CONTINUOUS DEVULCANIZATION OF GROUND TIRE RUBBER OF DIFFERENT PARTICLE SIZES USING AN ULTRASONIC TWIN-SCREW EXTRUDER

A Thesis

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

Tian Liang

May, 2013
CONTINUOUS DEVULCANIZATION OF GROUND TIRE RUBBER OF DIFFERENT PARTICLE SIZES USING AN ULTRASONIC TWIN-SCREW EXTRUDER

Tian Liang

Thesis

Approved: 

Advisor 
Dr. Avraam I. Isayev

Department Chair 
Dr. Robert Weiss

Committee Member 
Dr. Thein Kyu

Dean of the College 
Dr. Stephen Cheng

Committee Member 
Dr. Erol Sancaktar

Dean of the Graduate School 
Dr. George Newkome

Date

ii
ABSTRACT

Continuous ultrasonic devulcanization of ground tire rubber (GTR) of 10 mesh and 30 mesh from Rondy Co., as well as whole truck tire rubber of 40 mesh (40TR), 140 mesh (140TR), 200 mesh (200TR), mixture of 40 and 80 meshes (84TR) and truck tire buffing rubber of 80 mesh (80BU) from Lehigh Technologies, Inc. were studied. The devulcanization process was conducted using an ultrasonic co-rotating twin-screw extruder at ultrasonic amplitudes from 5 to 13 µm and a frequency of 40 kHz.

Ultrasonic power consumption and die pressure during devulcanization, curing behavior of devulcanized rubber, gel fraction and rheological properties of devulcanized and revulcanized rubbers, crosslink density and mechanical properties of revulcanized rubbers were obtained. It was found that GTR of 10 mesh devulcanized less than GTR of 30 mesh. Similarly, GTR of 40TR experienced less devulcanization than that of 84TR. This effect is attributed to a higher surface area in finer particles. Two groups of devulcanized rubbers exhibiting the smooth and rough extrudates were observed during the devulcanization of GTR of 10 and 30 meshes. The smooth extrudates were obtained at higher amplitudes due to more devulcanization. The revulcanizates of smooth extrudates had a higher elongation at break, but a lower modulus at 100% elongation and tensile strength.

The devulcanized and revulcanized rubbers of 140TR were found to have a lower gel fraction than the devulcanized and revulcanized rubbers of 200TR. The elongation
at break, modulus at 100% elongation and tensile strength of the revulcanized rubber of 140TR were found to be lower compared to those of the revulcanized rubber of 200TR.

Gel fraction measurement indicated that the devulcanization of GTR of 30 mesh, 40TR and 200TR increased with an increase of the ultrasonic amplitude. In contrast, 84TR and 140TR exhibited less devulcanization at intermediate amplitudes due to prevailing effect of revulcanization over devulcanization.

The 80BU was found to be less sensitive to ultrasonic treatment than other GTR with structures and properties of the devulcanized rubber being less dependent on ultrasonic amplitudes. Among various GTR, the revulcanizates of 80BU exhibited the highest elongation at break and tensile strength.
ACKNOWLEDGEMENTS

The author is grateful to his advisor, Dr. Avraam I. Isayev, for his kind instructions on research and course. The author also would like to express his thanks to Dr. Jaesun Choi, Mr. Todd M. Lewis, Dr. Niknezhad Setareh and Mr. Keyuan Huang for their selfless and patient help.
TABLE OF CONTENTS

LIST OF FIGURES........................................................................................................... ix

CHAPTER

I. INTRODUCTION......................................................................................................... 1

II. LITERATURE SURVEY.......................................................................................... 3

  2.1. Recycling of used tire rubber ........................................................................ 3
  2.2. Reclamation methods for used rubbers .......................................................... 4
    2.2.1. Mechanical methods .............................................................................. 4
    2.2.2. Chemical methods ............................................................................... 5
    2.2.3. Mechanochemical methods .................................................................... 6
    2.2.4. Microwave methods ............................................................................ 8
    2.2.5. Continuous ultrasonic methods ............................................................. 9
    2.2.6. Biological methods ................................................................................ 10
  2.3. Devulcanization of virgin rubbers with ultrasonic extruders .................... 10
  2.4. Preparation of polymer blends with ultrasonic extruder ......................... 13
  2.5. Preparation of polymer composites with ultrasonic extruder ................. 14

III. EXPERIMENTAL.................................................................................................. 17

  3.1. Materials ......................................................................................................... 17
  3.2. Ultrasonically aided devulcanization reactor .............................................. 17
  3.3. Extrusion and compounding ......................................................................... 19
VI. SUMMARY .................................................................................................................. 78

REFERENCES ................................................................................................................. 80
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1. Schematic of ultrasonic twin-screw extruder</td>
<td>18</td>
</tr>
<tr>
<td>3.2. Percentage of weight residue during TGA analysis of rubbers of 40TR, 84TR, 80BU, 140TR, 200TR, 10 mesh and 30 mesh as a function of temperature</td>
<td>21</td>
</tr>
<tr>
<td>4.1. Die pressure vs. ultrasonic amplitude during devulcanization of rubbers of 10 and 30 meshes at a temperature of 250°C</td>
<td>26</td>
</tr>
<tr>
<td>4.2. Photograph of rubber of 30 mesh devulcanized at amplitudes of (from left to right) 5 µm, 7.5 µm, 10 µm and 13 µm at a temperature of 250°C</td>
<td>27</td>
</tr>
<tr>
<td>4.3. Ultrasonic power consumption vs. ultrasonic amplitude during devulcanization of rubbers of 10 and 30 meshes at temperatures of 250°C and 180°C</td>
<td>29</td>
</tr>
<tr>
<td>4.4. Die temperature vs. ultrasonic amplitude during devulcanization of rubbers of 10 and 30 meshes at a temperature of 250°C</td>
<td>31</td>
</tr>
<tr>
<td>4.5. Crosslink density vs. ultrasonic amplitude of devulcanized and revulcanized rubbers of 10 and 30 meshes at devulcanization temperatures of 250°C and 180°C</td>
<td>32</td>
</tr>
<tr>
<td>4.6. Gel fraction vs. ultrasonic amplitude of devulcanized and revulcanized rubbers of 10 and 30 meshes at devulcanization temperatures of 250°C and 180°C</td>
<td>33</td>
</tr>
<tr>
<td>4.7. Normalized gel fraction vs. normalized crosslink density of devulcanized rubbers of 10 and 30 meshes obtained at various ultrasonic amplitudes at a temperature of 250°C</td>
<td>35</td>
</tr>
<tr>
<td>4.8. Complex viscosity (a) and (b) and storage moduli (c) and (d) of devulcanized and revulcanized rubbers of 10 and 30 meshes vs. frequency obtained at various ultrasonic amplitudes at temperatures of 250°C and 180°C, respectively</td>
<td>37</td>
</tr>
<tr>
<td>4.9. Loss moduli (a, c) and (b, d) and loss tangent (e) and (f) of devulcanized and revulcanized rubbers of 10 and 30 meshes vs. frequency obtained at various ultrasonic amplitudes at temperatures of 250°C and 180°C, respectively</td>
<td>38</td>
</tr>
<tr>
<td>4.10. Complex viscosity vs. ultrasonic amplitude of devulcanized and revulcanized rubbers of 10 and 30 meshes at a frequency of 9.3 rad/s and temperatures of 250°C and 180°C</td>
<td>40</td>
</tr>
</tbody>
</table>
4.11. Flow consistency index vs. ultrasonic amplitude of devulcanized and revulcanized rubbers of 10 and 30 meshes. The power-law index $n=0.06$ for devulcanized, and $n=0.02$ for revulcanized rubbers of 10 and 30 meshes. The devulcanization temperatures were 250°C and 180°C ...................................... 41

4.12. Cole-Cole plots of devulcanized and revulcanized rubbers of 10 and 30 meshes obtained at various ultrasonic amplitudes at temperatures of 250°C (a) and 180°C (b) ................................................................. 42

4.13. Curing curves of devulcanized rubbers of 10 and 30 meshes obtained at various ultrasonic amplitudes at temperatures of 250°C (a) and 180°C (b) ................................................................. 44

4.14. Stress-strain curves of revulcanized rubbers of 10 (a) and 30 (b) meshes obtained at various ultrasonic amplitudes and a temperature of 250°C, and of revulcanized rubbers of 10 and 30 (c) meshes obtained at various ultrasonic amplitudes and a temperature of 180°C ................................................................. 46

4.15. Modulus at 100% elongation (a), tensile strength (b) and elongation at break (c) of devulcanized rubbers of 10 and 30 meshes vs. ultrasonic amplitudes. The devulcanization temperatures were 250°C and 180°C ...................................... 47

5.1. Die pressure vs. ultrasonic amplitude during devulcanization of 40TR, 84TR, 80BU, 140TR and 200TR ................................................................................................. 52

5.2. Power consumption vs. ultrasonic amplitude during devulcanization of 40TR, 84TR, 80BU, 140TR and 200TR ................................................................................................. 54

5.3. Gel fraction of devulcanized and revulcanized 40TR, 84TR, 80BU, 140TR, 200TR at various amplitudes and tire powder ................................................................................................. 56

5.4. Crosslink density of revulcanized 40TR, 84TR, 80BU, 140TR and 200TR at various amplitudes ..................................................................................................................... 59

5.5. Storage moduli (a), complex viscosity (b), loss tangent (c) of devulcanized and revulcanized 40TR and 84TR, and loss moduli of devulcanized (d) and revulcanized (e) 40TR and 84TR vs. frequency at various amplitudes .......... 60

5.6. Storage moduli (a), complex viscosity (b), loss tangent (c) of devulcanized and revulcanized 140TR and 200TR, and loss moduli of devulcanized (d) and revulcanized (e) 140TR and 200TR vs. frequency at various amplitudes .......... 61

5.7. Storage moduli (a), complex viscosity (b), loss tangent (c) of devulcanized and revulcanized 80BU, and loss moduli of devulcanized (d) and revulcanized (e) 80BU vs. frequency at various amplitudes ........................................ 63

5.8. Complex viscosity of devulcanized and revulcanized 40TR, 84TR, 80BU, 140TR and 200TR at a frequency of 9.3 rad/s and various amplitudes........ 64

5.9. Curing curve of devulcanized 40TR and 84TR obtained at various amplitudes .. 66
5.10. Curing curve of devulcanized 140TR and 200TR obtained at various amplitudes 
........................................................................................................................................ 67

5.11. Curing curve of devulcanized 80BU obtained at various amplitudes.............. 68

5.12. Elongation at break of revulcanized 40TR, 84TR, 80BU, 140TR and 200TR obtained at various amplitudes................................................................. 70

5.13. Modulus at 100% elongation of revulcanized 40TR, 84TR, 80BU, 140TR and 200TR obtained at various amplitudes .................................................. 71

5.14. Tensile strength of revulcanized 40TR, 84TR, 80BU, 140TR and 200TR obtained at various amplitudes ................................................................. 72

5.15. The stress-strain curves of revulcanized rubbers of 40TR (a), 84TR (b), 80BU (c), 140TR (d) and 200TR (e) obtained at various amplitudes. ...................... 73
CHAPTER I
INTRODUCTION

Rubber is widely used in our daily life and industry. As an elastic and flexible material, rubber is widely applied in manufacturing of tires, conveyor belts, shoes, pads and other products. Raw rubber cannot be utilized until it is vulcanized. Typically raw rubber is compounded with processing oil, fillers, antioxidants and other additives. Compounding can help to disperse additives, strengthen the rubber, reduce the cost, and lengthen its service life and so on. Vulcanization ingredients are also compounded with rubber, followed by the vulcanization of rubber. During vulcanization the crosslinks are formed to make rubber insoluble, infusible and inflowable. After vulcanization the mechanical properties are further improved. Crosslinks play a crucial role in the application of rubber, but hinder its recycling. In the recent years, a large amount of used tires are burnt to provide energy or disposed in landfill rather than recycled. This is a huge waste of the valuable rubbers. One way to avoid this waste is to retread used tires. But this process is not easy to be automated, and requires a lot of human labor.

