DEVULCANIZATION OF WASTE EPDM RUBBER AND MANUFACTURING OF POLYPROPYLENE (PP)/ WASTE EPDM THERMOPLASTIC ELASTOMERS USING ULTRASONICALLY AIDED EXTRUSION

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

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

Hui Dong
May, 2015
DEVULCANIZATION OF WASTE EPDM RUBBER AND MANUFACTURING OF POLYPROPYLENE (PP)/ WASTE EPDM THERMOPLASTIC ELASTOMERS USING ULTRASONICALLY AIDED EXTRUSION

Hui Dong

Thesis

Approved:                        Accepted:

Advisor
Dr. Avraam I. Isayev

Department Chair
Dr. Sadhan C. Jana

Committee Member
Dr. Kevin Cavicchi

Dean of the College
Dr. Eric J. Amis

Committee Member
Dr. Mark D. Soucek

Interim Dean of the Graduate School
Dr. Rex Ramsier

Date
ABSTRACT

Waste ethylene propylene diene monomer (EPDM) rubber from postindustrial scrap is significant environmental problem. In attempt to solve this problem, a technology for its recycling and utilization is required. In the present study, the devulcanization of waste EPDM rubber was conducted by means of an ultrasonic twin screw extruder operating at a frequency of 40 kHz and ultrasonic amplitudes varying from 0 to 13 μm. Screw configurations with and without kneading elements were utilized in devulcanization. Die pressure and ultrasonic power consumption during devulcanization EPDM rubber were recorded. Curing behavior, dynamic properties and gel fraction of devulcanized EPDM and crosslink density, gel fraction, dynamic and mechanical properties of revulcanized EPDM were measured. It was found that higher ultrasonic amplitudes generally led to more devulcanization improving mechanical properties of revulcanizates. Specifically, the revulcanizates prepared from devulcanized EPDM obtained at an ultrasonic amplitude of 13 μm showed the tensile strength of 9 MPa and the elongation at break of 200%, but a lower modulus at 100% elongation. The complex viscosity of ultrasonically treated EPDM rubber at an ultrasonic amplitude of 13 μm decreased significantly and correlated with the gel fraction of the devulcanized EPDM rubber.

Compounding waste EPDM from postindustrial scrap with polypropylene (PP) is an ideal way to manufacture thermoplastic elastomers and to recycle waste EPDM to solve a significant environmental problem. Accordingly, the present study also focuses on the
effect of PP/EPDM mixing ratio, manufacturing methods and ultrasound on the rheological and mechanical properties of PP/EPDM blends. PP and EPDM were compounded at ratios of 75/25, 50/50, and 25/75. The one step (OS), two step (TS) methods and the dynamic revulcanization (DR) method were applied by using an ultrasonic twin screw extruder at ultrasonic amplitudes varying from 0 to 13 μm. In the OS method PP and waste EPDM particles were compounded into the extruder with and without ultrasonic treatment. In the TS and DR methods the waste EPDM particles were fed into the extruder and devulcanized without and with ultrasonic treatment. Then, in the TS method devulcanized EPDM was compounded with PP in the extruder without imposition of ultrasound. In the DR method, devulcanized EPDM after compounding with curatives was mixed with PP and dynamically revulcanized in the extruder without imposition of ultrasound. Die pressure during compounding were recorded. It is noteworthy that mechanical properties of blends obtained in OS and TS methods did not improve. At the same time, dynamically revulcanized PP/EPDM blends showed a significant increase of the tensile strength and elongation with ultrasonic amplitude and a slight decrease of the Young’s modulus. In particular, the tensile strength of 30 MPa and the elongation at break of 400% were achieved at an amplitude of 13 μm for the PP/EPDM blend at ratio of 75/25. The complex viscosity, storage modulus and loss modulus of dynamically revulcanized PP/EPDM blends increased with ultrasonic amplitude, and the loss tangent of dynamically revulcanized PP/EPDM blends decreased with ultrasonic amplitude while results for blends obtained by the OS and TS methods showed an opposite trend. These findings were supported by SEM studies of various blends.
ACKNOWLEDGEMENTS

The author is grateful to his advisor, Dr. Avraam I.Isayev, for his patient and kind instructions on research and courses. The author also would like to express his thanks to Mr. Jing Zhong, Mr. Tian Liang, Mr Keyuan Huang, Mr. Xiang Gao and Mr. Jiaxi Li for their help.
# TABLE OF CONTENTS

<p>| LIST OF FIGURES | viii |
| CHAPERS |
| I. INTRODUCTION | 1 |
| II. LITERATURE SURVEY | 4 |
| 2.1. Rubber Recycling | 4 |
| 2.2. Ultrasound | 5 |
| 2.3. Effect of ultrasound on degradation polymer | 6 |
| 2.4. Devulcanization of rubber by ultrasound | 6 |
| 2.5 Thermoplastic Elastomers (TPEs) | 8 |
| 2.6 Thermoplastic vulcanizates (TPVs) | 9 |
| III DEVULCANIZATION OF WASTE EPDM RUBBER FROM POST INDUSTRIAL SCRAP USING AN ULTRASONIC TWIN-SCREW EXTRUDER: EFFECT OF SCREW DESIGN | 11 |
| 3.1. Introduction | 11 |
| 3.2. Experimental | 12 |
| 3.2.1. Materials | 12 |
| 3.2.2. Twin screw extruder with ultrasonic treatment | 12 |
| 3.2.3. Screw design | 13 |
| 3.2.4. Extrusion and compounding | 14 |
| 3.2.5. Characterization methods | 15 |</p>
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Ultrasound cavitation bubble growth and collapse</td>
<td>5</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic of the overstressed network fragment around the collapsing bubble</td>
<td>7</td>
</tr>
<tr>
<td>3.1</td>
<td>Schematic drawing of twin screw extruder</td>
<td>13</td>
</tr>
<tr>
<td>3.2</td>
<td>Schematics of the kneading (a) and conveying (b) screws. The flow direction is from left to right</td>
<td>14</td>
</tr>
<tr>
<td>3.3</td>
<td>Die pressure (a) and ultrasonic power consumption (b) as a function of the ultrasonic amplitude during extrusion of EPDM in TSE containing kneading (filled symbols) and conveying (open symbols) screws</td>
<td>18</td>
</tr>
<tr>
<td>3.4</td>
<td>Gel fraction (a) and crosslink density (b) of the devulcanized and revulcanized EPDM as a function of the ultrasonic amplitude from TSE containing kneading (filled symbols) and conveying (open symbols) screws</td>
<td>20</td>
</tr>
<tr>
<td>3.5</td>
<td>Storage modulus of the devulcanized and revulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE containing kneading and conveying screws</td>
<td>22</td>
</tr>
<tr>
<td>3.6</td>
<td>Loss moduli (a) and loss tangent (b) of the devulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE containing kneading (filled symbols) and conveying (open symbols) screws</td>
<td>23</td>
</tr>
<tr>
<td>3.7</td>
<td>Loss modulus (a) and loss tangent (b) of the revulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE containing kneading (filled symbols) and conveying (open symbols) screws</td>
<td>24</td>
</tr>
<tr>
<td>3.8</td>
<td>Complex viscosity of the devulcanized and revulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE containing kneading (a) and conveying (b) screws</td>
<td>25</td>
</tr>
<tr>
<td>3.9</td>
<td>Curing curves of the devulcanized EPDM at various ultrasonic amplitudes from TSE containing kneading (solid lines) and conveying (dash lines) screws</td>
<td>26</td>
</tr>
</tbody>
</table>
3.10. Stress-strain curves of the revulcanized EPDM rubber at different ultrasonic amplitudes from TSE containing kneading (a) and conveying (b) screws ............28

3.11. Elongation at break (a), tensile strength (b) and modulus at 100% elongation (c) of the revulcanized EPDM as a function of the ultrasonic amplitude from TSE containing kneading (filled symbols) and conveying (open symbols) screws ..........29

4.1. Schematics of the ultrasonic (a) and mixing (b) screws. The flow direction is from left to right .................................................................34

4.2. Die pressure as a function of ultrasonic amplitude of PP/EPDM blends prepared by the OS (a), TS (b) and DR (c) methods .................................................................40

4.3. Complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) at a function of the frequency for pure PP, devulcanized EPDM and PP/EPDM blends prepared by the OS method .................................................................43

4.4. Complex viscosity (a), storage moduli (b), loss moduli (c) and loss tangent (d) at a function of the frequency for pure PP, devulcanized EPDM and PP/EPDM blends prepared by the TS method .................................................................46

4.5. Complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) at a function of the frequency for pure PP, devulcanized EPDM and PP/EPDM blends prepared by the DR method .................................................................49

4.6. Complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) at a function of the frequency for PP/EPDM 75/25 blends prepared by the OS, TS and DR methods .................................................................53

4.7. Complex viscosity (a), storage moduli (b), loss moduli (c) and loss tangent (d) as a function of the frequency for PP/EPDM 50/50 blends prepared by the OS, TS and DR methods .................................................................57

4.8. Complex viscosity (a), storage moduli (b), loss moduli (c) and loss tangent (d) at a function of the frequency for PP/EPDM 25/75 blends prepared by the OS, TS and DR methods .................................................................61

4.9. The stress-strain curves of PP/EPDM 75/25 (a), 50/50 (b) and 25/75 (c) blends prepared at different ultrasonic amplitudes by the OS method .........................63

4.10. Elongation at break (a), tensile strength (b) and Young’s modulus (c) as a function of the ultrasonic amplitude for PP/EPDM blends prepared by the OS method ........64

4.11. The stress-strain curves of PP/EPDM 75/25 (a), 50/50 (b) and 25/75 (c) blends prepared at different ultrasonic amplitudes by the TS method .........................67
4.12. Elongation at break (a), tensile strength (b) and Young’s modulus (c) as a function of different ultrasonic amplitudes for PP/EPDM blends prepared by the TS method ..........................................................68

