler hindering the crystallization of the oils. T\textsubscript{g} of various CB-filled SBR vulcanizates increases compared to those of the unfilled SBR vulcanizates. The CB-filled SBR/NO vulcanizate has a T\textsubscript{g} of -38.8°C, the CB-filled SBR/SO has a T\textsubscript{g} of -42.3°C, which is by 3.5°C lower than that of the CB-filled SBR/NO vulcanizate. Similar to the unfilled vulcanizates, only CB-filled SBR/30MSO and SBR/45MSO vulcanizates exhibit higher T\textsubscript{g} than that of the CB-filled SBR/NO vulcanizate. Results show that the SBR/SO and SBR/MSO vulcanizates could have better low temperature performance than the SBR/NO vulcanizate.
4.4 Curing behaviors

Curing properties of unfilled and CB-filled SBR compounds are measured by APA2000 at 160°C. The curing curves are shown in Figure 4.16 and Figure 4.17, respectively.

4.4.1 Unfilled SBR

The unfilled SBR compound without oil shows the highest maximum torque ($M_{HH}$), it’s $T_{95}$ is 36.5 min. The SBR/NO compound shows a much lower maximum torque and a slightly increased curing time compared to the SBR compound without oil. This is due to the dilution effect of the NO. The SBR/SO compound exhibits a shorter induction period than those of the SBR and SBR/NO compounds. Also the SBR/SO compound shows a marching torque during the overcure period. According to previous study\textsuperscript{46}, it is probably attributed to the additional reactive fatty acid in the SO solubilizing the ZnO more and giving a stronger ZnO/fatty acid activator system.

For the unfilled SBR/MSOs, with an increase of the modification level, the induction period and $T_{95}$ become longer, and the $M_{HH}$ decreases. The SBR/5MSO-2 and SBR/10MSO-2 show similar behavior and the $M_{HH}$ increases compared to the SBR/5MSO and SBR/10MSO. It can also be observed that instead of a plateau on the curing curves, reversion occurs at higher modification level. This is probably due to the covalcanization of the MSOs with SBR by sulfur creating more polysulfidic crosslinks.
Figure 4.16 Curing curves of various unfilled SBR compounds at 160°C
Figure 4.17 Curing curves of various CB-filled SBR compounds at 160°C
4.4.1 CB-filled SBR

Figure 4.17 shows curing curves of CB-filled SBR compounds. The CB-filled SBR compound without oil has the shortest induction period, the highest initial and final torque. Other CB-filled SBR compounds have similar but longer induction period, lower initial and final torque. This indicates that the CB-filled oil-extended SBR could have a better process safety than SBR without oil. In addition, a lower initial torque can benefit the processing. Also, the $M_H$ of the CB-filled SBR/5MSO-2 and SBR/10MSO-2 are close to that of the SBR/NO.

The $T_{95}$ is determined from curing curves. The results are shown in Table 4.3. All the CB-filled SBR compounds show a significant decrease in the induction time and $T_{95}$ compared to the corresponding unfilled samples. This is because that the CB could act as a catalyst during the vulcanization\textsuperscript{64}. SBR/5MSO-2 and SBR/10MSO-2 compounds showed the shortest curing time, due to their higher amount of curatives. SBR/SO had the longest $T_{95}$ (25.2 min) due to the marching torque at the overcure period. This phenomenon was similar to the unfilled SBR/SO compound.