A more economical way is to grind used rubbers. Before the grinding of rubber products, the non-rubber composition, e.g., metals and fibers in tires, are separated. Rubbers are left, with carbon black, silica, zinc oxide and other chemicals which are not easy to be separated physically. Rubbers are then ground to small particles for further use. The ground rubbers can be blended with fresh rubber and used for new products.
They can also be further processed to break the crosslinks, which may restore better properties. This process is called reclamation. Many reclamation methods have been developed\textsuperscript{2}. Among them the continuous ultrasonic devulcanization is a very promising method with a feasibility to be scaled up for industrial production. During the ultrasonic devulcanization, the compressive and extensive mechanical waves are induced by the ultrasonic horn and imposed to rubber, creating bubbles around impurities and voids\textsuperscript{3}. This process overstresses the crosslinks, providing enough energy to break them\textsuperscript{3}. The effect of devulcanization conditions, as well as the ultrasonic extruder parameters on the structures and properties of devulcanized and revulcanized GTR have been studied in the earlier research\textsuperscript{3, 4, 5, 6}.

There are several kinds of GTR with different particle sizes provided by manufacturers. A comparison of devulcanization of GTR with different particle sizes is currently an unexplored area. At different particle sizes, the difference is not only the physical size, because some other influences in addition to the different particle sizes cannot be ignored. Due to the different manufacturing processes for making GTR with different sizes, the differences of some other properties such as gel fraction and solid content may also take place. It is not easy to avoid the influence of these differences, since GTR supplied by the industry inherently have differences. Thus, a comparative research of GTR with different particle sizes, as well as different gel fraction and solid contents, is very useful for practical purpose. Accordingly, this thesis is focused on the comparison of continuous ultrasonic devulcanization of GTR with different particle sizes having different gel fraction and solid contents.
2.1. Recycling of used tire rubber

According to Rubber Manufacturers Association\(^1\), there were 5.18 million tons of scrap tires generated in the United States in 2009. It is an important issue to optimize the recycling of this huge amount of used tires, which can both benefit human society economically and ecologically. Generally, there are three ways to recycle and reuse used tires: retreading, grinding and reclamation.

Retreading is a process to use new tread to replace the old one of a used tire, which is more economical compared to produce a new tire. But retreading process requires a lot of labor, which is becoming less and less economical considering the ever increasing labor cost.

Grinding is a process which physically reduces the particle size of used tires. The ground tires can be used to blend with fresh rubber and become raw materials for new rubber products. Grinding is an economical way to recycle used tires, but the rubbers are not chemically devulcanized, i.e. most of the crosslinks in the rubber are not broken. Thus, for safety consideration and quality control of products, especially for manufacturing of tires, only a small amount of ground rubber can be used to make new products.
The purpose of reclamation of used rubbers is to chemically break the crosslinks in rubbers and restore their flowability. In this case, a better dispersion of the reclaimed rubbers in fresh rubber can be expected, the interfaces between them can be improved. A larger amount of recycled rubbers can be used for new products, as well as better properties can be achieved.

2.2. Reclamation methods for used rubbers

The final purpose of reclamation is to break the chemical bonds (crosslinks). Thus reclamation process can also be called as devulcanization process. The key for successful devulcanization of used rubbers is to break the crosslinks in rubbers, while damage as less as possible the main chains. The following devulcanization methods have been developed for the reclamation of waste rubbers.

2.2.1. Mechanical methods

Mechanical devulcanization of used rubbers involves the using of mechanical force, especially shear force, to break crosslinks in rubber vulcanizates. This method is a very fast process, and it does not require any chemicals. This reduces the costs and saves the efforts of disposing used chemicals. But the mechanical devulcanization has the disadvantages of degrading polymers during the process, because the high shear stress in the devulcanization system can damage the macromolecular chains. Thus, the optimization of devulcanization conditions is very important.

Typically, pan mill or twin-screw extruder are used to apply the mechanical force to GTR. Zhang et al. studied the devulcanization of GTR with a pan mill reactor. After revulcanization, the blend of devulcanized GTR with fresh Natural Rubber (NR)
showed a significantly better mechanical properties than the blend of GTR and NR. This was attributed to the homogeneous distribution of devulcanized GTR in NR, which was confirmed by SEM. The devulcanization of waste tire using a twin-screw extruder was studied by Yazdani et al. The effects of the barrel temperature of extruder and screw rotation speed were studied. These parameters can be used for the optimization of the devulcanization conditions.

2.2.2. Chemical methods

All reclamation methods are essentially chemical methods because the purpose is to break crosslinks. The chemical methods in this section are designated for those methods where certain chemicals are used as reagents or solvents.

De et al. reported the devulcanization of GTR with tetra methyl thiuram disulfide (TMTD). TMTD served as the reclamation reagent during the devulcanization of GTR with a two-roll mill. After devulcanization, TMTD was also used as a curative during the revulcanization process. The revulcanizates of reclaim rubber showed better aging properties than NR without reclaim rubber.

As a chemical process, the selection of reactants for chemical devulcanization methods is very important. For better delivery of the reclamation reagent to the crosslinks, proper organic solvents are needed. However, the using of organic solvents may cause environmental problems. Therefore, environment-friendly solvents are preferred. Supercritical fluids of carbon dioxide, which can penetrate solids while carrying certain chemicals is a proper candidate.

Kojima et al. used supercritical carbon dioxide as a medium to carry the reclamation reagent, diphenyl disulfide, for the devulcanization of carbon black filled
natural rubber and truck tires containing natural rubber. A loading up to 40 phr of
devulcanized tire rubbers in fresh rubber restored 90% tensile strength.

Jiang et al.\textsuperscript{12} also used supercritical carbon dioxide as the medium and diphenyl
disulfide (DD) as the devulcanization reagent to study the devulcanization of butyl
rubber vulcanizates, as well as its structure and mechanical properties.

2.2.3. Mechanochemical methods

The mechanochemical methods combines the utilization of mechanical shear
force and the selectivity of reclamation reagents. Cavalieri et al.\textsuperscript{13} introduced a method
of using fresh NR to chemically activate GTR, followed by mechanical devulcanization.
A toluene solution of fresh NR was mixed with GTR, and after the evaporation of
solvent, the mixture was subjected to ball milling under inert atmosphere. The fresh NR
with a loading of 10 wt% activated GTR achieved almost the same mechanical
properties as 100% fresh NR after vulcanization.

Lu et al.\textsuperscript{14} studied the mechanochemical devulcanization of fluoroelastomer
(FKM) using a pan mill machine. The devulcanization process improved the
mechanical properties of FKM/nitrile-butadiene rubber (NBR) blends after
revulcanization, compared to raw FKM. TGA data showed the devulcanized FKM also
improved the thermal stability of NBR.

The restoration of rubber properties by devulcanization process is not limited to
mechanical properties. The improvement of acoustic absorption and the foamability of
GTR/polyurethane (PU) composites was found by Zhang et al.\textsuperscript{15}. The improved
acoustic absorption ability was attributed to the fact that the pan mill devulcanization
process improved the chain flexibility of the molecules in GTR. This can be seen from the increase of the dampening properties, which was confirmed by DMA study.

Yehia et al.\textsuperscript{16} devulcanized waste rubber powder in a Brabender premixer in the presence of various reclamation reagents. The devulcanized rubber was blended with fresh NR and with styrene-butadiene rubber (SBR). The testing showed that the mechanical properties stayed about the same at a replacement of fresh rubber with devulcanized rubber from 10\% to 30\%.

For some mechanochemical reactions which take a long time, batch process equipment such as ball mill, pan mill, two-roll mixer or internal mixer is necessary. But for those reactions which only take a time scale from a few seconds to a few minutes, continuous process can be considered, which can produce devulcanized rubber with a more stable quality, especially when the process is enhanced to an industrial scale. For that purpose continuous manufacturing equipment such as extruder used in polymer processing industry is suitable.

Many studies have been conducted using the mechanochemical devulcanization process in an extruder. Sutanto et al.\textsuperscript{17} used a co-rotating twin-screw extruder in the mechanochemical devulcanization of ethylene propylene diene monomer (EPDM) rubber. The devulcanized EPDM rubber can be used to replace the virgin rubber with a fraction up to 25\%. Jalilvand et al.\textsuperscript{18} used diphenyl disulphide as the devulcanization reagent and a co-rotating twin-screw extruder as the devulcanization reactor to devulcanize EPDM rubber. The effect of devulcanization reagent as well as extruder conditions such as a rotation speed of screws and barrel temperature were studied. The mechanical properties of revulcanizates almost restored to the value of those of the virgin sample.
2.2.4. Microwave methods

Microwave is an electromagnetic wave with a frequency between 300 MHz to 300 GHz. It can interact with polar chemicals and induce their orientation. During the orientation process, the electromagnetic energy is transferred to thermal energy, which can be used as a heating source. Due to the fact that microwave does not interact with non-polar groups, the heat is localized at the vicinity of polar groups\textsuperscript{19}, which minimizes the thermal degradation of main chains. From the basic mechanism, the microwave devulcanization is very similar to the thermal devulcanization, but with the thermal energy delivered more accurately.