4.13. The stress-strain curves of PP/EPDM 75/25 (a), 50/50 (b) and 25/75 (c) blends prepared at different ultrasonic amplitudes by the DR method ............................................70

4.14. Elongation at break (a), tensile strength (b) and Young’s modulus (c) as a function of ultrasonic amplitude for PP/EPDM blends prepared by the DR method ..........71

4.15. Optical micrographs of original EPDM powder ..........................................................73

4.16. SEM micrographs of PP/EPDM 50/50 blends without (a) and with ultrasonic treatment at an amplitude of 13 μm (b) prepared by the OS method .........................74

4.17. SEM micrographs of PP/EPDM 50/50 blends without (a) and with ultrasonic treatment at an amplitude of 13 μm (b) prepared by the TS method .........................74

4.18. SEM micrographs of PP/EPDM 50/50 blends without (a) and with ultrasonic treatment at an amplitude of 13 μm (b) prepared by the DR method .........................74
CHAPTER I
INTRODUCTION

Rubber is widely used in industry and daily life. Generally, raw rubber cannot be utilized until it is vulcanized. During vulcanization the crosslinks are formed to make rubber inflowable, insoluble and infusible. After vulcanization the mechanical properties are highly improved. Thus, crosslinks play an important role in the application of rubber, but hinder its recycling. The waste rubber can be processed by breaking crosslinks. This process is called reclamation. Many reclamation methods were developed\textsuperscript{1} and among them the continuous ultrasonic devulcanization is a very useful method. During the ultrasonic devulcanization, the compression and extension mechanical waves are induced by the ultrasonic horn and imposed to rubber, creating bubbles around impurities and voids.\textsuperscript{2} This process can provide enough local energy to break the crosslinks in the rubber. Development of recycling of waste ethylene propylene diene monomer (EPDM) is gaining more and more attention in industry, including ultrasound,\textsuperscript{2} microwave\textsuperscript{1} methods. Yun and Isayev carried out research on ultrasonic devulcanization of carbon black-filled EPDM rubber.\textsuperscript{3} In their study, the recycling of carbon black filled EPDM rubber was carried out by using a continuous ultrasonic grooved-barrel reactor. The crosslink density and gel fraction measurements indicated that more devulcanization was achieved at higher ultrasonic amplitude. Also, Yun and Isayev carried out research on superior mechanical properties of ultrasonically recycled EPDM rubber.\textsuperscript{4} In their study,
the devulcanization of EPDM rubber was carried out by using an ultrasonic single screw extruder. It was found that an increase of the ultrasonic amplitude and a decrease of the gap size increased the degree of devulcanization for EPDM vulcanizates.

In general, the development of thermoplastic elastomers (TPEs) is cost-effective and practically valuable. They provide a new horizon to the field of polymer science and engineering. Thermoplastic elastomers consist of materials with both thermoplastic and elastomeric properties. TPEs are used for a wide range of applications, including electrical, and medical industries. In the practical application, TPEs have both advantages and disadvantages over vulcanized rubber.

Advantages:

(1) It is easy for processing, such as injection molding, blow molding.

(2) Change the ratio of the components of the TPES can control the properties of the products.

Disadvantages:

(1) TPEs melt or soften at raised temperature above which they lose their rubbery behavior.

(2) TPEs exhibit creep behavior on extended use.

The dynamic vulcanization method was first introduced by Gessler in 1962. The first TPEs based on a crosslinked rubber-thermoplastic composition presented to the marketplace in 1972, which was derived from W.K.Fisher’s innovation of partially crosslinking the EPDM phase of PP/EPDM with peroxide. In 1978 Coran, Das and Patel attained the important enhancements of the properties of these blends by fully vulcanizing the rubber phase, while keeping the thermoplasticity of these blends. In 1982
these blends were further developed by Sabet Abdou – Sabet and Fath\textsuperscript{11} by the use of phenolic resins as curatives, improving the rubber-like properties and the processing features.

In earlier studies, enhanced ultrasonic compatibilization of PE/PS\textsuperscript{12}, PP/PS\textsuperscript{13}, PMMA/PS\textsuperscript{14} and PP/rubber blends\textsuperscript{15} was reported. It could be found that during mixing ultrasound can improve compatibilization and interfacial adhesion between diverse phases. Feng and Isayev carried out research about in situ compatibilization of PP/EPDM blends during ultrasound aided extrusion.\textsuperscript{16} They found that the mechanical properties of ultrasonically treated PP/EPDM TPEs were improved, and FTIR results of treated samples showed that PP/EPDM blends were compatibilized due to the formation of copolymer during ultrasonic treatment. Feng and Isayev also carried out research about in situ ultrasonic compatibilization of dynamically vulcanized PP/EPDM blends.\textsuperscript{17} The mechanical properties of the compression-molded samples of dynamically vulcanized PP/EPDM blends increased. However, these blends consisted of PP with virgin EPDM. In the earlier studies for PP/waste EPDM blends,\textsuperscript{18} the mechanical properties of ultrasonically treated PP/waste EPDM blends decreased. Nevertheless, these TPEs were not dynamically revulcanized. Therefore, it is necessary and interesting to study the effect of ultrasonic treatment on the mechanical and rheological properties of the dynamically revulcanized PP/waste EPDM blends.
CHAPTER II
LITERATURE SURVEY

2.1 Rubber Recycling

Recycling of waste rubber is a significant environmental issue in industrial society. Directly reprocessing and recycling of waste tires and vulcanized rubber are almost impossible due to the 3-dimensional networks in the rubber. In general, there are three methods for recycling vulcanized rubber and turning them into new materials: retreading, grinding and reclamation. Reclamation method can create high-value products. Reclamation is to recycle waste rubber by breaking crosslinks. A lot of techniques were proposed for recycling waste rubbers including ultrasound,\textsuperscript{2} and microwave.\textsuperscript{1} Microwave method provides the heat on the waste rubber fast. This method employs the application of a controlled amount of microwave energy to devulcanize a sulfur vulcanized elastomer, containing polar groups or components. Another method is ultrasonically aided extrusion.\textsuperscript{19} During the ultrasonic devulcanization, the compression and extension mechanical waves are induced by the ultrasonic horn and imposed to rubber, creating bubbles around impurities and voids.\textsuperscript{2} This process can provide local energy sufficient to break the crosslinks in the rubber.
2.2 Ultrasound

Ultrasound is an oscillating sound pressure wave with a frequency above the limitation of the human hearing range, i.e. > 16 KHz. Ultrasound is applied in several fields, including chemistry, biology, geology and polymers.

Ultrasound provides huge potential in the processing of liquids and melts, by improving the mixing and chemical reactions in many practical applications. Like all sound waves, ultrasound waves have cycles of compression and expansion. Compression generates positive pressure on the molecules by pushing them together. Expansion exerts negative pressure on the molecules by pulling them apart. Ultrasound generates changing high-pressure and low-pressure waves in liquids, which lead to the formation and violent collapse of small vacuum bubble. This phenomenon is called cavitation causing high speed impinging liquid jets and strong hydrodynamic shear-forces. The cavitation mechanism is made of three steps: formation, growth and collapse of bubbles, as shown in Figure 2.1. During cavitation, bubble collapse produces intense heating and high pressures at very short time.

![Figure 2.1 Ultrasound cavitation bubble growth and collapse](image)

Figure 2.1 Ultrasound cavitation bubble growth and collapse
2.3 Effect of ultrasound on degradation polymer

In earlier studies, it was found that in polymer solution, polymer degradation was induced by ultrasound. Price and Smith\textsuperscript{22,23,24} found the effect of various ultrasonic irradiation conditions on the molecular weight change of polystyrene in solution. In these studies, it was pointed out that the molecular weight degrades more for higher molecular weight polymer reaching a limiting molecule weight, below which no further degradation happens. Besides, molecular weight decreases with increasing ultrasound intensity, however, the dependence of degradation rate on ultrasound intensity is not monotonous increase. The rate of polymer degradation increases to maximum and then drops. It is because the radius of the bubble is proportional to the square root of the ultrasound intensity, and increasing ultrasound intensity causes larger number of bubbles per unit volume of solution leading to the higher shear forces on collapse, lower molecular weight and higher degradation rate. However, with an increase of the number of bubbles, ultrasound field is unable to pass through the solution efficiently resulting in less cavitation, so the degradation rate decreases at very high ultrasound intensity.

2.4 Devulcanization of rubber by ultrasound

Ultrasonic devulcanization is considered to be induced by the cavitation, and during the process of devulcanization, the existence of cavitational bubbles in solid polymer was verified.\textsuperscript{25,26} The effect of ultrasound on devulcanization of rubber was studied by many researchers, as summarized in the review by Isayev.\textsuperscript{1}
When ultrasound is applied to rubber, cavitation bubbles expand and contract because of the pulsating force. Thus a large amount of energy is released leading to the rupture of intermolecular bonds.

![Figure 2.2 Schematic of the overstressed network fragment around the collapsing bubble](image)

Extensive work on ultrasonic devulcanization has been done by Isayev and co-workers. The first study of SBR devulcanization with an ultrasonic extruder was carried out in 1995. SBR was devulcanized at different ultrasonic amplitudes and flow rates. It was found that gel fraction and viscosity decreased with increasing ultrasonic amplitude and decreasing flow rate, indicating better devulcanization. The mechanical properties of the revulcanized SBR also were improved. The effect of different ultrasonic amplitude, gap and flow rate on the devulcanization of ground tire rubber (GTR) was carried out by Tukachinsky et al. The devulcanization of GTR was characterized by crosslink density and gel fraction. It was shown that the degree of devulcanization was more significant with the increasing ultrasonic amplitude. Yun and Isayev carried out research about ultrasonic devulcanization of carbon black-filled EPDM rubber. The crosslink density and gel fraction of EPDM rubber indicated that much more devulcanization was achieved.
at higher amplitude. Yun and Isayev also studied the recycling of roofing membrane rubber by ultrasonic devulcanization.\textsuperscript{28} In their study, the mechanical properties of revulcanized EPDM rubber were exhibited to be controlled by devulcanization conditions and cure recipes, and rheological properties showed that devulcanized EPDM rubber were more elastic than uncured virgin EPDM rubber. Also, Yun and Isayev carried out research on superior mechanical properties of ultrasonically recycled EPDM rubber.\textsuperscript{4} In their study, the devulcanization of EPDM rubber was carried out by using an ultrasonic single screw extruder. It was found that the degree of devulcanization for EPDM vulcanizates increased with an increase of the ultrasonic amplitude and a decrease of the gap size.