The values of the $M_H$ of both unfilled and CB-filled compounds correlate well with the crosslink density test results, as described later.
<table>
<thead>
<tr>
<th></th>
<th>T$_{95}$ of Unfilled SBR (min)</th>
<th>T$_{95}$ of CB-filled SBR (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>36.5</td>
<td>16.1</td>
</tr>
<tr>
<td>SBR/NO</td>
<td>37.5</td>
<td>18.2</td>
</tr>
<tr>
<td>SBR/SO</td>
<td>45.3</td>
<td>25.2</td>
</tr>
<tr>
<td>SBR/5MSO</td>
<td>23.5</td>
<td>14.4</td>
</tr>
<tr>
<td>SBR/10MSO</td>
<td>27.2</td>
<td>11.5</td>
</tr>
<tr>
<td>SBR/30MSO</td>
<td>28.3</td>
<td>12.8</td>
</tr>
<tr>
<td>SBR/45MSO</td>
<td>31.1</td>
<td>13.0</td>
</tr>
<tr>
<td>SBR/5MSO-2</td>
<td>22.0</td>
<td>7.6</td>
</tr>
<tr>
<td>SBR/10MSO-2</td>
<td>22.2</td>
<td>7.6</td>
</tr>
</tbody>
</table>
4.5 Swelling test

4.5.1 Gel Fraction

Gel fractions of unfilled and CB-filled SBR vulcanizates are shown in Figure 4.18. All the CB-filled vulcanizates show higher gel fraction than the unfilled ones due to the presence of the CB.

Among various unfilled vulcanizates, the unfilled SBR vulcanizate without any oil shows the highest gel fraction of 98.3%. Due to the presence of the extender oils, all the unfilled oil-extended vulcanizates show lower gel fraction compared to that of the unfilled SBR vulcanizate without oil. Under assuming all the oils were extracted, the calculated gel fraction of the oil-extended unfilled SBR vulcanizates is 78.20%. The unfilled SBR/SO vulcanize has a gel fraction of 79.31%, slightly higher than that of the unfilled SBR/NO vulcanizate with its value being 79.18%. With an increase of the modification extent, the gel fraction of the SBR/MSOs is slightly increased. The gel fraction of the unfilled SBR/5MSO, SBR/10MSO, SBR/30MSO and SBR/45MSO are 79.40%, 79.56%, 79.64% and 79.68%, respectively. The slight increase is probably due to the covalcanization of the SO and MSOs with rubber. After increasing the amount of sulfur and CBTS in the recipe, the gel fraction of the SBR/5MSO-2 and SBR/10MSO-2 increases to 79.97% and 80.08%, respectively, which is higher compared to those of the vulcanizates with original recipe.

The CB-filled SBR vulcanizates without any oil had a gel fraction of 98.96%. The theoretical gel fraction for the CB-filled SBR vulcanizates with oil is 84.87%. All the CB-filled oil-extended SBR vulcanizates with 2 phr of sulfur and 1.3 phr of CBTS show a similar gel fraction around 84.80% to 84.90%. After increasing the sulfur and CBTS
Figure 4.18 Gel fraction of various unfilled and CB-filled SBR vulcanizates.
content, the gel fraction of SBR/5MSO-2 and SBR/10MSO-2 is increased to 85.50% and 85.33%, respectively.

4.5.2 Crosslink density

The crosslink densities of various unfilled and CB-filled SBR vulcanizates are shown in Figure 4.19. The unfilled SBR vulcanizate has a crosslink density of 0.136 Kmol/m$^3$. The crosslink density of unfilled SBR/NO vulcanizate is 0.086 Kmol/m$^3$ due to the presence of the oil plasticizer. The unfilled SBR/SO vulcanizate has a crosslink density of 0.053 Kmol/m$^3$. The unfilled SBR/5MSO, SBR/10MSO, SBR/30MSO and SBR/45MSO have crosslink density of 0.052 Kmol/m$^3$, 0.048 Kmol/m$^3$, 0.039 Kmol/m$^3$ and 0.033 Kmol/m$^3$, respectively. It can be seen that the unfilled SBR/SO and all the SBR/MSO vulcanizates show lower crosslink density compared to that of the unfilled SBR/NO vulcanizates. This may probably be attributed to the fact that the SO and MSO could react with curatives and thus consume certain amount of sulfur, therefore causing the drop in the crosslink density of the SBR vulcanizates\textsuperscript{48}. After increasing the curative content, the crosslink density of the unfilled SBR/5MSO-2 and SBR/10MSO-2 is increased to 0.085 Kmol/m$^3$ and 0.080 Kmol/m$^3$, respectively.