The microwave devulcanization of various kinds of rubbers used in non-tire applications were studied since 1970s. Fix\textsuperscript{20} studied microwave devulcanization of EPDM and butyl rubber. In his research, the rubber particles of a particle size from 6 mm to 10 mm were fed to the microwave device continuously. After treatment, the rubber was blended with fresh rubbers. The blends showed a comparable mechanical properties with the control samples.

Landini and coworkers\textsuperscript{19} used microwave to devulcanize BIIR in a batch process. They studied the effect of microwave irradiation time and microwave power on the devulcanization of BIIR.

Crespo and coworkers\textsuperscript{21} used microwave to devulcanize SBR with a particle size between 20 and 35 mesh under stirring. SBR particles exposed to microwave for different times were compared with the control sample. It was found that the temperature right after exposure to microwave increased proportionally with the exposure time, and the gel fraction decreased with an increase of the exposure time. After revulcanization, sample with the best mechanical properties was obtained from
SBR exposed to microwave for 3 minutes. The tensile strength of the best sample was 25% of the control sample and the tear strength of the best sample was 41% of the control sample.

2.2.5. Continuous ultrasonic methods

Continuous ultrasonic devulcanization of tire rubbers with an ultrasonic extruder is a promising technology which can be feasibly scaled up for industrial application. It was first introduced by Isayev\(^3\) and his coworkers in 1995. GTR can be devulcanized in a short time. The devulcanized rubber was reprocessable and reshapable. It can be vulcanized again to produce new rubber products without adding any fresh rubbers.

A typical ultrasonic devulcanization reactor includes two critical parts: an extruder and an ultrasonic device. The extruder is used to heat rubber up and provide rubber flow to the ultrasonic device. The ultrasonic device is used to impose mechanical vibration wave at a frequency range of ultrasound to rubber through a metal horn.

The mechanism of ultrasonic devulcanization was explained in the following way\(^3\). When rubber is subjected to ultrasonic treatment, rapid extension and contraction induced by high frequency vibration of ultrasonic horn produces pulsating bubbles in the vicinity of voids and impurities in the rubber. High strains and high stresses are generated, breaking chemical bonds, including crosslinks.

Several kinds of continuous ultrasonic reactors have been developed by Isayev and his coworkers, including an ultrasonic reactor with cross-head die\(^3\), an ultrasonic reactor with coaxial die\(^3\), an ultrasonic barrel reactor\(^4\), an ultrasonic grooved barrel reactor\(^22\), and an ultrasonic twin-screw extruder that used in this thesis. Although these ultrasonic reactors are different in design, they share some common points in the
devulcanization of waste rubbers. The energy imposed per unit weight of rubber was found to be the most important parameter determining the mechanical properties of revulcanized rubber, and rubber subjected to either insufficient or overdosed ultrasonic energy would not display the best properties\(^4\).

2.2.6. Biological methods

To avoid the unnecessary degradation of polymer main chains during the devulcanization process, highly selective methods are preferred. Besides chemical devulcanization, another method which can focus the breakage on the sulfur crosslinks was developed\(^2, 3, 4, 5, 6, 7\). Certain microbial agents can change the sulfur at the crosslinks to another form. Although biological devulcanization process typically takes a couple of weeks, it provides another research direction for the disposal of used rubber.

2.3. Devulcanization of virgin rubbers with ultrasonic extruders

Devulcanization of waste rubbers involves the study of materials provided by industry, with the composition details typically unknown and roughly estimated. For a better insight into the mechanism about how the ultrasonic waves affect the structures and properties of rubbers, and for a more clear indication for the optimization of devulcanization conditions, the research on devulcanization of mere virgin rubber vulcanizates is very important. Since virgin rubber vulcanizates are vulcanized by the researcher, in this case the specific composition is clear.

The first study of SBR devulcanization with an ultrasonic extruder was carried out in 1995\(^3\). SBR was devulcanized at different ultrasonic amplitudes and flow rates. It was found that an increase of the amplitude and a decrease of the flow rate resulted in a
lower gel fraction and a lower viscosity, indicating more devulcanization along with the main chain degradation. The mechanical properties of the revulcanized SBR, even without addition of fresh rubber, were comparable with the control sample.

Later the influence of ultrasonic amplitude and gap size on the crosslink density and gel fraction of devulcanized SBR was studied. The gap size is the distance between the ultrasonic horn and the internal surface of die defining the thickness of rubber layer. The rubber under treatment is supposed to flow through the gap. Thus the gap size is very important. This research showed that the crosslink density and gel fraction of the devulcanized SBR decreased with an increase of the amplitude and a decrease of the gap size. After normalization with respect to the crosslink density and gel fraction of virgin vulcanizates, the normalized crosslink density and normalized gel fraction can be fitted into a universal master curve, regardless of the devulcanization conditions. As suggested by the authors this is an indication that all SBR devulcanized at different amplitudes and gap sizes shared the same chain fracture mechanism.

Besides SBR, the devulcanization of another widely used rubber, NR, was also researched by Tapale and Isayev. The effect of key parameters during ultrasonic devulcanization process, including ultrasonic amplitude, material feeding rate and barrel temperature of extruder, on the structures and properties of devulcanized rubber was systematically studied. The results showed that the ultrasonic treatment had quite different effect on unfilled NR vulcanizates, compared to its effect on SBR vulcanizates. Unlike the consistent enhanced devulcanization with an increase of the amplitude, the devulcanization of NR vulcanizates showed a competition between devulcanization and gel reformation. At certain high amplitude, the crosslink density and gel fraction of
devulcanized rubber are even higher than those of rubber devulcanized at lower amplitude.

The research of ultrasonic devulcanization was also extended to silicone rubber\textsuperscript{30}. Compared to SBR, the similarities of silicone rubber devulcanization include that the crosslink density and gel fraction of devulcanized rubber decreased with an increase of the amplitude and a decrease of the material feeding rate and the gap size. But due to the fact that the main chain composition of silicone rubber is different, the devulcanized silicone rubber showed different responses to the change of ultrasonic conditions. The master curve of normalized gel fraction versus normalized crosslink density was plotted. It showed that for silicone rubber, the gel fraction with respect to the crosslink density after devulcanization did not drop as much as that of devulcanized SBR at lower amplitude. This was attributed to the fact that silicone rubber vulcanizates have a larger difference of bond energy level between main chain bonds and crosslink bonds, compared to that of SBR vulcanizates, making the main chain breakage less probable.

The properties of pure rubber are not qualified for real applications, and most rubbers are compounded with fillers such as carbon black and silica in the manufacturing process. Therefore, the research of devulcanization of filled rubber vulcanizates is also very important.

Hong and Isayev\textsuperscript{31} studied the devulcanization of filled NR vulcanizates. They found that the competition between devulcanization and gel reformation of ultrasonically treated NR vulcanizates still existed in the filled system. Different compounding recipes were used to optimize the mechanical properties of the revulcanizates. The best sample with a tensile strength of 50\% of the virgin vulcanizates and an elongation at break of 70\% of virgin vulcanizates were obtained.
2.4. Preparation of polymer blends with ultrasonic extruder

Oh and Isayev\textsuperscript{32} used an ultrasonic extruder equipped with two horns to treat the blends of polypropylene (PP) and GTR. The research proved that, while at higher amplitudes the ultrasonic treatment may degrade polymers, at lower ultrasonic amplitudes, the treated blends were well compatibilized. After dynamic vulcanization, the mechanical properties were better compared to those of untreated blends which were studied in earlier work\textsuperscript{33}.

Chen et al. \textsuperscript{34} studied the ultrasonic compatibilization of high-density polyethylene (HDPE) and polystyrene (PS). The morphology study showed that the polymer micro-domains were more homogeneously distributed compared to the untreated sample. Ultra-violet characterization and extraction test provided an evidence for copolymerization between HDPE and PS, which was suggested by the authors as the reason for improved compatibility. As a result, the mechanical properties such as impact strength and elongation at break were increased significantly after ultrasound treatment.

In 2003, an informative paper was published by Isayev and Hong\textsuperscript{35}. The ultrasound was used to treat a series of polymer blends including NR/SBR, HDPE/NR, HDPE/SBR, HDPE/EPDM, PP/NR and PP/EPDM. The mechanical properties, such as tensile strength, elongation at break and impact energy, of treated blends were increased compared to untreated ones. The authors attributed these improvement to the better interfacial adhesion between different polymer phases, as well as the possible in-situ copolymerization, which was supported by the results of GPC, AFM and extraction test.
A later work by Oh, Isayev and Rogunova\textsuperscript{36} systematically studied the ultrasound-aided compatibilization of NR and PP. The AFM and SEM studies showed the ultrasonic treated blends had a thicker and rougher interface than untreated blends, which indicates the possible copolymerization at the interfaces and explains the better mechanical properties.

The ultrasonically treated PP/polyamide 6 of specific blending ratios achieved the tensile toughness and impact strength twice higher than those of the control sample\textsuperscript{37}. Although the ultrasound may induce degradation, by controlling the ultrasonic treatment conditions such as ultrasonic amplitude, the degradation effect can be minimized.

2.5. Preparation of polymer composites with ultrasonic extruder

Zhao et al. \textsuperscript{38} reported the compatibilization of PP with montmorillonite using ultrasonic oscillation. The ultrasonic treatment decreased the dimension of montmorillonite and increased the dispersion of montmorillonite. As a result, mechanical properties such as elongation at break and impact strength were significantly increased.

The ultrasonic compatibilization of PP and clay nanocomposites was studied by Lapshin et al. \textsuperscript{39}. Before the ultrasonic treatment, PP and clay were mixed with a twin-screw extruder to increase dispersing of the system. The mixed PP/clay system was processed with ultrasonic single-screw extruder. Ultrasound helped the exfoliation of clay and the intercalation of PP between clay layers, but at some conditions degradation of the PP/clay system occurred. To avoid degradation, a one-step process was developed\textsuperscript{40}. In this process, PP/clay nanocomposites were treated using a
single-screw extruder with mixing screw designed for the purpose of increasing mixing
effect. After the single-step ultrasonic treatment, better exfoliation of clay layers as well
as intercalation of PP into clay were achieved. The elongation at break of one-step
treated composites processed at certain conditions was improved in comparison with
untreated ones. Based on the rheological data, the degradation of the one-step treated
composites were reduced compared to the two-step treated samples.

Nanocomposites of HDPE and clay were also prepared with ultrasonic extruder\textsuperscript{41}. The oxygen permeability was decreased and mechanical properties were improved.
Ultrasonic-aided processing was also found to be useful for the compatibilization of
PA6 and montmorillonite\textsuperscript{42}, HDPE and montmorillonite\textsuperscript{43}, as well as PA6 and clay\textsuperscript{44,45}.