2.5 Thermoplastic Elastomers (TPEs)

The appearance of thermoplastic elastomers (TPEs) took place in the late 1950s. They are a class of copolymers or a physical mix of polymer usually consisting of materials with both thermoplastic and elastomeric properties. In practical use, TPEs have both advantages and disadvantages.\textsuperscript{7}

Advantages:

(1) It is easy for processing, such as injection molding, blow molding.

(2) Change the ratio of the components of the TPES can control the properties of the products.

Disadvantages:

(1) TPEs melt or soften at raised temperature above which they lose their rubbery behavior.
(2) TPEs exhibit creep behavior on extended use.

Also, ultrasound has been proven to be useful in improving the interfacial adhesion between two different incompatible phases. The application of ultrasound on the polymer blends induces the stresses because of the cavitation, leading to homolytic cleavage of polymeric chains. In situ compatibilization of PP/EPDM blends using ultrasound aided extrusion was studied by Feng and Isayev.\textsuperscript{16} The elongation at break increased from 1100 to 1370% resulting from ultrasound, and the tensile strength increased from 20 to 26 MPa. SEM microimages showed that domain size decreased for ultrasonically treated PP/EPDM than that of the untreated sample.

2.6 Thermoplastic vulcanizates (TPVs)

The dynamic vulcanization is a process during which elastomer particles are vulcanized and dispersed in the thermoplastic matrix during dynamic vulcanization. If the elastomer particles are small and are well vulcanized, then the properties of the blends are improved. The improvements are as follows:

1. Better mechanical properties
2. Better elastic recovery
3. Improved high temperature utility
4. Higher melt strength

The dynamic vulcanization method was first introduced by Gessler in 1962.\textsuperscript{8} The first TPEs based on a crosslinked rubber-thermoplastic composition presented to the marketplace in 1972, which was derived from W.K.Fisher’s\textsuperscript{9} innovation of partially crosslinking the EPDM phase of PP/EPDM with peroxide. In 1978 Coran, Das and
Patel\textsuperscript{10} attained the important enhancements of the properties of these blends by fully vulcanizing the rubber phase, while keeping the thermoplasticity of these blends. In 1982 these blends were further developed by Sabet Abdou – Sabet and Fath\textsuperscript{11} by the use of phenolic resins as curatives, improving the rubber-like properties and the processing features. Possible applications of thermoplastic elastomers and thermoplastic vulcanizates are flexible diaphragms, bumpers, seals, plugs, wire and cable insulation.

In-situ ultrasonic compatibilization of unvulcanized and dynamically vulcanized PP/EPDM blends was carried out by Feng and Isayev.\textsuperscript{17} It was found that ultrasonic treatment improved the processing of dynamically vulcanized PP/EPDM blends by decreasing the die pressure. The mechanical properties of the compression-molded samples of dynamically vulcanized PP/EPDM blends improved. However, these blends consist of PP with virgin EPDM. Therefore, it is necessary and interesting to study the effect of ultrasonic treatment on the mechanical and rheological properties of the dynamically revulcanized PP/waste EPDM blends.
CHAPTER III
DEVLUCANIZATION OF WASTE EPDM RUBBER FROM POST INDUSTRIAL SCRAP USING AN ULTRASONIC TWIN-SCREW EXTRUDER: EFFECT OF SCREW DESIGN

3.1 Introduction

Rubber is widely used in industry and daily life. Generally, raw rubber cannot be utilized until it is vulcanized. During vulcanization the crosslinks are formed to make rubber inflowable, insoluble and infusible. After vulcanization the mechanical properties are highly improved. Thus, crosslinks play an important role in the application of rubber, but hinder its recycling. The waste rubber can be processed by breaking crosslinks. This process is called reclamation. Many reclamation methods were developed\(^1\) and among them the continuous ultrasonic devulcanization is a very useful method. During the ultrasonic devulcanization, the compression and extension mechanical waves are induced by the ultrasonic horn and imposed to rubber, creating bubbles around impurities and voids.\(^2\) This process can provide enough local energy to break the crosslinks in the rubber. Development of recycling of waste ethylene propylene diene monomer (EPDM) is gaining more and more attention in industry, including ultrasound,\(^2\) microwave\(^1\) methods. Yun and Isayev carried out research on ultrasonic devulcanization of carbon black-filled EPDM rubber.\(^3\) In their study, the recycling of carbon black filled EPDM
rubber was carried out by using continuous ultrasonic grooved-barrel reactor. The crosslink density and gel fraction measurements indicated that more devulcanization was achieved at higher ultrasonic amplitude. Also, Yun and Isayev carried out research on superior mechanical properties of ultrasonically recycled EPDM rubber. In their study, the devulcanization of EPDM rubber was carried out by using an ultrasonic single screw extruder. It was found that an increase of the ultrasonic amplitude and a decrease of the gap size increased the degree of devulcanization for EPDM vulcanizates. In the present study, the devulcanization of waste EPDM rubber was conducted by means of an ultrasonic twin screw extruder at ultrasonic amplitudes varying 0 to 13 μm.

3.2 Experimental

This section includes materials, twin screw extruder with ultrasonic treatment, screw design, extrusion and compounding and characterization methods.

3.2.1 Materials

Waste EPDM rubber from Post Industrial Scrap of 40 meshes (MD-184-EPDM) manufactured by Lehigh Technologies was used.

3.2.2 Twin screw extruder with ultrasonic treatment

Ultrasonically aided devulcanization was carried out with a co-rotating twin-screw extruder (Prism USALAB 16, Thermo Electron Co., Waltham, MA) modified with an ultrasonic horn attached onto the barrel. Schematic of this ultrasonic twin-screw extruder is shown in Figure 3.1. Two screws with a diameter of 16 mm were used to convey and
decrosslink the EPDM. The EPDM was fed into the hopper. Ultrasonic waves with a frequency of 40 kHz were applied to the EPDM by a horn. The horn has a 28 mm x 28 mm square cross section. It was mounted in the barrel and connected to a booster, which was connected to a converter, where electrical energy from a power supply was transferred to mechanical energy for devulcanization. The converter was driven by a Branson 2000bdc power supply (Branson Ultrasonic Co., Danbury, CT). The gap between the horn tip and screws was 2.5 mm, and the volume of the ultrasonic treatment zone was 1.9 cm$^3$. The die of the extruder had a diameter of 4 mm and a length of 11 mm. The ultrasonic horn was cooled by water at 45°C coming from a thermostat (GP-100, NESLAB Instruments Inc., Newington, NH). Also, the converter was cooled by compressed air.

![Figure 3.1 Schematic drawing of twin screw extruder](image)

3.2.3 Screw design

Figure 3.2 shows schematics of two screw designs. The first design (a) contained kneading elements and forward and reverse conveying elements and called kneading
screws. The cylindrical elements were used to provide a gap between the screw and the ultrasonic horn in the ultrasonic zone. The second design (b) only contained forward and reverse conveying elements and called conveying screws.

Reverse Conveying Elements

\[ 5 \times 60^\circ + 4 \times 90^\circ \quad 5 \times 90^\circ \quad 4 \times 90^\circ + 3 \times 30^\circ \text{Reverse} \]

(a)

Reverse Conveying Elements

(b)

Figure 3.2 Schematics of the kneading (a) and conveying (b) screws. The flow direction is from left to right.

3.2.4 Extrusion and compounding

The EPDM rubber was devulcanized using the ultrasonic co-rotating twin-screw extruder (TSE). Ultrasonic amplitudes of 0 μm, 7.5 μm, 10 μm, and 13 μm were used. The EPDM rubber was fed into the twin-extruder by a feeder (K-Tron Co., Glassboro, NJ). The rotation speed of the twin-screw extruder was 200 rpm, the flow rate of EPDM rubber was 8 g/min. Zone temperatures from the entrance of the extruder to the die were 150/180/190/190/190/190 °C. During ultrasonic treatment, die pressure and power consumption were recorded. However, when the kneading screws were used to devulcanize EPDM rubber, die pressure cannot be recorded at the ultrasonic amplitudes
of 0 μm and 7.5 μm, because the torque reached a limit, so the die was removed from the extruder.

After extrusion, the devulcanized EPDM rubber was compounded with curatives using a two roll mill (Reliable Rubber & Plastic Machinery Co., North Bergen, NJ) with a gap size of 5 mm. A rotor speed of 20 rpm and a cooling water temperature of 40 °C were used. The compounding recipe used was as follows: 100 phr devulcanized EPDM rubber, 1 phr sulfur, 2 phr zinc oxide, 1 phr stearic acid, 0.75 phr TMTD and 0.375 phr MBT. To get mechanical testing samples, the devulcanized EPDM rubber was cured into slabs with a mold of dimensions 152 mm x 152 mm x 1.5 mm, using a compression-molding press (Carver, Wabash, IN) at 160 °C under pressure of 13.8 MPa.