The CB-filled SBR vulcanizate without oil has a crosslink density of 0.199 Kmol/m$^3$. The CB-filled SBR/NO has a crosslink density of 0.117 Kmol/m$^3$, while the CB-filled SBR/SO has a crosslink density of 0.065 Kmol/m$^3$. The CB-filled SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO vulcanizates show crosslink density of 0.050 Kmol/m$^3$, 0.042 Kmol/m$^3$, 0.027 Kmol/m$^3$ and 0.024 Kmol/m$^3$, respectively. Obviously, the crosslink density of the CB-filled SBR/SO and SBR/MSO vulcanizates decreases
Figure 4.19 Crosslink densities of various unfilled and CB-filled SBR vulcanizates.
with an increase of modification level. The reason to this phenomenon is similar to the unfilled SBR/SO and SBR/MSO vulcanizates that the sulfur is consumed by the reaction with the oils.

The behavior of the crosslink density of the unfilled and CB-filled SBR vulcanizates correlates with curing behaviors of compounds and dynamic and mechanical properties of vulcanizates. With the decrease of the crosslink density, the $M_H$ during the curing, the moduli and abrasion resistance of the vulcanizates are decreased.

### 4.5.3 Bound rubber fraction

Figure 4.20 shows the result of bound rubber measurements of compounds. The SBR/CB compound has the highest bound rubber fraction of 38.7%. After mixing with 30 phr of various processing oil, the bound rubber fraction of the CB-filled oil-extended SBR compound is decreased. The CB-filled SBR/NO compound has a bound rubber fraction of 23.5%. The CB-filled SBR/SO compound has a bound rubber fraction of 25.5%. The bound rubber fraction of the CB-filled SBR/5MSO, SBR/10MSO, SBR/30MSO and SBR/45MSO is 25.1%, 21.5%, 18.7% and 16.8%, respectively. It is observed that the CB-filled SBR/SO and CB-filled SBR/5MSO compounds have a higher bound rubber fraction than the CB-filled SBR/NO compound. With the increase of the modification level, the bound rubber fraction of the CB-filled SBR/MSO compounds decreases. This is probably due to the microplasticization effect and the coupling effect of the SO and MSO with SBR and CB. The ester groups of the oils could interact with the surface of the CB and the fatty acid chains could blend with the SBR chains. These effects could enhance the interaction between the rubber and the CB, and therefore better
Figure 4.20 Bound rubber fraction of various CB-filled SBR compounds.
mechanical properties such as abrasion resistance\textsuperscript{42,43}. After further modification, the coupling effect is weakened and the bound rubber fraction is decreased.

4.6 Reaction of MSO

As discussed in Chapter II, vegetable oil such as soybean oil has large amount of carbon-carbon double bonds on the fatty acid chains, and can be polymerized through various methods. Previous studies had claimed that during vulcanization of rubbers, the vegetable oils could possibly be covulcanized to the rubber matrix, and the sulfur may be consumed by the oils\textsuperscript{43,48}. To study the reaction of SO and MSO with curatives, oils with curatives at the same ratio as in the rubber compound and oils without curatives were heated in the DSC at 160°C.

Figure 4.21 shows the DSC curves of oils without curatives (a) and with curatives (b) at 160°C. The DSC curves of the oils without any curatives have smooth curves. However, the DSC curves with curatives show exothermic peaks. This indicates that the oils reacted with the curatives and cured. The exothermic peak of 30MSO with curatives has the largest curing peak among the three samples, followed by 10MSO with curatives, and SO with curatives having the smallest peak. This implies that the higher level of modification of the SO, the more the oil could react with the curatives.

The viscosity of the SO, 10MSO and 30MSO with and without curatives were measured by DHR. All the samples were heated in a vacuum oven at 160°C for 60 min to simulate the condition during the vulcanization. After the heating, no obvious color
Figure 4.21 DSC curves for SO, 10MSO and 30MSO at 160°C (a), and SO/Curatives, 10MSO/Curatives and 30MSO/Curatives at 160°C (b).
change is observed for the oils without curatives. The samples remain as transparent light yellow liquid. However, all the oil with curatives become opaque brown color liquid.