In 2009, an ultrasonic twin-screw extruder was developed\textsuperscript{46}. The nanocomposites
of polyetherimide (PEI) and multi-walled carbon nanotubes (MWNTs) were treated
with this twin-screw extruder. The rheological data and HRSEM confirmed a better
dispersion of MWNTs in the polymer matrix of treated samples. At certain conditions,
the tensile strength of the nanocomposites were increased with the help of ultrasound.

The ultrasonic twin-screw extruder was also used to treat the composites of carbon
nanofiber (CNF) and a liquid crystal polymer (LCP) \textsuperscript{47}. The electrical percolation
threshold was decreased for the samples processed with ultrasound. This observation
was explained as a better dispersion of CNF in LCP introduced by ultrasound, which
was confirmed by SEM study.

Later, the efforts of using ultrasonic extruder to increase the compatibilization
between plastics and fillers were also extended to the field of rubbers mixing with
fillers.
Choi and Isayev\textsuperscript{48} studied the processing of unfilled SBR and SBR filled with carbon black. The electrical percolation threshold and the abrasion loss were decreased after treatment, due to a better interaction between SBR and the filler. Subsequently, these researchers studied the ultrasonic extrusion of SBR with CNF and CNT\textsuperscript{49}. With an increase of the ultrasonic amplitude, the glass transition temperature of vulcanizates was increased and the loss tangent at glass transition temperature of the vulcanizates was decreased. Vulcanizates of the treated samples showed a decreased electrical percolation threshold, as well as a better interaction between SBR and fillers.
CHAPTER III
EXPERIMENTAL

3.1. Materials

GTR of 10 and 30 meshes were manufactured by Rondy Co. (Akron, OH). GTR of 40, 80, 140, 200 meshes and the mixture of 40 and 80 mesh were manufactured by Lehigh Technologies, Inc. (Tucker, GA). The 40, 140 and 200 meshes GTR were made from whole truck tires, and are named 40TR, 140TR and 200TR by the manufacturer, respectively. The 80 mesh GTR was made from truck buffings, and is named 80BU. The mixture of 40 mesh and 80 mesh was made from whole truck tires, containing 40% of 40TR and 60% percent of 80TR, is named 84TR. Details of tire rubber composition is unknown, but since it was made from tires, it is mainly composed of natural rubber (NR), styrene-butadiene rubber (SBR) and butadiene rubber (BR). Other possible ingredients include carbon black, inorganic additives and process oil.

3.2. Ultrasonically aided devulcanization reactor

Ultrasonically aided devulcanization was carried out with a co-rotating twin-screw extruder (Prism USALAB 16, Thermo Electron Co., UK) modified with installing an ultrasonic horn in the barrel. This modification with the ultrasonic device
was designed by Mr. Todd M. Lewis. Schematic of this ultrasonic twin-screw extruder is shown in Figure 3.1. The rubber particles were fed into the hopper and heated in the barrel. Two screws with a diameter of 16 mm were used to convey and mix the rubbers. Devulcanization took place in ultrasonic zone, where ultrasonic wave with a frequency of 40 kHz were imposed to the rubber by a horn. The horn with a 28 mm×28 mm square cross section is mounted in the barrel, and connected to a booster. The booster is connected to a converter where electrical energy from a power supply is transferred to mechanical energy for devulcanization. The converter is driven by a Branson 2000bdc power supply (Branson Ultrasonic Co., Danbury, CT). The gap between the horn tip and screws is 2.5 mm and the volume of ultrasonic treatment zone is 1.9 cm$^3$. The rubber passing through the gap is subjected to the longitudinal ultrasonic wave perpendicular to the flow direction. The die of the extruder has a diameter of 4 mm and a length of 11 mm. The barrel temperature was monitored by several thermocouples inserted and mounted in the barrel, and the die temperature was monitored by a thermocouple inserted and mounted in the die. A pressure transducer (PT460E-5M-6, Dynisco Instruments, Sharon, MA) was flush mounted in the die. The barrel in the feed
section was cooled by tap water. The ultrasonic horn was cooled by water from a thermostat (GP-100, NESLAB Instruments Inc., Newington, NH) set at 30°C for the devulcanization of 10 and 30 meshes, and set at 50°C for the devulcanization of 40TR, 84TR, 80BU, 140TR and 200TR. The converter was cooled by compressed air.

3.3. Extrusion and compounding

Rubbers of 10 mesh, 30 mesh, 40TR, 84TR, 80BU, 140TR and 200TR were devulcanized using the ultrasonic co-rotating twin-screw extruder described above. Ultrasonic amplitudes of 5 µm, 7.5 µm, 10 µm and 13 µm were used. The rubbers were fed into the extruder by a feeder (K-Tron Co., Glassboro, NJ). The flow rate of rubbers was set at 0.095 g/s. For the devulcanization of 10 and 30 meshes, the barrel temperatures from the entrance of the extruder to the die were set at 250°C, 250°C, 250°C, 250°C, 200°C and 150°C, respectively. A rotation speed of the twin-screw extruder was 200 rpm. An attempt was also made to carry out devulcanization at a barrel temperature of 180°C. However, at this temperature the torque on the extruder reached a limit. For this reason, the die was removed from the extruder and the rotation speed of screws was reduced to 50 rpm to carry out devulcanization of rubbers of 10 and 30 meshes at a temperature of 180°C. For the devulcanization of 40TR, 84TR, 80BU, 140TR and 200TR, the barrel temperatures from the entrance of the extruder to the die were set at 180°C, 180°C, 180°C, 180°C, 170°C and 150°C, respectively. A rotation speed of the twin-screw extruder was 200 rpm. During ultrasonic treatment, the die pressure and power consumption were recorded.

After extrusion, the devulcanized tire rubber was compounded with curatives using a two roll-mill (Reliable Rubber & Plastic Machinery Co., North Bergen, NJ).
For the compounding of devulcanized rubbers of 10 and 30 meshes, the temperature of the rolls was set at 25°C, since at higher temperatures the devulcanized rubbers can stick on the rolls. And the temperature of rolls was set at 40°C for the compounding of devulcanized rubbers of 40TR, 84TR, 80BU, 140TR and 200TR. The rotation speed of rolls was set at 15 rpm, and the compounding time was approximately 10 minutes. Rubbers devulcanized at 5 µm and 7.5 µm at a temperature of 180°C cannot be processed with two-roll mill due to insufficient ultrasonic treatment. The compounding recipe was 1 phr sulfur, 1 phr N-cyclohexyl-2-benzothiazole sulfenamide, 1.25 phr zinc oxide and 0.25 phr stearic acid.

3.4. Characterization methods

3.4.1. Thermogravimetric analysis

Thermogravimetric analysis was done with a Hi-RES TGA 2950 Thermogravimetric Analyzer (New Castle, DE). The temperature was increased from room temperature to 530°C at a heating rate of 10°C/min in nitrogen atmosphere, followed by an isothermal process for 10 minutes. The percentage of weight residue during TGA analysis of rubbers of 40TR, 84TR, 80BU, 140TR, 200TR, 10 mesh and 30 mesh as a function of temperature is shown in Figure 3.2. The solid fraction, Θ, was calculated using the following equation:

\[
Θ = \frac{\text{weight of residue}}{\text{weight of sample before test}}
\]  

(3.1)

The solid content fraction was found to be 33 wt% for both rubbers of 10 and 30 meshes, while the solid content fraction of 40TR, 84TR, 80BU, 140TR and 200TR was found to be 33.6 wt%, 35.5 wt%, 35.6 wt%, 39.0 wt% and 39.8 wt%, respectively.
Figure 3.2 Percentage of weight residue during TGA analysis of rubbers of 40TR, 84TR, 80BU, 140TR, 200TR, 10 mesh and 30 mesh as a function of temperature

3.4.2. Swelling test

Swelling tests for devulcanized and revulcanized rubbers to measure the crosslink density and gel fraction were carried out using a Soxhlet extraction apparatus. A sample of 0.5-1 gram was used for swelling test. Benzene was used to extract the sol part from the sample as well as to swell it. After 48 hours, the swollen sample was taken out and weighed, followed by placing in a vacuum oven for another 48 hours to dry at 65°C. Flory-Rehner equation\(^{51}\) were used to calculate the crosslink density:

\[
\nu_e = - \frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_1 \left( \frac{1}{V_r^{\frac{3}{2}}} - 0.5V_r \right)}
\]  

(3.2)

where \(\nu_e\) is the crosslink density, \(V_r\) is the volume fraction of rubber in the swollen sample, and \(\chi\) is the polymer-solvent interaction parameter. The \(\chi\) for NR/benzene,
BR/benzene and SBR/benzene is 0.42, 0.4 and 0.4, respectively. Since tire rubber typically contains NR, BR and a large amount of SBR, the $\chi$ of tire rubber is assumed to be 0.4. The molar volume of benzene, $V_1$, is taken as $8.834 \times 10^{-5}$ m$^3$/mol.

Since a large amount of carbon black is contained in the sample, Kraus correction was also employed:

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

(3.3)

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 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. In this thesis, C is taken as 1.17, assuming the carbon black in GTR is high abrasion furnace carbon black. The solid content of rubbers required for the Kraus correction was measured by thermogravimetric analysis as mentioned earlier. The crosslink density of original tire rubbers of 10 and 30 meshes was measured to be 0.195 kmole/m$^3$ and 0.181 kmole/m$^3$, respectively.

Due to the fact that the 40TR, 84TR, 80BU, 140TR, 200TR devulcanized at 180°C were in a powder form after swelling, and the amount of solvent in the swollen sample cannot be determined, thus the crosslink density is not available for the rubbers devulcanized at 180°C.

The gel fraction, $\xi$, for the all kinds of rubbers was determined using the following equation:

$$\xi = \frac{\text{weight of rubber after drying} - \text{weight of solid}}{\text{weight of rubber before swelling} - \text{weight of solid}}$$

(3.4)
Gel fraction of rubbers of 10 and 30 meshes was measured to be 81.8% and 81.7%, respectively. Gel fraction of 40TR, 84TR, 80BU, 140TR and 200TR was measured to be 85.2%, 87.0%, 81.1%, 69.4%, and 81.9%, respectively.

3.4.3. Dynamic rheology test

Advanced Polymer Analyzer (APA 2000, Alpha Technologies, Akron, OH) was used to determine curing curves during revulcanization of devulcanized rubbers at a temperature of 160°C, a frequency of 1.6 Hz and a strain amplitude of 0.042. APA 2000 was also used to obtain dynamic properties of devulcanized rubbers at a temperature of 120°C, and a strain amplitude of 0.042 within a frequency range from 0.00318 Hz to 31.8 Hz. To obtain dynamic properties of the revulcanized rubbers, the devulcanized rubbers with curatives were cured in APA 2000 at 160°C, and then tested with APA 2000 at a temperature of 120°C, a strain amplitude of 0.042, and within a frequency range from 0.00318 Hz to 31.8 Hz.