3.2.5 Characterization methods

Swelling tests for original waste EPDM powder, devulcanized and revulcanized EPDM rubber to measure the crosslink density and gel fraction were carried out using a Soxhlet extraction apparatus for 24 h. Toluene was used to extract the sol part from the samples and to swell it. The swollen sample was placed in a vacuum oven for 12 h and dried at 70°C. The Flory-Rehner equation\(^{29}\) and Kraus correction\(^{30}\) were used to calculate the crosslink density of samples. Since a large amount of carbon black was contained in the sample, Kraus correction should be employed. In this case, it was assumed that the carbon black as filler in EPDM rubber was HAF (high abrasion furnace) carbon black.

The Advanced Polymer Analyzer (APA 2000, Alpha Technologies, Akron, OH) was used to measure the curing curves during revulcanization of devulcanized rubber at 160 °C.
0°C, a frequency of 10 rad/s, and a strain amplitude of 4.2%. Also, the dynamic properties of devulcanized and revulcanized EPDM rubber were measured by APA2000 at 120 °C, and a strain amplitude of 4.2%, and within a frequency range from 0.06 rad/s to 200 rad/s. In order to obtain dynamic properties of revulcanized rubber, the devulcanized rubber with curatives was cured in APA2000 at 160°C and then cooled down and tested at 120 °C.

Mechanical properties of revulcanizates were tested using an Instron Tensile Tester (model 5567, Instron, Canton, MA) at an elongation rate of 500 mm/min. An extensometer was used.

3.3 Results and discussion

This section includes die pressure, power consumption, swelling tests, dynamic properties, curing behavior and tensile tests.

3.3.1 Die pressure, power consumption

Figure 3.3 shows the die pressure (a) and ultrasonic power consumption (b) as a function of the ultrasonic amplitude during the extrusion of EPDM using TSE with two different screw configurations depicted in Figure 3.2. Die pressure decreased with the ultrasonic amplitude. According to earlier study^{19}, the decrease of the die pressure is due to the fact that the higher amplitude induced more devulcanization and reduced the viscosity of devulcanized rubber, as shown later in the section on complex viscosity (Figure 3.8). At 10 μm and 13 μm, the die pressure in TSE containing the kneading screws was only slightly lower than that in TSE containing the conveying screws. As
shown below in section on gel fraction (Figure 3.4 (a)) and crosslink density (Figure 3.4 (b)), the TSE containing the kneading screws was more effective in reducing the gel fraction and crosslink density of the devulcanized EPDM in comparison with the TSE containing the conveying screws.

It is seen from Figure 3.3 (b) that the ultrasonic power consumption was affected by screw design and increased with the ultrasonic amplitude due to an increase of the acoustic pressure.\(^3\) The power consumption in TSE containing the kneading screws was higher than the power consumption in TSE containing the conveying screws. This can be explained that in the kneading screw design, the reverse conveying elements and kneading elements after ultrasonic zone could provide higher pressure leading to the higher power consumption.
Figure 3.3 Die pressure (a) and ultrasonic power consumption (b) as a function of the ultrasonic amplitude during extrusion of EPDM in TSE containing kneading (filled symbols) and conveying (open symbols) screws.

3.3.2 Swelling tests

Figure 3.4 shows both the gel fraction (a) and crosslink density (b) of devulcanized and revulcanized EPDM as a function of ultrasonic amplitude. The gel fraction of the original waste EPDM powder was also indicated. It can be seen that the gel fraction of devulcanized EPDM rubber was significantly reduced even when the EPDM rubber passed through the extruder without being treated by ultrasound due to the mechanical devulcanization. It is noteworthy that the crosslink density of the devulcanized samples
cannot be determined because the extrudate disintegrated during swelling. The crosslink density of revulcanized EPDM rubber and the gel fraction of devulcanized and revulcanized EPDM rubber using two different screw configurations decreased with increasing ultrasonic amplitude due to the breakage of crosslinks by ultrasound.\textsuperscript{19} A more devulcanization was achieved at an amplitude of 10 $\mu$m and 13 $\mu$m in TSE containing kneading screws. This is in accordance with the storage modulus shown in Figure 3.5 and loss tangent shown in Figure 3.6 (b) and Figure 3.7 (b). When the ultrasound was applied, TSE containing the kneading screws was more effective in decreasing both the gel fraction and crosslink density of the devulcanized EPDM than TSE containing the conveying screws. It can be explained that the kneading elements provided more shear stress to EPDM leading to the more devulcanization.

Huang and Isayev studied ultrasonic decrosslinking of crosslinked high-density polyethylene (XHDPE) using different screw designs.\textsuperscript{31} Their compounding screw design contained kneading elements and forward conveying elements. The decrosslinking screw design contained forward and reverse conveying elements, which is same as conveying screw design in the present study. They reported that TSE containing the decrosslinking screws was more effective in decreasing both the gel fraction and crosslink density of decrosslinked XHDPE than TSE containing the compounding screws. The reason is that the compounding screws did not contain the reverse conveying elements leading to the less residence time and lower pressure during the extrusion resulting in the less effective in decrosslinking.
3.3.3 Dynamic properties

Figure 3.5 shows the storage modulus of devulcanized and revulcanized samples as a function of the frequency at different ultrasonic amplitudes from TSE using two different screw configurations. For devulcanized EPDM, the values of the storage modulus decreased with an increase of ultrasonic amplitude. At 13 μm, the devulcanized EPDM
from TSE containing the kneading screws exhibited a lowest storage modulus. This is attributed to the fact that more devulcanization happened for EPDM devulcanized at higher ultrasonic amplitudes and more devulcanization occurred for EPDM devulcanized using kneading screws. More devulcanization led to the breakage of more crosslinks in EPDM due to the higher ultrasonic amplitudes and higher shear stress during the extrusion. This created more sol, and resulted in decreased elasticity, which is accordance with gel fraction shown in Figure 3.4 (a) and crosslink density shown in Figure 3.4 (b). Figure 3.6 shows the loss modulus (a) and loss tangent (b) of devulcanized samples as a function of the frequency at different ultrasonic amplitudes from TSE using two different screw configurations. Figure 3.7 shows the loss modulus (a) and loss tangent (b) of revulcanized samples as a function of the frequency at different ultrasonic amplitudes from TSE using two different screw configurations. Figure 3.8 shows the complex viscosity of devulcanized and revulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE using kneading screws (a) and conveying screws (b). The devulcanized and revulcanized EPDM from TSE using kneading screws had a lower complex viscosity and loss modulus and a higher loss tangent than those of devulcanized and revulcanized EPDM from TSE using conveying screws. This also can be explained by the fact that more devulcanization was achieved at an amplitude of 10 μm and 13 μm in TSE containing kneading screws. It is in accordance with the gel fraction and crosslink density shown in Figure 3.4.
Figure 3.5 Storage modulus of the devulcanized and revulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE containing kneading and conveying screws.
Figure 3.6 Loss moduli (a) and loss tangent (b) of the devulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE containing kneading (filled symbols) and conveying (open symbols) screws.
Figure 3.7 Loss modulus (a) and loss tangent (b) of the revulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE containing kneading (filled symbols) and conveying (open symbols) screws.
Figure 3.8 Complex viscosity of the devulcanized and revulcanized EPDM as a function of the frequency at different ultrasonic amplitudes from TSE containing kneading (a) and conveying (b) screws.
3.3.4 Curing behavior

Torque as a function of curing time of devulcanized EPDM rubber from TSE containing the kneading and conveying screws is shown in Figure 3.9. The values of torque decreased with the increasing ultrasonic amplitude. At an amplitude of 13 μm, the devulcanized EPDM from TSE containing the kneading screws exhibited the lowest torque due to more devulcanization experienced by these rubbers. This is accordance with the data on the gel fraction shown in Figure 3.4 (a), crosslink density shown in Figure 3.4 (b), storage modulus shown in Figure 3.5 and complex viscosity shown in Figure 3.8.

![Curing curves of the devulcanized EPDM at various ultrasonic amplitudes from TSE containing kneading (solid lines) and conveying (dash lines) screws.](image)

Figure 3.9 Curing curves of the devulcanized EPDM at various ultrasonic amplitudes from TSE containing kneading (solid lines) and conveying (dash lines) screws.
3.3.5 Tensile tests

The tensile stress-strain curves of revulcanized EPDM rubber obtained from devulcanized rubbers at different ultrasonic amplitudes from TSE containing the kneading (a) and conveying (b) screws are shown in Figure 3.10. Figure 3.11 shows the elongation at break (a), tensile strength (b) and modulus at 100% (c) as a function of ultrasonic amplitude. The elongation at break and tensile strength of revulcanized rubber increased, but the modulus at 100% decreased with the increasing ultrasonic amplitude. This generally corresponds to the decreasing crosslink density and gel fraction of the revulcanizates with an increase of the amplitude shown in Figure 3.4. According to previous study, the elongation at break and the modulus at 100% elongation of revulcanized rubber correlates with the gel fraction and crosslink density of revulcanizates, as can be seen from the Figure 3.4. At high ultrasonic amplitude, the elongation at break and tensile strength of the revulcanized EPDM rubber from TSE containing the kneading screws was higher, which is a result of the lower gel fraction and lower crosslink density of the revulcanizates. The M100 of the untreated revulcanized EPDM rubber from TSE containing the kneading screws cannot be achieved because its elongation of break was less than 100%. The M100 of the revulcanized EPDM rubber had the lowest value at an amplitude of 13 μm due to the lowest gel fraction and crosslink density of vulcanizates at an amplitude of 13 μm, shown in Figure 3.4. At an amplitude of 13 μm, the M100 of the revulcanized EPDM rubber from TSE containing the kneading screws was lower than that of the revulcanized EPDM rubber from TSE containing the conveying screws due to the lower gel fraction and crosslink density of vulcanizates from TSE containing the kneading screws, shown in Figure 3.4. At an amplitude of 7.5 μm, the
M100 of the revulcanized EPDM rubber from TSE containing the kneading screws was higher due to the lower sol fraction shown in Figure 3.4 (b). Therefore, one can conclude that more devulcanization would adversely affect the modulus of revulcanizates.