Figure 4.22 shows the viscosity data of oils with and without curatives. All the samples showed Newtonian behavior in the test range. After the reaction, the viscosity of SO with curatives, 10MSO with curatives and 30MSO with curatives is increased 24.2%, 29.8% and 45.9%, respectively. The latter demonstrates that with an increase of the modification level, the oil could react more with curatives leading to higher increase in the viscosity.

The presented experimental data show that the SO and MSO could react with curatives causing consumption of the curatives, leading to a lower crosslink density of the SBR/SO and various SBR/MSO vulcanizates. Figure 4.23 shows the possible crosslink structures between the rubber chains. The SO and MSO can probably cured on the rubber chains and also vulcanized with each other. The MSOs have more reactive double bonds compared to SO and therefore could react more during the curing. The MSOs play an important role in the curing process of the rubber compounds. They could be covulcanized in the crosslink network, and possibly alter the crosslink structure of the vulcanizates, creating more polysulfidic crosslinks. The polysulfidic crosslinks could slip under high stress, cleave and reform and prevent the premature breakage of the overstressed rubber chains. Therefore, it could result in improved room temperature tensile properties of vulcanizates\textsuperscript{65,66}. 
Figure 4.22 Viscosity as a function of shear rate of SO, 10MSO and 30MSO, SO/Curatives, 10MSO/Curatives and 30MSO/Curatives at 35°C.
Figure 4.23 Schematic picture of possible crosslinks between rubber chains
4.7 Mechanical properties

4.7.1 Tensile properties

Tensile properties including the M100, M300, elongation at break and tensile strength of unfilled and CB-filled SBR vulcanizates were obtained.

Figure 4.24 shows the strain-stress curves of the unfilled SBR vulcanizates. The M100, M300, elongation at break and tensile strength of these vulcanizates are shown in Figure 4.25 (a) to (d). The unfilled SBR vulcanizate without oil had the highest modulus and tensile strength but the lowest elongation at break among all the unfilled SBR vulcanizates. It has an elongation of 321.3% and a tensile strength of 1.69 MPa. All the unfilled oil-extended SBR vulcanizates exhibit lower moduli but higher elongation at break compared to those of the pure SBR vulcanizate. The unfilled SBR/NO vulcanizate has an elongation at break of 326.3% and a tensile strength of 0.933 MPa. The unfilled SBR/SO has an elongation at break of 402.5% and a tensile strength of 0.902 MPa, it also has a lower modulus than that of the SBR/NO vulcanizate. For the various unfilled SBR/MSO vulcanizates, the elongation at break and tensile strength values are 477.2% and 0.967 MPa for SBR/5MSO, 489.6% and 0.912 MPa for SBR/10MSO, 674.5% and 1.021 MPa for SBR/30MSO and 744.9% and 1.091 MPa for SBR/45MSO. With an increase of the modification level, the M100 and M300 of the samples decreases, but the elongation at break increases tremendously with an increase of modification level. The tensile strength is similar or higher compared to the SBR/NO vulcanizate. After increasing the amount of curatives recipe, the unfilled SBR/5MSO-2 vulcanizate has an elongation at break of 363.1%, and a tensile strength of 1.139 MPa. The unfilled
Figure 4.24 Strain-stress curves of unfilled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates.
Figure 4.25 M100 (a), M300 (b), elongation at break (c) and strength (d) of the unfilled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates.
SBR/10MSO-2 vulcanizate has an elongation at break of 392.9% and a tensile strength of 1.158 MPa, with the modulus being comparable to that of the SBR/NO vulcanizate.