3.4.4. Tensile test

After compounding, the devulcanized tire rubber was cured into slabs with a mold of dimensions 152 mm×152 mm×1.5 mm, using a compression-molding press (Carver, Wabash, IN) at 160°C, and the curing time was based on t95. The cured slabs were cut into dumbbell shape specimens using Die C described in ASTM D412. Mechanical properties of revulcanizates were tested based on ASTM D412 using an Instron tensile tester (Model 5567, Instron, Canton, MA) at an elongation rate of 500 mm/min. The tests were conducted at room temperature.
CHAPTER IV
CONTINUOUS ULTRASONIC DEVULCANZIATION OF RUBBERS OF 10 AND 30 MESHES

4.1. General

Since the manufacturer of rubbers of 10 and 30 meshes is different from 40TR, 84TR, 80BU, 140TR and 200TR, the study of rubbers of 10 and 30 meshes will be discussed in this chapter separately. Since the gel fraction and solid content fraction of rubbers of 10 and 30 meshes are very close to each other, the difference in particle size is the main difference between rubbers of 10 mesh and 30 mesh. Therefore it will be easier for us to see the effect of particle size in this chapter. The die pressure, power consumption, die temperature, gel fraction, crosslink density, dynamic rheological data and mechanical properties are presented. It is found that rubber of 30 mesh experienced more devulcanization than rubber of 10 mesh at a temperature of 250°C, while at a temperature of 180°C, the devulcanization experienced by rubber of 10 mesh and rubber of 30 mesh are very close. At each temperature, the devulcanized and revulcanized rubbers can be sorted into two groups with different structures and exhibiting very different rheological and mechanical properties.
4.2. Die pressure

Die pressure measured during the ultrasonic treatment of rubbers of 10 and 30 meshes at a temperature of 250°C as a function of ultrasonic amplitude is shown in Figure 4.1. The die pressure decreased with increasing amplitude. This is due to the fact that the higher amplitude is inducing more devulcanization and lowering the viscosity of devulcanized rubbers, as shown later in section on rheology. Therefore, after ultrasonic treatment zone, viscous forces in the devulcanized rubber and friction forces between the rubber and barrel decreased, resulting in a lower die pressure. It is interesting to note that rubber of 30 mesh yielded a lower die pressure than rubber of 10 mesh at almost all amplitudes. This is because the particle size of rubber of 30 mesh is finer and has a larger specific surface area than that of rubber of 10 mesh. Therefore, it can absorb more energy during the ultrasonic treatment. Accordingly, rubber of 30 mesh experienced more devulcanization and had a lower viscosity. From Figure 4.1 one can divide the die pressure of eight samples devulcanized at 250°C in two groups exhibiting smooth and rough extrudates. The smooth extrudates group includes the rubber of 10 mesh devulcanized at 13µm and the rubber of 30 mesh devulcanized at 10 µm and 13 µm. The rough extrudates group includes the rest of samples. These two groups of devulcanized tire rubbers came out in two different forms, samples in the former group came out continuously in a string with the smooth surface, and samples in the latter group came out with the rough surface, and extrudate was periodically broken. Figure 4.2 shows the appearance of 30 mesh tire rubber devulcanized at a temperature of 250°C. A dramatic drop of the die pressure was observed during transition from the rough extrudates to the smooth extrudates. This is evidently related to more devulcanization of the smooth extrudates, since more devulcanization will produce
Figure 4.1 Die pressure vs. ultrasonic amplitude during devulcanization of rubbers of 10 and 30 meshes at a temperature of 250°C
Figure 4.2 Photograph of rubber of 30 mesh devulcanized at amplitudes of (from left to right) 5 µm, 7.5 µm, 10 µm and 13 µm at a temperature of 250°C
more sol part, which can significantly decrease the viscosity of devulcanized rubbers and correspondingly the die pressure. At a devulcanization temperature of 180°C, extrudates of 10 and 30 meshes exited the extruder in a cohesive powder form at an amplitude of 10 µm and in a sticky extrudate form at an amplitude of 13 µm. Since the die was removed from the extruder, die pressure cannot be measured during the ultrasonic treatment at a devulcanization temperature of 180°C.

4.3. Power consumption

During ultrasonically aided extrusion, power consumption varied with ultrasonic amplitude, devulcanization temperature and mesh size of tire rubber (Figure 4.3). For the same tire rubber, more ultrasonic power was consumed at the higher ultrasonic amplitude, which was due to the higher strain amplitude imposed on rubber leading to more power transmitted to tire rubber\(^{54}\). It is often seen that at higher devulcanization temperatures power consumption is reduced. At a temperature of 250°C, for the same amplitude, devulcanization of rubber of 30 mesh consumed more power than devulcanization of rubber of 10 mesh. However, at 180°C that situation is reversed, possibly due to changes of the acoustic properties of material, such as the velocity of wave propagation and attenuation. It should be noted that these properties are highly affected by ambient pressure, temperature, void density, surface area of particle, modulus and tangent loss of rubber. Similar to the die pressure, the power consumption of rubbers can also be divided into two groups: exhibiting smooth and sticky extrudates, and rough extrudates and cohesive powder. Different power consumption of these two groups resulted in a tremendous difference in the molecular structure and further
Figure 4.3 Ultrasonic power consumption vs. ultrasonic amplitude during devulcanization of rubbers of 10 and 30 meshes at temperatures of 250°C and 180°C
influenced rheological properties and mechanical properties, which will be introduced in the following sections.

4.4. Die temperature

At a devulcanization temperature of 250°C, the die temperature during the ultrasonic treatment of rubbers of 10 and 30 meshes as a function of ultrasonic amplitude are presented in Figure 4.4. Surprisingly, the die temperature decreased with increasing ultrasonic amplitude. This is due to the fact that the sample devulcanized at a higher amplitude experienced more devulcanization and exhibited a lower viscosity, thus a lower viscous dissipation in the die. The die temperature during the treatment of rubber of 30 mesh was lower than that during the treatment of rubber of 10 mesh. This is also due to the fact that finer powder experienced more devulcanization and exhibited a lower viscosity, thus lower viscous dissipation in the die. Since the die was not equipped with cooling system, the die temperature exceeded the set temperature of 150°C in all cases due to viscous dissipation. Therefore, lower friction generated less heat, and resulted in a lower die temperature. Due to the die removal, the die temperature cannot be measured at a devulcanization temperature of 180°C.

4.5. Swelling test

Figure 4.5 shows the crosslink density of devulcanized and revulcanized rubbers of 10 and 30 meshes as a function of ultrasonic amplitude, and Figure 4.6 shows the gel fraction of devulcanized and revulcanized rubbers of 10 and 30 meshes as a function of ultrasonic amplitude. It should be noted that the crosslink density of devulcanized sample of 180°C cannot be determined because the extrudate disintegrated during
Figure 4.4 Die temperature vs. ultrasonic amplitude during devulcanization of rubbers of 10 and 30 meshes at a temperature of 250°C
Figure 4.5 Crosslink density vs. ultrasonic amplitude of devulcanized and revulcanized rubbers of 10 and 30 meshes obtained at devulcanization temperatures of 250°C and 180°C
Figure 4.6 Gel fraction vs. ultrasonic amplitude of devulcanized and revulcanized rubbers of 10 and 30 meshes obtained at devulcanization temperatures of 250°C and 180°C.
swelling. The crosslink density and the gel fraction of devulcanized and revulcanized rubbers of 10 and 30 meshes are seen to decrease with increasing ultrasonic amplitude. Generally, devulcanized rubbers of 30 mesh show lower crosslink density and gel fraction than that of rubber of 10 mesh. This indicates that the rubber of 30 mesh experienced more devulcanization than the rubber of 10 mesh. One exception is rubber of 10 mesh devulcanized at 250°C and 5 µm, as seen from Figure 4.5. At this amplitude the die temperature increased by about 32°C, possibly leading to the thermal degradation and more breakage of crosslinks creating more sol. Also, it should be noted that the crosslink density and gel fraction of the smooth and sticky extrudates are much lower than those of the rough extrudates and cohesive powder. Again, samples can be sorted into two groups based on their crosslink density and gel fraction. In one group, the crosslink density and gel fraction of each sample are quite close, while in the other group crosslink density and gel fraction differ significantly. This indicates that the smooth extrudates and sticky extrudates experienced more devulcanization than the rough extrudates and cohesive powder. After curing, the crosslink density of revulcanized rubbers of 10 and 30 mesh increased by almost one order of magnitude, and the gel fraction increased by approximately 30%. The increase of both the crosslink density and gel fraction of rubber of 30 mesh is larger than that of rubber of 10 mesh, which means more crosslinks were generated during the curing process of devulcanized rubber of 30 mesh. Figure 4.7 shows the normalized crosslink density versus the normalized gel fraction of rubbers of 10 and 30 meshes devulcanized at a temperature of 250 °C. Normalization was done with respect of the crosslink density and gel fraction of the original tire rubbers. These results were fitted to a function indicated in the field of that figure and shown by solid line. It can be seen from Figure 4.7 that the
Figure 4.7 Normalized gel fraction vs. normalized crosslink density of devulcanized rubbers of 10 and 30 meshes obtained at various ultrasonic amplitudes at a temperature of 250°C.
results can be correlated by a universal master curve, which was also observed in several papers for other rubbers\textsuperscript{5,30,55}. Since the master curve is related to the molecular network breakage mechanism\textsuperscript{28}, one can conclude that 10 and 30 mesh tire rubbers share the same network devulcanization breakage mechanism due to the fact that their chemical composition is basically the same\textsuperscript{28}, because both tire powders were produced by the same manufacturer.