Figure 3.10 Stress-strain curves of the revulcanized EPDM rubber at different ultrasonic amplitudes from TSE containing kneading (a) and conveying (b) screws.
Figure 3.11 Elongation at break (a), tensile strength (b) and modulus at 100% elongation (c) of the revulcanized EPDM as a function of the ultrasonic amplitude from TSE containing kneading (filled symbols) and conveying (open symbols) screws.
3.4 Conclusion

Devulcanization of waste EPDM was carried out by using TSE containing kneading and conveying screws without and with ultrasonic treatment at various ultrasonic amplitudes. The gel fraction and dynamic properties of devulcanized EPDM rubber, and the gel fraction, crosslink density, mechanical properties and dynamic properties of revulcanized EPDM rubber were measured. The higher efficiency of kneading screws in devulcanization was observed due to higher pressure generated by the presence of kneading elements. Also, it was found that higher ultrasonic amplitudes generally led to more devulcanization improving mechanical properties of revulcanizates. Among various samples, the revulcanizates prepared from devulcanized EPDM obtained at an ultrasonic amplitude of 13 μm showed highest performance with the tensile strength of 9 MPa and the elongation at break of 200%. However, this revulcanizate showed a lower modulus at 100% elongation in comparison with those revulcanizates obtained at lower amplitude. The lowest complex viscosity of ultrasonically treated EPDM rubber was obtained at an ultrasonic amplitude of 13. This correlated with the lowest gel fraction and the lowest minimum and maximum curing torque upon revulcanization of the devulcanized EPDM rubber. It was found that ultrasonic amplitude did not affect the induction time during revulcanization.
4.1 Introduction

In general, the development of thermoplastic elastomers (TPEs) is cost-effective and practically valuable. They provide a new horizon to the field of polymer science and engineering. Thermoplastic elastomers consist of materials with both thermoplastic and elastomeric properties. Also, dynamic vulcanization is a process during which elastomer particles are vulcanized and dispersed in the thermoplastic matrix. If the elastomer particles are small and are well vulcanized, then the properties of the blends are improved. The dynamic vulcanization method was first introduced by Gessler in 1962. The first TPEs based on a crosslinked rubber-thermoplastic composition presented to the marketplace in 1972, which was derived from W.K.Fisher’s innovation of partially crosslinking the EPDM phase of PP/EPDM with peroxide. In 1978 Coran, Das and Patel attained the important enhancements of the properties of these blends by fully vulcanizing the rubber phase, while keeping the thermoplasticity of these blends. In 1982 these blends were further developed by Sabet Abdou – Sabet and Fath by the use of phenolic resins as curatives, improving the rubber-like properties and the processing features.

Feng and Isayev carried out research about in situ compatibilization of PP/EPDM blends during ultrasound aided extrusion. They found that the mechanical properties of
ultrasonically treated PP/EPDM TPEs were improved, and FTIR results of treated samples showed that PP/EPDM blends were compatibilized due to the formation of copolymer during ultrasonic treatment. Feng and Isayev also carried out research about in situ ultrasonic compatibilization of dynamically vulcanized PP/EPDM blends. The mechanical properties of the compression-molded samples of dynamically vulcanized PP/EPDM blends were improved. However, these blends consisted of PP with virgin EPDM. In this thesis, waste EPDM rubber was used. In the earlier studies for PP/waste EPDM blends, the mechanical properties of ultrasonically treated PP/waste EPDM blends decreased. Nevertheless, these TPEs were not dynamically revulcanized. Therefore, in this thesis PP/EPDM blends were dynamically revulcanized. It is necessary and interesting to study the effect of ultrasonic treatment on the mechanical and rheological properties of the dynamically revulcanized PP/waste EPDM blends.

4.2 Experimental

This section includes materials, twin screw extruder with ultrasonic treatment, preparation of PP/waste EPDM TPEs, molding and characterization methods.

4.2.1 Materials

The PP used for preparing PP/waste EPDM blends is metallocene based polypropylene PP3825 supplied by Exxon Chemical Company. Its melt flow rate is 32g/10min, and molecular weight is 144,800. Waste EPDM rubber from Post Industrial Scrap of 40 meshes (MD-184-EPDM) manufactured by Lehigh Technologies was used.
4.2.2 Twin screw extruder with ultrasonic treatment

Devulcanization and compounding was carried out using an ultrasonic co-rotating twin-screw extruder (Prism USALAB 16, Thermo Electron Co., Waltham, MA). Schematic of this ultrasonic twin-screw extruder (TSE) is shown in Figure 3.1. Two screws with a diameter of 16 mm were used to convey and mix the EPDM rubber with PP. Ultrasonic waves with a frequency of 40 kHz were applied to the EPDM rubber by a horn. The horn has a 28 mm x 28 mm square cross section. It was mounted in the barrel and connected to a booster, which equipped with a converter. The converter is driven by a Branson 2000bdc power supply (Branson Ultrasonic Co., Danbury, CT) and electrical energy from it is transferred to mechanical energy for devulcanization. The gap between the horn and screws is 2.5 mm, and the volume of the ultrasonic treatment zone is 1.9 cm$^3$. The circular die of the extruder has a diameter of 4 mm and a length of 11 mm. The ultrasonic horn was cooled by water at 45 °C coming from a thermostat (GP-100, NESLAB Instruments Inc., Newington, NH). Also, the converter is cooled by compressed air. Figure 4.1 shows schematics of two screw designs. The first design (a) was ultrasonic screw design containing conveying and kneading elements, and the cylindrical elements were used in the ultrasonic zone. The second design (b) was mixing design containing conveying and kneading elements.
4.2.3 Preparation of PP/Waste EPDM TPEs

Three different methods to manufacture PP/waste EPDM thermoplastic elastomers were used. The first method was called one step (OS) method. In this method, the PP pellets were fed into the hopper using a feeder (K-Tron Soder, USA) and the waste EPDM was also fed into the same hopper using a high precision twin screws feeder (MT-2, Brabender Technologie GmbH & Co. KG, Germany) using ultrasonic screws without and with ultrasonic treatment under amplitudes of 7.5, 10 and 13 μm. The ratio of PP/waste EPDM is 75/25, 50/50 and 25/75. For PP/EPDM at a ratio of 75/25, the flow rate of PP was 6 g/min and the flow rate of EPDM was 2 g/min. For PP/EPDM at a ratio of 50/50, the flow rate of PP was 4 g/min and the flow rate of EPDM was 4 g/min. For PP/EPDM at a ratio of 25/75, the flow rate of PP was 2 g/min and the flow rate of EPDM was 6 g/min. The screw speed was 200 rpm, and zone temperatures from the entrance of the extruder to the die were 150/180/190/190/190/190 °C. The extrudates from extruders were cooled, dried, finally crushed into particles using a pelletizer (Scheer Bay Company, Bay City, MI). The second method was called two steps (TS) method. In this method,
waste EPDM was fed into extruder using ultrasonic screws at a flow rate of 8 g/min and devulcanized without and with ultrasonic treatment at amplitude of 7.5, 10 and 13 μm. Then, PP/devulcanized EPDM blends of 75/25, 50/50 and 25/75 composition were physically mixed and fed to the TSE using mixing screws at a flow rate of 8 g/min without the ultrasonic treatment. The screw speed and zone temperature are same as the OS method. The third method was called dynamic revulcanization (DR) method. In this method, waste EPDM was fed into extruder independently using ultrasonic screws at a flow rate of 8 g/min and devulcanized without and with ultrasonic treatment at amplitude of 7.5, 10 and 13 μm. After extrusion, the devulcanized EPDM rubber was compounded with curatives using a two roll mill (Reliable Rubber & Plastic Machinery Co., North Bergen, NJ) with a gap size of 5 mm. A rotor speed of 20 rpm and a cooling water temperature of 40 °C were used. Then, it was crushed into particles using a grinder (Weima). The compounding recipe was as follows: 100 phr devulcanized EPDM rubber, 1 phr sulfur, 2 phr zinc oxide, 1 phr stearic acid, 0.75 phr TMTD and 0.375 phr MBT. Finally, PP/devulcanized EPDM blends of 75/25, 50/50 and 25/75 composition were physically mixed and then fed to the TSE using mixing screws at a flow rate of 8 g/min without imposition of ultrasound. The screw speed and zone temperature are same as in the OS method. The extrudates from extruders were then cooled, dried, finally crushed into particles using a pelletizer (Scheer Bay Company, Bay City, MI). The size of these particles was about 2 mm.
4.2.4 Molding

This section includes injection molding and compression molding, and the details are as follows.

4.2.4.1 Injection molding

For characterization, tensile samples for PP/EPDM blends at ratios of 75/25 and 50/50 were prepared by injection molding with a mini-jet injection molding machine (DSM Research B.V). A cylinder temperature of 200 °C and a mold temperature of 60 °C at a pressure of 6 MPa were used. The PP/EPDM blends obtained from the OS, TS and DR methods at a ratio of 25/75 cannot be prepared by injection molding due to the high viscosity.

4.2.4.2 Compression molding

For rheological characterization, specimens of pure PP and PP/EPDM blends were molded at 180 °C under a pressure of 25 MPa for 5 minutes using a compression molding press (Carver, Inc). The samples had a diameter of 25 mm and thickness of 2 mm. Besides, tensile samples for PP/EPDM blends obtained from the OS, TS and DR methods at a ratio of 25/75 were prepared by a compression - molding press (Carver, Wabash, IN) at 180 °C under pressure of 13.8 MPa with a mold of dimensions 90 mm x 60 mm x 1.5 mm.
4.2.5 Characterization methods

This section includes tensile tests, rheological tests, and morphological tests. The details are as follows.

4.2.5.1 Tensile tests

The tensile tests of pure PP and PP/EPDM blends were conducted by an Instron-5567 at room temperature at an elongation rate of 50 mm/min. An extensometer was not used. The tests were operated according to ASTM D638 standard.