Figure 4.26 shows the strain-stress curves of the various CB-filled SBR vulcanizates. The M100, M300, elongation at break and tensile strength of these vulcanizates are shown in Figure 4.27 (a) to (d). Similar to the unfilled samples, the CB-filled SBR vulcanizate has the highest modulus and tensile strength, but its elongation at break is the lowest than that of the CB-filled oil-extended SBR vulcanizates. The tensile strength of the CB-filled SBR is 21.00 MPa, and the elongation at break is 243.8%. Due to the plasticization effect, all the CB-filled oil-extended SBR vulcanizates show an increase in the elongation at break and decrease in modulus and tensile strength compared to the CB-filled SBR without oil. The CB-filled SBR/NO vulcanizate had an elongation of 321.3% and a tensile strength of 13.57 MPa, the CB-filled SBR/SO has an elongation of 427.3% and a tensile strength of 15.76 MPa. Clearly it has both the higher elongation at break and tensile strength compared to that of the CB-filled SBR/NO vulcanizate. Previous study also observed that the rubber containing soybean oil showed increase in both elongation at break (from 401.4% to 543.4%) and tensile strength (from 19.54 MPa to 23.93 MPa) compared to the rubber containing petroleum oil. For various CB-filled SBR/MSO vulcanizates, the elongation at break and strength are 671.8% and 17.08 MPa for SBR/5MSO, 755.2% and 16.56 MPa for SBR/10MSO, 943.0% and 13.05 MPa for SBR/30MSO and 776.1% and 10.07 MPa for SBR/45MSO. After adjusting the recipe, the moduli of the CB-filled SBR/5MSO-2 and SBR/10MSO-2 vulcanizates are close to that of the CB-filled SBR/SO vulcanizate. These vulcanizates have an elongation at break and tensile strength of 512.5% and 18.63 MPa and 560.0% and 19.27 MPa, respectively.
Figure 4.26 Strain-stress curves of the CB-filled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates.
Figure 4.27 M100 (a), M300 (b), elongation (c) and strength (d) of CB-filled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates
It is observed that after the modification of the SO, the CB-filled SBR/MSO vulcanizates have a tremendous increase in the elongation at break. The CB-filled SBR/30MSO vulcanizate showed the highest elongation at break, which is about three times of the CB-filled SBR/NO vulcanizate. Also the CB-filled SBR/5MSO and SBR/10MSO have a higher tensile strength and elongation at break compared to that of the CB-filled SBR/NO and SBR/SO vulcanizates. The CB-filled SBR/45MSO has a similar elongation at break as the CB-filled SBR/10MSO vulcanizate and has the lowest tensile strength among all the samples due to its low crosslink density. The CB-filled SBR/10MSO-2 vulcanizate has a tensile strength comparable to that of the CB-filled SBR vulcanizate without oil, and has a much higher elongation at break at the same time.

Due to their different structures and properties, the extender oils, the SO and MSOs can influence the curing process creating more polysulfidic crosslinks, thus leading to different crosslink densities and mechanical properties.

4.7.2 Hardness and abrasion

Table 4.4 shows the hardness of various unfilled and CB-filled SBR vulcanizates. Hardness was measured by a pocket Durometer Type A. For both unfilled and CB-filled SBR vulcanizates, the hardness of SBR without oils is the highest among all the vulcanizates. The SBR/SO vulcanizate has a lower hardness than the SBR/NO vulcanizate, which was observed in previous study. For various SBR/MSO vulcanizates, with an increase of the modification level, the hardness of the vulcanizates increased. The hardness of the SBR/5MSO-2 and SBR/10MSO-2 vulcanizates is increased with
increased amount of the curatives compared to the SBR/5MSO and SBR/10MSO vulcanizates.

Figure 4.28 depicts the results of CB-filled SBR abrasion test. In the 40 m abrasion tests, the CB-filled SBR Vulcanizate has the lowest weight loss among all the vulcanizates. The CB-filled SBR/5MSO vulcanizate has a slightly better abrasion resistance than that of CB-filled SBR/NO vulcanizate, which in agreement with the previous report\textsuperscript{45}. It is probably attributed to the coupling effect of the SO between the CB and the SBR. With an increase of the modification level, the CB-filled SBR/MSO vulcanizates show an increase in weight loss. The CB-filled SBR/5MSO vulcanizate shows similar value of weight loss compared to that of the CB-filled SBR/NO vulcanizate. The CB-filled SBR/5MSO-2 vulcanizate shows the best abrasion resistance among all the oil-extended vulcanizates.