4.6. Rheology

Figure 4.8 shows the complex viscosity (a and b) and storage moduli (c and d) of devulcanized and revulcanized samples as a function of frequency at various ultrasonic amplitudes and temperatures of 250°C and 180°C, respectively. Figure 4.9 shows the loss moduli (a, c and b, d) and loss tangent (e and f) of devulcanized and revulcanized samples as a function of frequency at various ultrasonic amplitudes at temperatures of 250°C and 180°C, respectively. Values of the complex viscosity, storage and loss moduli of devulcanized and revulcanized 10 and 30 meshes were lower at higher devulcanization temperature and ultrasonic amplitude. Values of the loss tangent were higher at higher devulcanization temperature and ultrasonic amplitude. This is due to the fact that the higher devulcanization temperature led to more devulcanization. The devulcanized and revulcanized rubber of 30 mesh had a lower complex viscosity, storage and loss moduli and a higher loss tangent than those of devulcanized and revulcanized rubber of 10 mesh, respectively. This is attributed to the fact that more devulcanization happened for tire rubbers devulcanized at higher amplitudes and more devulcanization occurred in rubber of 30 mesh. Increased devulcanization led to the breakage of more crosslinks in rubber. This created more sol, thus resulting in
Figure 4.8 Complex viscosity (a) and (b) and storage moduli (c) and (d) of devulcanized and revulcanized rubbers of 10 and 30 meshes vs. frequency obtained at various ultrasonic amplitudes at temperatures of 250°C and 180°C, respectively
Figure 4.9 Loss moduli (a, c) and (b, d) and loss tangent (e) and (f) of devulcanized and revulcanized rubbers of 10 and 30 meshes vs. frequency obtained at various ultrasonic amplitudes at temperatures of 250°C and 180°C, respectively.
decreased elasticity and viscosity. The storage and loss moduli and viscosity of the smooth extrudates and sticky extrudates and their revulcanizates is lower and the loss tangent higher than those of the rough extrudates and cohesive powder and their revulcanizates.

The complex viscosity of devulcanized and revulcanized rubbers of 10 and 30 meshes obtained at a frequency of 9.3 rad/s as a function of the ultrasonic amplitude is specified in Figure 4.10. It is seen that the complex viscosity of devulcanized rubbers of 10 and 30 mesh separated in two groups of higher and lower viscosity depending on the level of devulcanization. The same trend was observed for the complex viscosity of revulcanized rubber of 10 and 30 meshes, which were also separated into two groups. It should be noted that the complex viscosity of all devulcanized rubbers exhibits a power-law behavior with a power-law index $n$ being around 0.06. The complex viscosity of all revulcanized rubbers also exhibits a power-law behavior but with a power-law index around 0.02. The consistency index $K$ of devulcanized and revulcanized rubber of 10 mesh is higher than that of devulcanized and revulcanized rubber of 30 mesh, respectively, as shown in Figure 4.11. The consistency index $K$ is lower for rubber devulcanized at higher temperature.

Figure 4.12 shows the Cole-Cole plots of devulcanized and revulcanized rubbers of 10 and 30 meshes, where the smooth extrudates and sticky extrudates, and the rough extrudates and cohesive powder and their revulcanizates exhibit distinctly different behavior. At the same loss moduli, the rough extrudates and cohesive powder and their revulcanizates have a higher storage moduli, which indicates that they are more elastic than the smooth extrudates and sticky extrudates and their revulcanizates. This again
Figure 4.10 Complex viscosity vs. ultrasonic amplitude of devulcanized and revulcanized rubbers of 10 and 30 meshes at a frequency of 9.3 rad/s and temperatures of 250°C and 180°C.
Figure 4.11 Flow consistency index vs. ultrasonic amplitude of devulcanized and revulcanized rubbers of 10 and 30 meshes. The power-law index $n=0.06$ for devulcanized, and $n=0.02$ for revulcanized rubbers of 10 and 30 meshes. The devulcanization temperatures were 250°C and 180°C.
Figure 4.12 Cole-Cole plots of devulcanized and revulcanized rubbers of 10 and 30 meshes obtained at various ultrasonic amplitudes at temperatures of 250°C (a) and 180°C (b).
confirms the significant differences in the molecular structure between the two groups of devulcanized rubbers and their revulcanizates.

4.7. Curing behavior

Torque as a function of curing time of rubbers of 10 and 30 mesh devulcanized at temperatures of 250°C and 180°C is shown in Figure 4.13 (a) and (b), respectively. It is seen that curing starts as soon as samples are heated. Evidently, the true induction period is absent. However, there is a pseudo induction time at the beginning, where curing is quite slow. Then curing speeds up and finally reaches a steady value indicating its completion.

During the pseudo induction period, rubbers of 10 and 30 mesh devulcanized at a higher temperature had a lower torque due to more devulcanization at higher temperature. Also rubbers of 10 and 30 mesh devulcanized at higher amplitudes had a lower torque due to more devulcanization experienced by these rubbers. This is in agreement with the storage modulus values showing lower values for rubbers devulcanized at higher temperature and higher amplitudes. At the completion of curing, maximum torques have the same trend indicating the lower maximum torques for rubbers devulcanized at higher temperature and amplitudes. The same amount of curatives were used in each sample, thus samples with a lower torque at the start of curing show a lower maximum torque. Again, curing curves can be divided into two groups. The rough extrudates and cohesive powder show higher torques at the pseudo induction period and higher maximum torque at the completion of curing than the smooth extrudates and sticky extrudates. This indicates that after revulcanization, the
Figure 4.13 Curing curves of devulcanized rubbers of 10 and 30 meshes obtained at various ultrasonic amplitudes at temperatures of 250°C (a) and 180°C (b).
rough extrudates and cohesive powder also have higher moduli than that of the smooth extrudates and sticky extrudates.

4.8. Tensile test

The stress-strain curves of revulcanized rubbers of 10 and 30 mesh are shown in Figure 4.14 (a) and (b) for rubbers devulcanized at 250°C, and (c) for rubber devulcanized at 180°C. Figure 4.15 shows the modulus at 100% elongation (a), tensile strength (b) and elongation at break (c) as a function of ultrasonic amplitude. Modulus at 100% elongation varied from 2.54 MPa to 3.71 MPa, the elongation at break varied from 131% to 183%, and the tensile strength varied from 4.38 MPa to 7.74 MPa. Revulcanized rubber of 30 mesh had a higher elongation at break, and generally, a higher tensile strength except revulcanized rubber devulcanized at an amplitude of 10 μm. The modulus at 100% elongation and the tensile strength of revulcanized rubbers of 10 and 30 meshes correlates with the crosslink density of revulcanizates, as can be seen from the comparison of Figure 4.5 and Figure 4.15. The modulus and strength increased with increasing crosslink density of devulcanized rubbers and revulcanizates for both rubbers of 10 and 30 mesh. The tensile strength was also related to the gel fraction of revulcanizates. With the increase of the gel fraction of vulcanizates, the strength was increased. Revulcanized 30 mesh tire rubbers had a lower modulus at 100% elongation, and the modulus of revulcanizates of both meshes decreased with the increase of amplitude. Again, the modulus of revulcanized rubbers can be divided into two groups corresponding to the smooth extrudates and sticky extrudates, and rough extrudates and cohesive powder. The revulcanizates of the smooth extrudates and sticky extrudates had significantly lower modulus than the revulcanizates of the rough
Figure 4.14 Stress-strain curves of revulcanized rubbers of 10 (a) and 30 (b) meshes obtained at various ultrasonic amplitudes and a temperature of 250°C, and of revulcanized rubbers of 10 and 30 (c) meshes obtained at various ultrasonic amplitudes and a temperature of 180°C
Figure 4.15 Modulus at 100% elongation (a), tensile strength (b) and elongation at break (c) of revulcanized rubbers of 10 and 30 meshes vs. ultrasonic amplitudes. The devulcanization temperatures were 250°C and 180°C.
extrudates and cohesive powder. This is also related to the crosslink density of revulcanizates. Namely, the revulcanizates of the smooth extrudates and sticky extrudates have a lower crosslink density. Therefore, their revulcanizates also have a lower modulus at 100% elongation. From the observations, one can conclude that the revulcanizates of the smooth extrudates and sticky extrudates have a lower modulus and strength, but a higher elongation at break. Therefore, during the ultrasonic aided devulcanization by the twin-screw extrusion, one can determine which extrudates to obtain based on the requirement for mechanical properties of the revulcanizates. The revulcanized rubbers of 10 and 30 mesh obtained at a higher devulcanization temperature showed a higher modulus at 100% elongation and a lower elongation at break and tensile strength. This may be due to the fact that the sol part of rubbers of 10 and 30 meshes devulcanized at a higher temperature had a lower molecular weight, which led to lower modulus at 100% elongation after revulcanization. But lower molecular weight led to a better flowability of devulcanized rubbers during curing, and resulted in a better tensile strength and elongation at break.

4.9. Conclusion

At the same ultrasonic amplitude, rubber of 30 mesh experienced more devulcanization during continuous ultrasonic extrusion than rubber of 10 mesh. Also, at a devulcanization temperature of 250°C, rubber of 30 mesh consumed more ultrasonic energy and exhibited a lower die pressure during devulcanization than rubber of 10 mesh. However, at a temperature of 180°C, rubber of 10 mesh consumed more ultrasonic energy than rubber of 30 mesh, possibly due to changes of the acoustic properties of the material. Devulcanized and revulcanized rubber of 30 mesh had a
lower crosslink density and a lower gel fraction. The lower die pressure of rubber of 30 mesh can be attributed to a lower gel fraction after devulcanization and a correspondingly a lower viscosity. The dependence of the normalized crosslink density on the normalized gel fraction of devulcanized rubbers of 10 and 30 meshes can be correlated by a universal master curve, which indicates that their network breakage mechanism is similar. The dynamic tests of devulcanized rubber of 30 mesh indicated a lower complex viscosity, storage and loss moduli, and higher loss tangent confirming that rubber of 30 mesh experienced more devulcanization than rubber of 10 mesh. Curing curves showed the pseudo induction period with the maximum torque of devulcanized rubber of 30 mesh being higher than that of devulcanized rubber of 10 mesh. The latter correlated with the modulus at 100% elongation. The highest elongation at break was obtained from the revulcanizate of rubber of 30 mesh devulcanized at 10 µm, and the highest tensile strength was obtained from the revulcanizate of rubber of 30 mesh devulcanized at 5 µm. Results of tensile tests generally showed that both the elongation at break and tensile strength of revulcanizates of 30 mesh were higher than those of 10 mesh, while the modulus of revulcanizates of 30 mesh was lower. The revulcanizates of rubbers devulcanized at a temperature of 180 °C showed a higher modulus at 100% elongation and a lower tensile strength and elongation at break. Therefore, from tensile tests, one can conclude that generally rubber of 30 mesh was a better material for devulcanization with a devulcanization temperature of 250°C providing better properties of revulcanizates.