4.2.5.2 Rheological tests

Small amplitude oscillatory shear (SAOS) test of the pure PP and PP/EPDM blends at ratios of 75/25 and 50/50 at a temperature of 180 °C was conducted by using a stress-controlled Discover Hybrid Rheometer (DHR-2, TA Instruments, New Castle, DE) equipped with 25 mm parallel plates. For PP/EPDM blends at a ratio of 75/25, the frequency sweep was in the range from 0.1 to 200 rad/s at a stress amplitude of 40 Pa. For PP/EPDM blends at a ratio of 50/50, the frequency sweep was in the range from 0.1 to 0.5 rad/s at a stress amplitude of 4 Pa, the frequency sweep was in the range from 0.5 to 10 rad/s at a stress amplitude of 10 Pa, and the frequency sweep was in the range from 10 to 200 rad/s at a stress amplitude of 40 Pa. It was confirmed that the stress amplitude is within the linear region. The rheological properties of PP/EPDM blends at ratio of 25/75 cannot be tested by DHR-2 due to the wall slip. The rheological properties of PP/EPDM blends at ratio of 25/75 can be achieved using the Advanced Polymer
Analyzer (APA 2000, Alpha Technologies, Akron, OH) at 180 °C with a strain amplitude of 4.2%, and within a frequency range from 0.01 rad/s to 200 rad/s.

4.2.5.3 Morphological tests

The size of original EPDM powder was observed using an optical transmission microscopy (Laborlux 12 POL S, Leitz Ltd., Midland, Ontario). The images were captured by a camera.

The phase morphology of PP/EPDM blends was observed using scanning electron microscopy (SEM, Hitachi S-1250). Etching technique was applied to extract PP phase because of the low contrast between EPDM and PP phases. The tensile samples from injection molding were fractured in liquid nitrogen. To remove the PP phase the samples were immersed in xylene at 90 °C for 30 minutes. Then, samples were dried at 70 °C for 12 hours in a vacuum. A sputter coater (K575X, Quorum Technologies, UK) was used to coat the surface with silver to provide the conductivity.

4.3 Results and discussion

This section includes die pressure, dynamic properties, mechanical properties and morphological tests.

4.3.1 Die pressure

The pressure measured in the die zone of PP/waste EPDM blends from twin screw extruder as a function of the ultrasonic amplitude is presented Figure 4.2 (a), (b) and (c) for OS, TS and DR methods, respectively. For the OS and TS methods, die pressure decreased with the increasing concentration of PP due to the lower viscosity of PP than
EPDM rubber, and reduced with an increase of the ultrasonic amplitude, which resulted in better processability of the melts. The decrease of the die pressure with amplitude is due to the degradation of PP and devulcanization of EPDM caused by the acoustic cavitation, shown in Figure 4.3. For the OS method (a), both of PP and EPDM were treated by ultrasound, so the degradation of PP due to the polymer chain scission and devulcanization of waste EPDM leading to the decreasing die pressure. For the TS method (b), devulcanization of waste EPDM led to the reduction of complex viscosity, which caused reduction of the die pressure. However, for the DR method (c), the die pressure increased with an increase of the ultrasonic amplitude. The reason is that during the dynamic revulcanization, sulfur generated the dense network in the EPDM phase of the blends leading to the higher complex viscosity. This is accordance with the results of measurements of the dynamic properties shown in Figure 4.5.
Figure 4.2 Die pressure as a function of ultrasonic amplitude of PP/EPDM blends prepared by the OS (a), TS (b) and DR (c) methods.
4.3.2 Dynamic properties

Figure 4.3 (a) shows the complex viscosity as a function of the frequency for pure PP, devulcanized EPDM and PP/EPDM blends at ratios of 75/25, 50/50 and 25/75, from TSE using the OS method. Firstly, the complex viscosity increased tremendously with increasing EPDM weight percentage. According to the earlier study, this occurs due to the higher viscosity of EPDM rubber than PP leading to the higher viscosity of PP/EPDM blends. This is in accordance with the die pressure trend shown in Figure 4.2 (a).

Secondly, it is seen that the complex viscosity of PP decreased with increasing ultrasonic amplitude, which is supportive evidence of the degradation of PP. Moreover, it is seen that the complex viscosity of PP/EPDM blends decreased with increasing ultrasonic amplitude at different weight ratios of PP/EPDM blends. The complex viscosity was affected by two factors: the devulcanization of EPDM and the degradation of PP. Specially, the complex viscosity of ultrasonically treated PP/EPDM blends at a ratio of 75/25 and at an amplitude of 13 μm decreased significantly. It was even lower than the complex viscosity of untreated pure PP. The storage modulus (Figure 4.3 (b)) and loss modulus (Figure 4.3 (c)) decreased dramatically at an amplitude of 13 μm for all ratios of PP/EPDM blends. The loss tangent (Figure 4.3 (d)) had largest value at an amplitude of 13 μm. According to the earlier study, these observations are due to higher ultrasonic amplitude leading to more devulcanization of EPDM and more degradation of PP. Both of the polymer degradation and ultrasonic devulcanization are considered to be induced by the ultrasonic cavitation.
Figure 4.3 Complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) at a function of the frequency for pure PP, devulcanized EPDM and PP/EPDM blends prepared by the OS method.
Figure 4.4 (a) depicts the complex viscosity as a function of the frequency for pure PP, pure EPDM and PP/EPDM blends of the ratios of 75/25, 50/50, 25/75 from TSE using the TS method. Firstly, the complex viscosity increased tremendously with increasing EPDM weight percentage due to the higher viscosity of EPDM rubber than pure PP leading to the higher viscosity of PP/EPDM blends. This is also in accordance with the die pressure trend shown in Figure 4.2 (b). Secondly, it is seen that the complex viscosity of PP/EPDM blends decreased with increasing ultrasonic amplitude at different weight ratios of PP/EPDM blends. However, at this time, the complex viscosity of blends is just dependent on one factor that is the devulcanization of EPDM because PP was not treated by ultrasound. Besides, the storage modulus (Figure 4.4 (b)) and loss modulus (Figure 4.4 (c)) decreased dramatically at an amplitude of 13 μm. The loss tangent (Figure 4.4 (d)) had largest value at an amplitude of 13 μm. These observations are due to higher ultrasonic amplitude leading to more devulcanization of EPDM, which is accordance with the gel fraction of devulcanized EPDM rubber shown in Figure 3.4 (a) and the storage modulus of devulcanized EPDM rubber shown in Figure 3.5. The ultrasonic devulcanization are considered to be induced by the ultrasonic cavitation.\textsuperscript{25,26}
Figure 4.4 Complex viscosity (a), storage moduli (b), loss moduli (c) and loss tangent (d) at a function of the frequency for pure PP, devulcanized EPDM and PP/EPDM blends prepared by the TS method.
Figure 4.5 (a) shows the complex viscosity as a function of the frequency for pure PP, devulcanized EPDM and PP/EPDM blends of the ratios of 75/25, 50/50 and 25/75 from TSE using the DR method. In this case, the complex viscosity still increased with increasing EPDM weight percentage because of the higher viscosity of EPDM rubber than pure PP causing the higher viscosity of PP/EPDM blends. However, unlike the OS and TS methods, at all different weight ratios of PP/EPDM blends, the complex viscosity increased with amplitudes at 10 and 13 μm. The storage modulus (Figure 4.5 (b)) and loss modulus (Figure 4.5 (c)) increased dramatically at an ultrasonic amplitude of 13 μm. The loss tangent (Figure 4.5 (d)) had lowest value at an ultrasonic amplitude of 13 μm. According to previous study, molecular transformations such as the formation of copolymer might occur during the dynamic revulcanization in the extrusion simultaneously with the generation of the dense network in the ultrasonically treated EPDM phase, which leading to an increase of viscosity. Also, compatibilization of PP/EPDM might lead to an increase of viscosity. Therefore, the relative contribution of these effects might define the final viscosity of these blends, and these effects are strongest at an amplitude of 13 μm due to the more devulcanization of EPDM rubber, shown in gel fraction (Figure 3.4 (a)) and crosslink density (Figure 3.4 (b)).
Figure 4.5 Complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) at a function of the frequency for pure PP, devulcanized EPDM and PP/EPDM blends prepared by the DR method.
Figure 4.6 shows the complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) as a function of the frequency for PP/EPDM blends of a ratio of 75/25 at the ultrasonic amplitudes of 0 μm and 13 μm from TSE using OS, TS and DR methods.

Firstly, at an ultrasonic amplitude of 0 μm, the complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the DR method was slightly higher than those of PP/EPDM blends using the TS method. The loss tangent of PP/EPDM blends using the DR method was slightly lower than that of PP/EPDM blends using the TS method. It can be explained that network generated by sulfur in the EPDM phase of the dynamically revulcanized PP/EPDM blends obtained from the DR method led to the better compatibilization between PP and EPDM rubber, which resulted in higher modulus, higher complex viscosity and lower loss tangent. The complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the OS method was lower than those of PP/EPDM blends using DR and TS methods. The loss tangent of PP/EPDM blends using the OS method was higher than that of PP/EPDM blends using the DR and TS methods. According to previous study,\(^{16}\) it can be explained that compatibilization between PP and EPDM rubber using the DR and TS methods might be better than that between PP and EPDM rubber using the OS method, which resulted in the lower modulus and viscosity of PP/EPDM blends using the OS method.