Table 4.4 Hardness of the unfilled and CB-filled SBR vulcanizates

<table>
<thead>
<tr>
<th></th>
<th>Unfilled (Shore A)</th>
<th>CB Filled (Shore A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR</td>
<td>41</td>
<td>81</td>
</tr>
<tr>
<td>SBR/NO</td>
<td>28</td>
<td>65</td>
</tr>
<tr>
<td>SBR/SO</td>
<td>26</td>
<td>61</td>
</tr>
<tr>
<td>SBR/5MSO</td>
<td>27</td>
<td>59</td>
</tr>
<tr>
<td>SBR/10MSO</td>
<td>27</td>
<td>59</td>
</tr>
<tr>
<td>SBR/30MSO</td>
<td>28</td>
<td>61</td>
</tr>
<tr>
<td>SBR/45MSO</td>
<td>29</td>
<td>63</td>
</tr>
<tr>
<td>SBR/5MSO-2</td>
<td>29</td>
<td>60</td>
</tr>
<tr>
<td>SBR/10MSO-2</td>
<td>29</td>
<td>61</td>
</tr>
</tbody>
</table>
Figure 4.28 Abrasion loss of the CB-filled SBR, SBR/NO, SBR/SO, SBR/5MSO, SBR/10MSO, SBR/30MSO, SBR/45MSO, SBR/5MSO-2 and SBR/10MSO-2 vulcanizates
4.8 DMA test and performance predictors

The dynamic properties of the unfilled and CB-filled rubber vulcanizates as a function of different temperature are evaluated using DMA. The results are used to predict the performance in tires.

Figure 4.29 to Figure 4.34 shows the temperature dependencies of $E'$, $E''$ and $\tan \delta$ of various unfilled and CB-filled SBR vulcanizates in a temperature range from -80°C to 80°C. Figure 4.29 shows the $E'$ of the unfilled vulcanizates in the glassy and rubbery state and transition region. The value of $E'$ in the glassy state corresponding to low temperature differs insignificantly. At high temperature region corresponding to the rubbery state, the unfilled SBR vulcanizate without any oil has the highest value of $E'$. Various unfilled SBR vulcanizates with oils exhibit values close to each other. Figure 4.30 shows the temperature dependencies of $E''$ of various unfilled SBR vulcanizates. It is seen that with an increase of modification level, the $E''$ values of the unfilled SBR/MSO vulcanizates increase in the rubbery state. After adjusting the recipe, the $E''$ values of unfilled SBR/5MSO-2 and SBR/10MSO-2 vulcanizates in the rubbery state decrease and close to that of unfilled SBR/NO vulcanizate. Figure 4.31 shows that all the unfilled oil-extended SBR vulcanizates have a single $\tan \delta$ peak with its position on temperature scale shifting to a lower glass transition temperature compared to that of the unfilled SBR vulcanizate without any oil. At high temperature, the $\tan \delta$ values of unfilled SBR/MSO vulcanizates increase with an increase of modification level.

Figure 4.32 shows the temperature dependencies of $E'$ of the CB-filled vulcanizates. The values of $E'$ in the glassy state of all the vulcanizates are similar to each other. At high temperature region corresponding to the rubbery state, the SBR vulcanizate without
any oil has the highest value of $E'$, followed by SBR/NO and SBR/SO vulcanizes. Various SBR/MSO vulcanizates exhibit values close to each other. Figure 4.33 shows the temperature dependences of $E''$ of various CB-filled SBR vulcanizates. The $E''$ values of all the CB-filled SBR vulcanizates in the glass state are similar to each other. In the rubbery state, the CB-filled SBR vulcanizate without any oil shows the highest value. After mixing with oils, the $E''$ values decrease, and with an increase of the modification level, the $E''$ values of CB-filled SBR/MSO slightly increase. Figure 4.34 shows that all the CB-filled SBR vulcanizates have a single tan $\delta$ peak. It is noted that the glass transition temperatures of both unfilled and CB-filled SBR vulcanizates from the DMA test show the same trend as the glass transition temperatures of these vulcanizates obtained from the DSC test. The tan $\delta$ value converges to a similar value at low temperature region. At high temperature region, the CB-filled SBR/MSO vulcanizates have higher values of tan $\delta$ compared to CB-filled SBR/NO, SBR/NO and SBR vulcanizates. Also, the tan $\delta$ values of the CB-filled SBR/MSO increase with an increase of modification level.