Interestingly, the properties of devulcanized and revulcanized rubbers of both meshes obtained at different amplitudes fell into two groups exhibiting the smooth and sticky extrudates, and rough extrudates and cohesive powder corresponding to different
levels of devulcanization. This was also indicated by the die pressure, power consumption, Cole-Cole plots, crosslink density and gel fraction. The elongation at break of the revulcanizates of the smooth and sticky extrudates was higher than that of those of the rough extrudates and cohesive powder, while the tensile strength and modulus at 100% elongation of the revulcanizates of the smooth and sticky extrudates was lower.
CHAPTER V
CONTINUOUS ULTRASONIC DEVULCANIZATION OF 40TR, 84TR, 80BU, 140TR AND 200TR

5.1. General

In this chapter, the devulcanization study of GTR of 40TR, 84TR, 80BU, 140TR and 200TR, manufactured by Lehigh Technologies, at a temperature of 180°C will be discussed. A low temperature in the ultrasonic zone should be used to minimize degradation effect. But at temperatures lower than 180°C, the torque during extrusion was too high to rotate the screws. Thus 180°C was chosen. For the purpose of comparison, 40TR, 84TR, 80BU, 140TR and 200TR were divided into three groups. Rubber particles of 40TR and 84TR were put into one group because they were made from whole truck tire, and their gel fraction and solid content were found to be close to each other. 140TR and 200TR were put in another group because their solid content was much higher than all of the other tire rubbers. 80BU was put in the third group because it was made from truck tire buffing.

5.2. Die pressure

The die pressure registered during the devulcanization of 40TR, 84TR, 80BU, 140TR and 200TR at different ultrasonic amplitudes is shown in Figure 5.1. Generally
Figure 5.1 Die pressure vs. ultrasonic amplitude during devulcanization of 40TR, 84TR, 80BU, 140TR and 200TR
the die pressure decreased with the increasing amplitude. In the case of 40TR, 84TR, 140TR and 200TR, when amplitude was low, the die pressure only slightly changed with an increase of the ultrasonic amplitude. At higher amplitudes an obvious drop of die pressure with an increase of the amplitude could be observed. This phenomenon can be explained by the fact that at higher amplitude the viscosity of treated rubbers significantly and resulted in a much lower die pressure\(^3\), as indicated by Figure 5.1 and described earlier in Figure 5.6 and Figure 5.7. For rubber of 80BU, the die pressure is less sensitive to the amplitude increase during ultrasonic treatment. The die pressure measured during the devulcanization of 40TR is higher than that measured during the devulcanization of 84TR, because 40TR was less devulcanized than 84TR as will be described later. This can be attributed to the smaller specific surface area of the rubber of 40TR. The die pressure measured during the ultrasonic treatment of 140TR was higher than that measured during the treatment of 200TR.

5.3. Power consumption

Another important parameter recorded during the ultrasonic extrusion process is the ultrasonic power consumption. Ultrasonic power consumption is the power consumed for the ultrasonic treatment of GTR. Figure 5.2 shows the dependence of the ultrasonic power consumed during the ultrasonic treatment of 40TR, 84TR, 80BU, 140TR and 200TR as a function of amplitudes. The power consumption increased with an increase of the amplitude, indicating that more power was transferred to induce the expansion and contraction of voids present in tire rubber during ultrasonic treatment\(^4\). It should be noted that higher power consumption does not necessarily result in more
Figure 5.2 Power consumption vs. ultrasonic amplitude during devulcanization of 40TR, 84TR, 80BU, 140TR and 200TR
devulcanization of tire rubbers. This is due to the fact that ultrasonic treatment does not only induce devulcanization, it can also lead to the reformation of gel, which was observed by Tapale and Isayev\textsuperscript{29} in their study of devulcanization of the unfilled natural rubber. Generally, power consumption during the devulcanization of 40TR is lower than that during devulcanization of 84TR. The power consumption during devulcanization of 140TR is much less than that during devulcanization of 200TR, possibly as a result of the much lower gel fraction of 140TR powder.

5.4. Swelling test

Figure 5.3 shows the gel fraction of devulcanized and revulcanized 40TR, 84TR, 80BU, 140TR and 200TR treated at various amplitudes, as well as the gel fraction of tire powders. The gel fraction of devulcanized 40TR and 200TR generally decreased with an increase of the ultrasonic amplitude. This observation can be explained by the occurrence of more devulcanization experienced by 40TR and 200TR at higher amplitudes. But for the devulcanized 84TR and 140TR, the gel fraction increased with the amplitude at first, then reached a maximum at intermediate amplitudes, followed by a drop when the amplitude further increased. This means gel reformation took place at certain intermediate amplitudes\textsuperscript{29}. For all tire rubbers except 80BU, the gel fraction of rubbers devulcanized at 13 \(\mu\text{m}\) is much lower than the gel fraction of those devulcanized at lower amplitudes. This indicates that an amplitude of 13 \(\mu\text{m}\) is sufficient for decreasing gel fraction. At this amplitude, devulcanization is more pronounced than gel reformation. The gel fraction of devulcanized 40TR is higher compared to devulcanized 84TR, due to more devulcanization of 84TR under ultrasonic treatment. This observation indicates that GTR with a smaller particle size is
Figure 5.3 Gel fraction of devulcanized and revulcanized 40TR, 84TR, 80BU, 140TR, 200TR at various amplitudes and tire powder.
easier to be devulcanized. The gel fraction of devulcanized 140TR is lower than that of
devulcanized 200TR mainly due to the lower gel fraction of powder of 140TR
compared to that of 200TR. The gel fraction of 80BU devulcanized at all amplitudes are
almost the same, due to a less sensitivity of 80BU to ultrasonic treatment.

Generally, variance of the gel fraction of the revulcanized 40TR, 84TR, 80BU,
140TR and 200TR with amplitude corresponds to the tendency of variance of gel
fraction of the devulcanized rubbers very well. This is obviously due to the same
amount of curatives were compounded for all devulcanized rubbers. For 40TR, 80BU
and 200TR, the gel fraction of the revulcanizates decreased with an increase of the
amplitude, which indicates that more sol was generated during the ultrasonic treatment
at higher amplitudes. For the revulcanized 84TR and 140TR, the gel fraction has a
maximum at 10 µm and 7.5µm, respectively, indicating more gel reformed at these
amplitudes. The gel fraction of revulcanized 40TR is about similar as that of
revulcanized 84TR, even devulcanization effect was different in mere rubbers. The gel
fraction of revulcanized 140TR is much lower than the gel fraction of revulcanized
200TR. This is because that the gel fraction of the raw powder of 140TR is much lower
than that of the raw powder of 200TR. However, the revulcanization reduced the
difference of gel fraction between 140TR and 200TR observed in tire powders. At an
amplitude of 13 µm, gel fraction of revulcanizates is much lower than revulcanizates
obtained from powder devulcanized at lower amplitudes. This indicates that at an
amplitude of 13 µm, some permanent damage was induced to tire powder, which
cannot be completely restored by revulcanization.

For 40TR, 84TR, 80BU, 140TR and 200TR, the crosslink density of devulcanized
rubbers are not available because they were disintegrated during swelling. The
crosslink density of the revulcanizates of 40TR, 84TR, 80BU, 140TR and 200TR treated at various amplitudes are shown in Figure 5.4. Generally, for the revulcanized 80BU, 140TR and 200TR, the crosslink density decreased with an increase of the ultrasonic amplitude. Again, the crosslink density of revulcanized 84TR shows a maximum at an amplitude of 10 µm, as a result of the strong effect of gel reformation at this amplitude. At each amplitude, the revulcanizates of 40TR have higher crosslink density compared to those of 84TR, due to more devulcanization experienced by 84TR.

5.5. Dynamic rheology data

Figure 5.5 shows the storage moduli (a), complex viscosity (b) and loss tangent (c) of devulcanized and revulcanized 40TR and 84TR, as well as the loss moduli of devulcanized (d) and revulcanized (e) 40TR and 84TR obtained at various amplitudes as a function of frequency. The storage moduli, complex viscosity and loss moduli of devulcanized and revulcanized 40TR at all amplitudes are higher than those of devulcanized and revulcanized 84TR, while the loss tangent of devulcanized and revulcanized 40TR at all amplitudes are lower than those of devulcanized and revulcanized 84TR, as a result of more devulcanization of 84TR. Figure 5.6 shows the storage moduli (a), complex viscosity (b), loss tangent (c) of devulcanized and revulcanized 140TR and 200TR, as well as the loss moduli of devulcanized (d) and revulcanized (e) 140TR and 200TR obtained at various amplitudes as a function of frequency. At lower amplitudes, the storage moduli, complex viscosity and loss moduli of devulcanized 140TR are slightly lower than those of devulcanized 200TR. The loss tangent of devulcanized 140TR and 200TR are very close to each other. At higher amplitudes, the storage moduli, complex viscosity and loss moduli of devulcanized
Figure 5.4 Crosslink density of revulcanized 40TR, 84TR, 80BU, 140TR and 200TR at various amplitudes
Figure 5.5 Storage moduli (a), complex viscosity (b), loss tangent (c) of devulcanized and revulcanized 40TR and 84TR, and loss moduli of devulcanized (d) and revulcanized (e) 40TR and 84TR vs. frequency at various amplitudes
Figure 5.6 Storage moduli (a), complex viscosity (b), loss tangent (c) of devulcanized and revulcanized 140TR and 200TR, and loss moduli of devulcanized (d) and revulcanized (e) 140TR and 200TR vs. frequency at various amplitudes.
140TR are higher, and the loss tangent of devulcanized 140TR are lower. The storage moduli and complex viscosity of revulcanized 140TR are higher than those of revulcanized 200TR, and the loss tangent of revulcanized 140TR are lower than those of revulcanized 200TR.

Figure 5.7 shows the storage moduli (a), complex viscosity (b), loss tangent (c) of devulcanized and revulcanized 80BU, as well as the loss moduli of devulcanized (d) and revulcanized (e) 80BU obtained at various amplitudes as a function of frequency. The less sensitivity of 80BU to the ultrasonic treatment resulted in the storage moduli, complex viscosity and loss moduli of devulcanize and revulcanized 80BU treated at different amplitudes are very close to each other. Only a slight trend of decreasing of the rheological properties with an increase of the amplitude is noted.