Secondly, at an amplitude of 13 μm, the complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the DR method was higher than those of PP/EPDM blends using the TS method. The loss tangent of PP/EPDM blends using the DR method was lower than that of PP/EPDM blends using the TS method. According to earlier
study, it can be explained that molecular transformations such as the formation of copolymer might occur during the dynamic revulcanization in the extrusion simultaneously with the generation of dense network in the EPDM phase of dynamically revulcanized PP/EPDM blends, while compatibilization between PP and EPDM rubber also might lead to an increase of modulus and viscosity of PP/EPDM blends using the DR method. Also, from morphology study shown in Figure 4.17 (b) and Figure 4.18 (b), the size of EPDM particles in PP/EPDM blends using the DR method was much smaller than that of EPDM particles in PP/EPDM blends using the TS method leading to the higher modulus and higher viscosity of PP/EPDM blends using the DR method. The complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the TS method was higher than those of PP/EPDM blends using the OS method. The loss tangent of PP/EPDM blends using the TS method was lower than that of PP/EPDM blends using the OS method. This is due to the degradation of PP in PP/EPDM blends using the OS method, but the degradation did not occur in the TS method because PP was not treated by the ultrasound.
Figure 4.6 Complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) at a function of the frequency for PP/EPDM 75/25 blends prepared by the OS, TS and DR methods.
Figure 4.7 shows the complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) as a function of the frequency for PP/EPDM blends of a ratio of 50/50 at the ultrasonic amplitudes of 0 μm and 13 μm from TSE using OS, TS and DR methods.

Firstly, at an ultrasonic amplitude of 0 μm, the complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the DR method was slightly higher than those of PP/EPDM blends using the TS method, and the loss tangent of PP/EPDM blends using the DR method was slightly lower than that of PP/EPDM blends using the TS method. It can be explained that sulfur generated network in the EPDM phase of the dynamically revulcanized PP/EPDM blends leading to the better compatibilization between PP and EPDM rubber, which resulted in higher modulus, higher complex viscosity and lower loss tangent. The complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the OS method was lower than those of PP/EPDM blends using DR and TS methods. The loss tangent of PP/EPDM blends using the OS method was higher than that of PP/EPDM blends using the DR and TS methods. According to previous study,\textsuperscript{16} it can be explained that compatibilization between PP and EPDM rubber using the DR and TS methods might be better than that between PP and EPDM rubber using the OS method, which resulted in the lower modulus and viscosity of PP/EPDM blends using the OS method.

Secondly, at an amplitude of 13 μm, the complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the DR method was higher than those of PP/EPDM blends using the TS method. The loss tangent of PP/EPDM blends using the DR method was lower than that of PP/EPDM blends using the TS method. According to earlier
study,\textsuperscript{17} it can be explained that molecular transformations such as the formation of copolymer might occur during the dynamic revulcanization in the extrusion simultaneously with the generation of dense network in the EPDM phase of dynamically revulcanized PP/EPDM blends, while compatibilization between PP and EPDM rubber also might lead to an increase of modulus and viscosity of PP/EPDM blends using the DR method. Also, from morphology study shown in Figure 4.17 (b) and Figure 4.18 (b), the size of EPDM particles in PP/EPDM blends using the DR method was much smaller than that of EPDM particles in PP/EPDM blends using the TS method leading to the higher modulus and higher viscosity of PP/EPDM blends using the DR method. The complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the TS method was higher than those of PP/EPDM blends using the OS method. The loss tangent of PP/EPDM blends using the TS method was lower than that of PP/EPDM blends using the OS method. This is due to the degradation of PP in PP/EPDM blends using the OS method, but the degradation did not occur in the TS method because PP was not treated by the ultrasound.
Figure 4.7 Complex viscosity (a), storage moduli (b), loss moduli (c) and loss tangent (d) as a function of the frequency for PP/EPDM 50/50 blends prepared by the OS, TS and DR methods.
Figure 4.8 shows the complex viscosity (a), storage modulus (b), loss modulus (c) and loss tangent (d) as a function of the frequency for PP/EPDM blends of a ratio of 25/75 at the ultrasonic amplitudes of 0 μm and 13 μm from TSE using OS, TS and DR methods.

Firstly, at an ultrasonic amplitude of 0 μm, the complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the DR method was slightly higher than those of PP/EPDM blends using the TS method. The loss tangent of PP/EPDM blends using the DR method was slightly lower than that of PP/EPDM blends using the TS method. It can be explained that sulfur generated network in the EPDM phase of the dynamically revulcanized PP/EPDM blends leading to the better compatibilization between PP and EPDM rubber, which resulted in higher modulus, higher complex viscosity and lower loss tangent. The complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the OS method was lower than those of PP/EPDM blends using DR and TS methods. The loss tangent of PP/EPDM blends using the OS method was higher than that of PP/EPDM blends using the DR and TS methods. According to previous study,\(^\text{16}\) it can be explained that compatibilization between PP and EPDM rubber using the DR and TS methods might be better than that between PP and EPDM rubber using the OS method, which resulted in the lower modulus and viscosity of PP/EPDM blends using the OS method.

Secondly, at an amplitude of 13 μm, the complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the DR method was higher than those of PP/EPDM blends using the TS method. The loss tangent of PP/EPDM blends using the DR method was lower than that of PP/EPDM blends using the TS method. According to earlier
study\textsuperscript{17}, it can be explained that molecular transformations such as the formation of copolymer might occur during the dynamic revulcanization in the extrusion simultaneously with the generation of dense network in the EPDM phase of dynamically revulcanized PP/EPDM blends, while compatibilization between PP and EPDM rubber also might lead to an increase of modulus and viscosity of PP/EPDM blends using the DR method. Also, from morphology study shown in Figure 4.17 (b) and Figure 4.18 (b), the size of EPDM particles in PP/EPDM blends using the DR method was much smaller than that of EPDM particles in PP/EPDM blends using the TS method leading to the higher modulus and higher viscosity of PP/EPDM blends using the DR method. The complex viscosity, storage modulus and loss modulus of PP/EPDM blends using the TS method was higher than those of PP/EPDM blends using the OS method, and the loss tangent of PP/EPDM blends using the TS method was lower than that of PP/EPDM blends using the OS method. This is due to the degradation of PP in PP/EPDM blends using the OS method, but the degradation did not occur in the TS method because PP was not treated by the ultrasound.
Figure 4.8 Complex viscosity (a), storage moduli (b), loss moduli (c) and loss tangent (d) at a function of the frequency for PP/EPDM 25/75 blends prepared by the OS, TS and DR methods.
4.3.3 Mechanical properties

Figure 4.9 shows the tensile stress – strain curves of PP/EPDM blends at ratios of 75/25 (a), 50/50 (b) and 25/75 (c) manufactured at different ultrasonic amplitudes by the OS method from TSE. Figure 4.10 indicates the elongation at break (a), tensile strength at break (b) Young’s modulus (c) at a function of the ultrasonic amplitude for PP/EPDM blends of different ratios. The Young’s modulus was not affected by an increase of the ultrasonic amplitude at three different ratios of PP/EPDM. The elongation at break and tensile strength decreased with an increase of the ultrasonic amplitude at three different ratios of PP/EPDM. The mechanical properties of PP/EPDM blends at an amplitude of 13 μm were poorest. This is because the complex viscosity of PP/EPDM blends was lowest at an amplitude of 13 μm shown in Figure 4.3, which resulted in the coalescence of EPDM in the PP phase during the extrusion. The coalescence of EPDM led to the agglomerates of EPDM in the PP phase shown below in the section on morphology (Figure 4.16 (b)). The agglomerates led to the poor dispersion of EPDM in the PP phase resulting in the poor mechanical properties. According to earlier study,\textsuperscript{18} Kim et al. compounded PP with ultrasonically treated waste EPDM rubber at a ratio of 25/75. The mechanical properties of the ultrasonically treated PP/waste EPDM decreased due to the low chemical interaction at the interface and poor adhesion between waste EPDM and PP.
Figure 4.9 The stress-strain curves of PP/EPDM 75/25 (a), 50/50 (b) and 25/75 (c) blends prepared at different ultrasonic amplitudes by the OS method.
Figure 4.10 Elongation at break (a), tensile strength (b) and Young’s modulus (c) as a function of the ultrasonic amplitude for PP/EPDM blends prepared by the OS method.
Figure 4.11 shows the tensile stress – strain curves of PP/EPDM blends at ratios of 75/25 (a), 50/50 (b) and 25/75 (c) manufactured at different ultrasonic amplitudes by the TS method from TSE. Figure 4.12 indicates the elongation at break (a), tensile strength at break (b) Young’s modulus (c) at a function of the ultrasonic amplitude for PP/EPDM blends of different ratios. The modulus was unchanged with an increase of the ultrasonic amplitude at three different ratios of PP/EPDM. The elongation at break and tensile strength were decreased for all treated samples. This is because the complex viscosity of PP/EPDM blends decreased for treated samples as shown in Figure 4.4, which resulted in the coalescence of EPDM in the PP phase during the extrusion. The coalescence of EPDM led to the agglomerates of EPDM in the PP phase as shown below in the section on morphology (Figure 4.17 (b)). The agglomerates led to the poor dispersion of EPDM in the PP/EPDM blends resulting in the poor mechanical properties. Kim et al.\textsuperscript{18} compounded PP with ultrasonically treated waste EPDM rubber at a ratio of 25/75. The size of original waste EPDM powder used in the Kim’s research was much smaller than that used in the present study. In Kim’s study, the size of original waste EPDM powder ranged from 5 to 20 μm, but in the present study the size of original waste EPDM powder ranged from 150 to 250 μm shown in the Figure 4.15. The smaller EPDM particles led to the good dispersion of EPDM particles in the PP phase, which resulted in the higher elongation at break and higher tensile strength. Thus, in Kim’s research, the elongation at break of the PP/waste EPDM blends decreased from 300% to 150% with the increasing ultrasonic amplitude and the tensile strength decreased from 12 MPa to 5 MPa with the increasing ultrasonic amplitude due to the low chemical interaction at the interface and poor adhesion between waste EPDM and PP according to Kim’s
explanation. In the present study, the elongation at break of the PP/waste EPDM blends at a ratio of 25/75 decreased from 130% to 50% with the increasing ultrasonic amplitude, and the tensile strength decreased from 7 MPa to 4 MPa with the increasing ultrasonic amplitude due to the agglomeration of EPDM particles in the PP phase.
Figure 4.11 The stress-strain curves of PP/EPDM 75/25 (a), 50/50 (b) and 25/75 (c) blends prepared at different ultrasonic amplitudes by the TS method.
Figure 4.12 Elongation at break (a), tensile strength (b) and Young’s modulus (c) as a function of different ultrasonic amplitudes for PP/EPDM blends prepared by the TS method.
Figure 4.13 shows the tensile stress–strain curves of PP/EPDM blends at ratios of 75/25 (a), 50/50 (b) and 25/75 (c) manufactured at different ultrasonic amplitudes by the DR method from TSE. Figure 4.14 indicates the elongation at break (a), tensile strength at break (b) Young’s modulus (c) at a function of the ultrasonic amplitude for PP/EPDM blends of different ratios. The elongation at break of PP/EPDM blends at different ratios increased with increasing ultrasonic amplitude. The tensile strength of PP/EPDM blends at ratios of 75/25 and 50/50 increased with increasing ultrasonic amplitude. According to previous study,¹⁷ molecular transformations such as the formation of copolymer might occur during the dynamic revulcanization in the extrusion simultaneously with the generation of the dense network in the ultrasonically treated EPDM phase. It is believed that the copolymer was formed at the interface of two phases, which reduced interfacial tension between the two components and improved the mechanical properties. This compatibilization between PP and EPDM rubber led to good dispersion of EPDM rubber creating smaller sizes of EPDM particles in the PP phase during dynamic revulcanization as shown in Figure 4.18 (b). Also, for PP/EPDM blends at a ratio of 25/75, the tensile strength slightly decreased with increasing ultrasonic amplitude, while the elongation at break slightly increased and the Young’s modulus was slightly decreased with increasing ultrasonic amplitude due to the higher sol fraction of devulcanized EPDM rubber at an amplitude of 13 μm as shown in Figure 3.4 (a).
Figure 4.13 The stress-strain curves of PP/EPDM 75/25 (a), 50/50 (b) and 25/75 (c) blends prepared at different ultrasonic amplitudes by the DR method.
Figure 4.14 Elongation at break (a), tensile strength (b) and Young’s modulus (c) as a function of ultrasonic amplitude for PP/EPDM blends prepared by the DR method.
4.3.4 Morphological tests