According to previous study$^{8,58}$, tan $\delta$ and $E'$ of the vulcanizates at certain temperatures could be used as a predictor for tire rubber performance. Figure 4.35 shows the normalized radar graph of various CB-filled oil-extended SBR vulcanizates. The CB-filled SBR/NO vulcanizate is used as a control sample. Figure 4.36 to Figure 4.39 show the comparison of the control sample, CB-filled SBR/NO and different CB-filled SBR/MSO vulcanizates. The results show that the CB-filled SBR/30MSO and SBR/45MSO vulcanizates have slightly higher tan $\delta$ at 10°C and -10°C indicating, respectively, a higher wet and snow traction performance compared to the CB-filled
Figure 4.29 Storage modulus as a function of temperature of various unfilled SBR vulcanizates
Figure 4.30 Loss modulus as a function of temperature of various unfilled SBR vulcanizates
Figure 4.31 Tan δ as a function of temperature of various unfilled SBR vulcanizates
Figure 4.32 Storage modulus as a function of temperature of various CB-filled SBR vulcanizates
Figure 4.33 Loss modulus as a function of temperature of various CB-filled SBR vulcanizates
Figure 4.34 Tan δ as a function of temperature of various CB-filled SBR vulcanizates
Figure 4.35 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of various CB-filled SBR vulcanizates.
Figure 4.36 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of CB-filled SBR/NO, SBR/SO, SBR/5MSO and SBR/5MSO-2 vulcanizates.
Figure 4.37 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of CB-filled SBR/NO, SBR/SO, SBR/10MSO and SBR/10MSO-2 vulcanizates.
Figure 4.38 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of CB-filled SBR/NO, SBR/SO and SBR/30MSO vulcanizates.
Figure 4.39 Rolling resistance, wet traction, dry handling, dry traction and snow traction predictors of CB-filled SBR/NO, SBR/SO and SBR/45MSO vulcanizates.
SBR/NO vulcanizates. However, the CB-filled SBR/SO, SBR/5MSO and SBR/10MSO vulcanizates have a lower wet and snow traction performance compared to the CB-filled SBR/NO vulcanizate. The CB-filled SBR/SO vulcanizate has a similar tan δ at 30°C indicating similar dry traction performance compared to the CB-filled SBR/NO vulcanizate, while the CB-filled SBR/MSO vulcanizates indicate an increase in the dry traction performance with the increase of modification level. All the CB-filled SBR/SO and SBR/MSO vulcanizates show a lower value of E’ at 30°C indicating a lower dry handling performance. The CB-filled SBR/SO and various SBR/MSO vulcanizates all had a higher tan δ at 60°C indicating a higher rolling resistance compared to the CB-filled SBR/NO vulcanizates. After adjusting the recipe of the curatives in the CB-filled SBR/5MSO-2 and SBR/10MSO-2 vulcanizates the predicted rolling resistance decreases and the predicted wet, snow and dry traction performances significantly improves becoming similar to those of the CB-filled SBR/NO vulcanizates of the original recipe.
CHAPTER V
SUMMARY

SO is modified through the reaction with dicyclopentadiene at 240°C and high pressure, the double bonds on the fatty acid chains are converted into norbornyl groups. Different levels of the MSO including 5%, 10%, 30% and 45% are obtained. The research evaluates the usage of NO, SO and various MSO in SBR compounds and vulcanizates. The process oil can lower the viscosity of SBR gums to provide ease in rubber processing. During the rubber compounding, the unfilled and CB-filled SBR/SO compounds showed the lowest power consumption and processing temperature rise. The power consumption and processing temperature increased with an increase of the modification level of the SO.