We can see that the storage moduli, complex viscosity and loss moduli of devulcanized 40TR and 200TR decreased with an increase of the ultrasonic amplitude. This can be explained as a result of the devulcanization effect increasing with an increase of the amplitude. For the devulcanized and revulcanized 84TR and 140TR, the storage moduli and complex viscosity increased with the increasing amplitude till 10 µm and 7.5 µm, respectively, and decreased when the amplitude was further increased. This can be explained as a result of the stronger gel reformation effect at certain intermediate amplitudes, with the devulcanization dominated at higher amplitudes. Figure 5.8 shows the complex viscosity at a frequency of 9.3 rad/s of devulcanized and revulcanized 40TR, 84TR, 80BU, 140TR and 200TR obtained at various amplitudes. The complex viscosity at a frequency of 9.3 rad/s of devulcanized and revulcanized rubbers shows the same trend with increasing amplitude, as the complex viscosity
Figure 5.7 Storage moduli (a), complex viscosity (b), loss tangent (c) of devulcanized and revulcanized 80BU, and loss moduli of devulcanized (d) and revulcanized (e) 80BU vs. frequency at various amplitudes.
Figure 5.8 Complex viscosity of devulcanized and revulcanized 40TR, 84TR, 80BU, 140TR and 200TR at a frequency of 9.3 rad/s and various amplitudes
obtained within a frequency range from 0.02 rad/s to 200 rad/s, which was described in this section earlier.

5.6. Curing behavior

During curing of all kinds of devulcanized tire rubbers, the induction period was absent, and instead, a pseudo induction period was observed, as discussed in the previous chapter. The torque during curing increased slightly during the pseudo induction period, followed by a fast increase at the end of pseudo induction period, then reached a maximum and stabilized.

Figure 5.9 shows the curing curves measured during revulcanization of 40TR and 84TR devulcanized at different ultrasonic amplitudes. Compared to 84TR, the torque measured during the pseudo induction period and the maximum torque measured during the curing of the devulcanized 40TR is higher because of more devulcanization experienced by 84TR. This behavior is similar to the behavior of dynamic properties of devulcanized and revulcanized 40TR and 84TR.

Figure 5.10 shows the curing curves measured during revulcanization of 140TR and 200TR devulcanized at different amplitudes. The torque during the pseudo induction period and the maximum torque obtained during revulcanization of devulcanized 140TR are higher, compared to those of 200TR.

Figure 5.11 shows the curing curves during revulcanization of devulcanized 80BU obtained at different amplitudes. The torque during the pseudo induction period and the maximum torque during the revulcanization of 80BU devulcanized at different amplitudes are very close. However, it can be observed that there is a slight decrease in torque with an increase of the amplitude.
Figure 5.9 Curing curve of devulcanized 40TR and 84TR obtained at various amplitudes
Figure 5.10 Curing curve of devulcanized 140TR and 200TR obtained at various amplitudes
Figure 5.11 Curing curve of devulcanized 80BU obtained at various amplitudes
For 40TR and 200TR, the torque during the pseudo induction period and the maximum torque during revulcanization decreased with an increase of amplitude, as a result of more devulcanization experienced at higher amplitudes. The torque during the pseudo induction period and the maximum torque during revulcanization of the devulcanized 84TR and 140TR have a maximum at 10 µm and 7.5µm, respectively, because of gel reformation at these intermediate amplitudes.

5.7. Tensile test

Figure 5.12, Figure 5.13 and Figure 5.14 show the elongation at break, the modulus at 100% elongation (M100), and the tensile strength of revulcanizates, respectively. The elongation at break of revulcanizates of various revulcanized tire rubbers ranges from 121.5% to 236.4%. The M100 of revulcanizates ranges from 1.97 MPa to 4.17 MPa, and the tensile strength of revulcanizates varies from 4.43 MPa to 9.28 MPa. Figure 5.15 shows the stress-strain curves of revulcanized 40TR (a), 84TR (b), 80BU (c), 140TR (d) and 200TR (e) obtained at various amplitudes.

Generally, the elongation at break of the revulcanizates increased with an increase of the ultrasonic amplitude. This is due to the fact that at higher amplitudes, more sol was created during the ultrasonic treatment, leading to an increase of the elongation at break of revulcanizates. The elongation at break of the revulcanized 40TR is lower, compared to those of the revulcanized 84TR. This is a result of the higher gel fraction and lower sol fraction of the revulcanized 40TR. The revulcanizates of 80BU exhibits a higher elongation at break than the revulcanizates of other kinds of tire rubbers. The revulcanizate of 80BU treated at 13 µm exhibits the highest elongation at break of
Figure 5.12 Elongation at break of revulcanized 40TR, 84TR, 80BU, 140TR and 200TR obtained at various amplitudes
Figure 5.13 Modulus at 100% elongation of revulcanized 40TR, 84TR, 80BU, 140TR and 200TR obtained at various amplitudes
Figure 5.14 Tensile strength of revulcanized 40TR, 84TR, 80BU, 140TR and 200TR obtained at various amplitudes
Figure 5.15 The stress-strain curves of revulcanized rubbers of 40TR (a), 84TR (b),
80BU (c), 140TR (d) and 200TR (e) obtained at various amplitudes.
236.4%. The elongation at break of the revulcanized 140TR is lower than that of the revulcanized 200TR.

For the revulcanized tire rubber of 40TR, 80BU, 140TR and 200TR, the M100 decreased with an increase of the amplitude. This generally corresponds to the decreasing crosslink density of the revulcanizates with increase of the amplitude shown in Figure 5.4, except the crosslink density of revulcanized 40TR obtained at 5µm. The M100 of the revulcanized 84TR had a maximum at 10 µm, due to the strong gel reformation occurring during the ultrasonic treatment at this amplitude. The M100 of the revulcanized 40TR are higher than those of the revulcanized 84TR. This is in agreement with the higher crosslink density of 40TR. The M100 of the revulcanized 140TR is lower than those of the revulcanized 200TR, due to a lower crosslink density of the revulcanized 140TR. It is quite interesting that the comparison of the storage modulus, complex viscosity of revulcanizates and the maximum torque during curing process showed an opposite trend that the revulcanized 140TR showed higher modulus than the revulcanized 200TR. The highest M100 was obtained from the revulcanize of 200TR treated at 5µm, with a M100 of 4.17 MPa.

The strength of the revulcanizates of each kind of tire rubber increased with the amplitude at first. After reaching a maximum, the strength decreased with the amplitude. This is possibly due to the fact that at lower amplitudes, the devulcanization was not sufficient, while at higher amplitudes, too much degradation took place. In both cases the tensile strength cannot be maximized. Thus, an optimization of the ultrasonic amplitude is critical to maximize the strength of the revulcanizates. The revulcanizates of 80BU showed the higher tensile strength compared to the revulcanizates of other tire rubbers. The highest tensile strength of 9.28MPa was obtained from the revulcanized
80BU treated at an amplitude of 10µm. The revulcanizates of 84TR and 140TR have a lower tensile strength. The strong gel reformation phenomena at intermediate amplitudes might be the reason for the lower tensile strength of revulcanized 84TR, and the low gel fraction may be the reason for the lower tensile strength of revulcanized 140TR.

5.8. Conclusion

The die pressure of devulcanized 40TR was found to be higher than that of 84TR, due to less devulcanization experienced by 40TR. The power consumption during the devulcanization of 40TR was lower compared to that during devulcanization of 84TR, meaning less energy was transferred to 40TR. The dynamic properties such as the storage modulus, complex viscosity and loss modulus of devulcanized and revulcanized 40TR are higher, compared to those of devulcanized and revulcanized 84TR, while the loss tangent of devulcanized and revulcanized 40TR are lower, indicating more devulcanization experienced by 84TR. The gel fraction of devulcanized and revulcanized 40TR is higher than that of the devulcanized rubber of 84TR, confirming that 84TR was more devulcanized during the ultrasonic treatment. This was explained as follows. The average particle size of 84TR is smaller than that of 40TR. Therefore, the specific surface area of 84TR is obviously larger than that of 40TR, which facilitate the transfer of ultrasonic energy to the GTR, and resulted in more devulcanization of tire rubber with a smaller particle size. Both the minimum torque and the maximum torque during curing of the devulcanized 40TR are higher than those during curing of the devulcanized 84TR. This observation is in agreement
with the dynamic properties. The revulcanizates of 40TR have a higher modulus at 100% elongation and tensile strength, and lower elongation at break.

During the ultrasonic extrusion, 140TR exhibited a higher die pressure than 200TR. During the ultrasonic treatment, more power was consumed by 200TR, which might be due to higher gel fraction. The gel fraction of both the devulcanized and revulcanized 140TR are lower compared to those of 200TR, due to a low gel fraction of 140TR powder. The elongation at break, modulus at 100% elongation and tensile strength of the revulcanized 140TR are all lower than those of the revulcanized 200TR.

The GTR of 80BU was less sensitive to the ultrasonic treatment, as confirmed by swelling test result and rheology data. The best tensile strength and elongation at break were achieved from the revulcanized 80BU. The revulcanizate with the highest tensile strength of 9.28MPa was obtained at an amplitude of 10µm. The highest elongation at break of 236.4% was obtained from the revulcanizates of 80BU treated at 13µm.
CHAPTER VI
SUMMARY

The studies described in this thesis are the first attempt to use an ultrasonic twin-screw extruder for the devulcanization of rubbers. Ground tire rubbers with different particle sizes were devulcanized using this ultrasonic twin-screw extruder. The differences in structure and properties among the devulcanized and revulcanized tire rubbers were compared. Since specific compositions of recycled tire rubbers were unknown, there is a huge obstacle to make clear the relation among processing, structure and properties. Even though, some understandings were achieved.

The comparison between rubbers of 10 and 30 meshes, and the comparison between 40TR and 84TR showed that tire rubbers with smaller particle sizes were easier to be devulcanized to produce devulcanized rubbers with lower gel fraction. Their revulcanizes had a higher elongation at break. A hypothesis was made regarding how the ground tire rubber with different particle sizes were treated differently under ultrasound, associating the difference in particle sizes to the difference in surface area.

The effect of ultrasonic amplitude was also studied, and the competition between devulcanization and gel reformation during the ultrasonic treatment was revealed. At higher amplitudes, devulcanization effect is stronger than gel reformation, resulting in highly devulcanized tire rubbers. But at higher amplitudes, severe
degradation may take place. Thus, the optimization of ultrasonic treatment is extremely important for producing the devulcanized rubber that neither undertreated nor overtreated.

140TR has much lower gel fraction than that of 200TR. This could be related to its manufacturing process. 80BU is less sensitive to ultrasonic treatment. This might be attributed to different material of 80BU. Mechanical properties such as the elongation at break and tensile strength of revulcanized 80BU are the best among all revulcanized GTR studied in this thesis.

In the future research, an optimization of the screw design could be considered. The current screw design involves some kneading element, which can damage main chains of rubbers considerably. A better screw design with more conveying elements can be considered to replace the current design.


22. Yun, J. S.; Isayev, A. I., Recycling of roofing membrane rubber by ultrasonic


34. Chen, G. S.; Guo, S. Y.; Li, H. L., Ultrasonic improvement of the


46. Isayev, A. I.; Kumar, R.; Lewis, T. M., Ultrasound assisted twin screw