Figure 4.15 shows the micrograph of original waste EPDM powder of 40 meshes obtained by the optical transmission microscopy. It indicates that the diameter of the EPDM powder ranges from 100 μm to 250 μm. Figure 4.16 shows the SEM micrographs of 50/50 PP/EPDM blends from TSE using the OS method without (a) and with ultrasonic treatment at amplitudes of 13 μm (b). Firstly, it can be observed from Figure 4.16 that particles in blends are much smaller than these of the original EPDM powder. This is because of the fact that the EPDM rubber underwent devulcanization during the extrusion. It is noteworthy that there are some agglomerates of EPDM in the 50/50 PP/EPDM blends treated at an amplitude of 13 μm. It can be explained that this high ultrasonic amplitude led to a lower viscosity causing the coalescence of the EPDM particles during the extrusion. The formation of these agglomerates led to the poor mechanical properties. Similar effect is seen for 50/50 PP/EPDM blends from TSE using the TS method without treatment and with ultrasonic treatment at amplitudes of 13 μm. This is seen in Figure 4.17 (a) and (b). The SEM micrographs of 50/50 PP/EPDM blends from TSE using the DR method without treatment (a) and with ultrasonic treatment at an amplitude of 13 μm (b), are presented in Figure 4.18. One can observe in Figure 4.18 (b) that EPDM rubber particles of blends under an amplitude of 13 μm exhibit much smaller sizes and are better distributed in the PP matrix. Accordingly, the mechanical properties of these blends obtained by the DR method achieved the highest improvement in mechanical properties, as shown in Figure 4.14.
Figure 4.15 Optical micrographs of original EPDM powder.
Figure 4.16 SEM micrographs of PP/EPDM 50/50 blends without (a) and with ultrasonic treatment at an amplitude of 13 μm (b) prepared by the OS method.

Figure 4.17 SEM micrographs of PP/EPDM 50/50 blends without (a) and with ultrasonic treatment at an amplitude of 13 μm (b) prepared by the TS method.

Figure 4.18 SEM micrographs of PP/EPDM 50/50 blends without (a) and with ultrasonic treatment at an amplitude of 13 μm (b) prepared by the DR method.
4.4 Conclusion

Compounding PP with waste EPDM using ultrasonically aided extrusion was carried out. The effect of (1) PP/waste EPDM mixing ratio, (2) type of compounding methods, (3) ultrasonic amplitude were considered. The one step (OS), two step (TS) methods and the dynamic revulcanization (DR) method were applied by using an ultrasonic twin screw extruder at ultrasonic amplitudes varying from 0 to 13 μm. PP and waste EPDM were compounded at ratios of 75/25, 50/50, and 25/75. In the OS method PP and waste EPDM particles were compounded in the extruder with and without ultrasonic treatment. In the TS and DR methods the waste EPDM particles were fed into the extruder and devulcanized without and with ultrasonic treatment. Then, in the TS method devulcanized EPDM was compounded with PP in the extruder without imposition of ultrasound. In the DR method, devulcanized EPDM after compounding with curatives was mixed with PP and dynamically revulcanized in the extruder without imposition of ultrasound. It is noteworthy that in the DR method, the mechanical properties of PP/EPDM blends increased with the increasing ultrasonic amplitude possibly due to the formation of copolymer, compatibilization between PP and EPDM rubber and good dispersion of EPDM particles in PP phase. In particular, the tensile strength of 30 MPa and the elongation at break of 400% were achieved at an amplitude of 13 μm for the PP/EPDM blend at ratio of 75/25. However, in the OS and TS methods, the mechanical properties of PP/EPDM blends decreased with the increasing ultrasonic amplitude due to the coalescence of devulcanized EPDM particles leading to the presence of agglomerates of EPDM particles in PP phase. These findings were supported by SEM studies of various blends. In the DR method, the complex viscosity increased with the increasing
ultrasonic amplitude due to the dense network in the EPDM phase of the PP/EPDM blends and the formation of copolymer. In the OS method, the complex viscosity decreased with the ultrasonic amplitude due to the degradation of PP and devulcanization of EPDM. In the TS method, the complex viscosity decreased with the ultrasonic amplitude due to the devulcanization of EPDM.
CHAPTER V

SUMMARY

Devulcanization of waste EPDM was carried out by using TSE containing kneading and conveying screws without and with ultrasonic treatment at various ultrasonic amplitudes. The gel fraction and dynamic properties of devulcanized EPDM rubber, and the gel fraction, crosslink density, mechanical properties and dynamic properties of revulcanized EPDM rubber were measured. The higher efficiency of kneading screws in devulcanization was observed due to higher pressure generated by the presence of kneading elements. Also, it was found that higher ultrasonic amplitudes generally led to more devulcanization improving mechanical properties of revulcanizates. Among various samples, the revulcanizates prepared from devulcanized EPDM obtained at an ultrasonic amplitude of 13 μm showed highest performance with the tensile strength of 9 MPa and the elongation at break of 200%. However, this revulcanizate showed a lower modulus at 100% elongation in comparison with those revulcanizates obtained at lower amplitude. The lowest complex viscosity of ultrasonically treated EPDM rubber was obtained at an ultrasonic amplitude of 13. This correlated with the lowest gel fraction and the lowest minimum and maximum curing torque upon revulcanization of the devulcanized EPDM rubber. It was found that ultrasonic amplitude did not affect the induction time during revulcanization. Compounding PP with waste EPDM using ultrasonically aided extrusion was carried out. The effect of (1) PP/waste EPDM mixing ratio, (2) type of compounding
methods, (3) ultrasonic amplitude were considered. The one step (OS), two step (TS) methods and the dynamic revulcanization (DR) method were applied by using an ultrasonic twin screw extruder at ultrasonic amplitudes varying from 0 to 13 \( \mu \text{m} \). PP and waste EPDM were compounded at ratios of 75/25, 50/50, and 25/75. In the OS method PP and waste EPDM particles were compounded in the extruder with and without ultrasonic treatment. In the TS and DR methods the waste EPDM particles were fed into the extruder and devulcanized without and with ultrasonic treatment. Then, in the TS method devulcanized EPDM was compounded with PP in the extruder without imposition of ultrasound. In the DR method, devulcanized EPDM after compounding with curatives was mixed with PP and dynamically revulcanized in the extruder without imposition of ultrasound. It is noteworthy that in the DR method, the mechanical properties of PP/EPDM blends increased with the increasing ultrasonic amplitude possibly due to the formation of copolymer, compatibilization between PP and EPDM rubber and good dispersion of EPDM particles in PP phase. In particular, the tensile strength of 30 MPa and the elongation at break of 400% were achieved at an amplitude of 13 \( \mu \text{m} \) for the PP/EPDM blend at ratio of 75/25. However, in the OS and TS methods, the mechanical properties of PP/EPDM blends decreased with the increasing ultrasonic amplitude due to the coalescence of devulcanized EPDM particles leading to the presence of agglomerates of EPDM particles in PP phase. These findings were supported by SEM studies of various blends. In the DR method, the complex viscosity increased with the increasing ultrasonic amplitude due to the dense network in the EPDM phase of the PP/EPDM blends and the formation of copolymer. In the OS method, the complex viscosity decreased with the ultrasonic amplitude due to the degradation of PP and
devulcanization of EPDM. In the TS method, the complex viscosity decreased with the ultrasonic amplitude due to the devulcanization of EPDM.
REFERENCES