The SO lowers the $T_g$ of the gums and vulcanizates leading to better low temperature properties. The SBR/SO gums and its vulcanizate have the lowest $T_g$. The $T_g$ of various SBR/MSO gums, compounds and vulcanizates increased with an increase of the modification level. The SBR/30MSO gum, compound and its vulcanizate show a $T_g$ similar to that of SBR/NO gum, compound and vulcanizate. The SBR/SO gum, compound and vulcanizate show the best thermal stability. The thermal stability decreases with an increase of the modification level, but all the SBR/MSO gums, compounds and vulcanizates exhibited better thermal stability than that of the SBR/NO gum, compound and vulcanizates, respectively.
The CB-filled SBR/SO and SBR/MSO compounds during curing have shorter curing time, similar induction period and lower maximum torque compared to those of the CB-filled SBR/NO compounds.

Experimental evaluations indicate that the unfilled and CB-filled oil-extended SBR vulcanizates all show a higher elongation at break, a lower modulus, and a lower tensile strength than the unfilled and CB-filled SBR vulcanizates without any oil. This effect is due to the plasticization effect of extender oils. The unfilled and CB-filled SBR/MSO vulcanizates both show a tremendous increase in elongation at break compared to the unfilled and CB-filled SBR/NO vulcanizates. The CB-filled SBR/30MSO vulcanizate has a more than a 200% increase in the elongation at break than that of the CB-filled SBR/NO and SBR/SO vulcanizates. The CB-filled SBR/5MSO and SBR/10MSO show an increase in both the elongation at break and the tensile strength. The CB-filled SBR/5MSO-2 and SBR/10MSO-2 vulcanizates exhibit a much higher elongation at break but almost a similar strength as the CB-filled SBR vulcanizate without any oil. Abrasion resistance of the CB-filled SBR/NO vulcanizate is better than that of the CB-filled SBR/NO vulcanizate. With an increase of the modification level, the abrasion resistance of various CB-filled SBR/MSO vulcanizates increases. The CB-filled SBR/5MSO vulcanizate has similar abrasion resistance to that of the CB-filled SBR/NO vulcanizate. The abrasion resistance of the SBR/MSO can be improved by increasing the curative content. Also, the CB-filled SBR/MSO vulcanizates all have a lower hardness compared to those of the CB-filled SBR/NO and SBR vulcanizates.

The DMA test predicts the performance of various CB-filled SBR vulcanizates compared to the CB-filled SBR/NO vulcanizate. With the increase of the modification
level of the SO, the CB-filled SBR/MSO vulcanizates would have better traction but higher rolling resistance. After adjusting the recipe, the CB-filled SBR/5MSO-2 and SBR/10MSO-2 vulcanizates exhibit similar predictors as the CB-filled SBR/NO vulcanizates, indicating a similar traction and rolling resistance performance.

The swelling test indicates that with an increase of the modification, the gel fraction of the SBR/MSO vulcanizates slightly increases, and the crosslink density decreases. The decrease in the crosslink density of the SBR/5SO and various SBR/MSO vulcanizates are probably due to the reaction of the SO and MSO with the curatives. The oil could probably consume certain amount of curatives altering the crosslink structure, resulting in a tremendous improvement in product properties.

The SBR/MSO vulcanizates has advantages in some aspects. The MSO addition to SBR has a promising possibility to replace part of or all of the petroleum extender oils in the product.
REFERENCES


7. USDA *Oil Crops Yearbook*; 2012.


50. Flanigan, C. M.; Perry, C. Rubber compositions containing an oil blend of a petroleum oil and a biobased oil and methods of making the same. US 8,034,859 B2, 2011.


57. Data sheet of Duradene HX739, Firestone Polymers.


60. Data sheet of Plasticizer LN, Akrochem Corporation.


63. Data sheet of Technical Grade RBD Soybean Oil, Cargill Industrial Oil & Lubricants.

