A PRELIMINARY DISCOURSE ON TUNABLE ROLLING RESISTANCE OF ELECTRORHEOLOGICAL FLUID REINFORCED POLYMER COMPOSITES

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements of the Degree

Doctor of Philosophy

Shuwen Chen

December, 2015
A PRELIMINARY DISCOURSE ON TUNABLE ROLLING RESISTANCE OF
ELECTRORHEOLOGICAL FLUID REINFORCED POLYMER COMPOSITES

Shuwen Chen
Dissertation

Approved:

Advisor
Dr. Shing-Chung Josh Wong

Committee Member
Dr. Xiaosheng Gao

Committee Member
Dr. Gregory N. Morscher

Committee Member
Dr. Ernian Pan

Accepted:

Department Chair
Dr. Sergio Felicelli

Interim Dean of the College
Dr. Mario R. Garzia

Dean of the Graduate School
Dr. Chand K. Midha

Date

Committee Member
Dr. Darrell H. Reneker
ABSTRACT

Rolling resistance contributes to 6-10% of the overall fuel consumption of vehicles. In order to enable future smart tire technology, rolling resistance needs to be responsible for environmental conditions. Materials with smart property are fabricated by composing smart filler.

In this research, a laboratory-scale pendulum-acoustic emission device is adopted to evaluate the rolling resistance coefficients and normalized damping for selected materials. At first, fibrous electrospun membranes (polyvinylidene fluoride, polycaprolactone and nylon 6) and different substrates were tested. As substrates, asphalt and rubber consistently give rise to the higher rolling resistance and the shorter damping time, while electrospun membranes produce the lower rolling resistance and the longer damping time. Electrospun polymer fabrics appeared to provide a tuning opportunity for changing the rolling resistance. From the test results, there has consistently positive correlation between elastic modulus and rolling resistance. For these four types of polymer electrospun membrane, the mechanical properties are studied.

Electrorheological fluid (ERF) is well known as solid-fluid transform under the effect of electrical voltage. It is used as a smart filler to reinforce silicon rubber and electrospun polymer membrane. Scanning Electron Microscope (SEM), Atomic Force Micrograph (AFM) and Energy Dispersive X-ray Spectroscopy (EDX) are utilized to
examine the incorporation of ERF in the silicon rubber and surface morphology. For the ERF reinforced silicon rubber composite, we prepared a series of composites with different ERF/rubber ratio and vulcanization voltages. The effect of different ERF concentrations is investigated. The obtained smart ERF reinforced silicone rubber composites show tunable coefficients of rolling resistance against external electric field. We also study the mechanical properties and surface characteristics of smart composites under different vulcanized conditions. Two classical rubber constitutive models: Mooney-Rivlin model and Ogden model are adopted to understand the mechanical behavior of ERF reinforced rubber. The interaction of mechanical properties and rolling resistance of the studied smart composite system is discussed.

For the ERF reinforced polymer electrospun membranes, we propose a co-electrospinning technology to prepare electrorheological fluid (ERF)/fabrics membranes composite. A wood-pendulum acoustic-emission device is used to evaluate the rolling resistance of ERF/fabrics membranes composite. Two different co-electrospinning smart composite systems are studied: ERF/PVDF and ERF/PCL. The tunable rolling resistance behavior of this smart composite system is studied through testing under different external electrical field. The surface morphology is also examined to further understand its interaction between rolling resistance.
ACKNOWLEDGEMENTS

I would like to express my appreciation to my advisor Dr. Shing-Chung Wong for his valuable guidance and continuously support throughout my graduate studies. He provided me with so many precious opportunities and experience to wide my vision, and which directed me to approach my long-term career goals.

I would also like to thank my graduate committee members: Dr. Xiaosheng Gao and Dr. Gregory N. Morscher from Mechanical Engineering, Dr. Ernian Pan from Civil Engineering, and Dr. Darrell Reneker from Polymer Science for their valuable time and advice. I am also thankful to Dr. Avraam I. Isayev for his helpful comments about my dissertation proposal.

I really want to thank Dr. Xiaomin Zhang and Dr. Haining Na for their help and suggestions on my graduate studying. Special thanks are also given to my fellow graduate students Guang Ji, Vishal Bhimrao Zade, Omar Ali Blandón, Yanfeng Lu, and Yanfei Zhao, for their help and friendship.

My deepest grateful goes to my family, especially Chao Zhang, for their continuous love and support during the journey. Unparalleled thanks dedicate to my boy, Kevin Zhang, you are giving me so much surprises to make my life colorful and huge power to complete my study.
TABLE OF CONTENTS

Page

LIST OF FIGURES .................................................................................................................. x

LIST OF TABLES ...................................................................................................................... xi

CHAPTER

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

  1.1 Background ...................................................................................................................... 1

  1.2 Introduction ..................................................................................................................... 3

II. LITERATURE REVIEW ......................................................................................................... 4

  2.1 Tire history and structure ................................................................................................. 4

    2.1.1 The history of natural rubber ................................................................................ 4

    2.1.2 Rubber Elasticity ..................................................................................................... 5

    2.1.3 Rubber in tire application ....................................................................................... 8

    2.1.4 Tire Structure .......................................................................................................... 9

    2.1.5 Tire functions ......................................................................................................... 12

    2.1.6 Magic triangle in tire performance ....................................................................... 12

  2.2 Filler reinforcement rubber in tire application ............................................................... 17

    2.2.1 Classification of filler as reinforcement ................................................................. 22

    2.2.2. Filler reinforce rubber mechanisms ................................................................. 26

    2.2.3 Improvement the tire rubber properties by adding fillers ................................. 28
2.3 Smart tire ........................................................................................................... 35
2.4 ER fluids ............................................................................................................ 39
   2.4.1 ER fluids concept ....................................................................................... 39
   2.4.2 ER preparation .......................................................................................... 40
   2.4.3 ER mechanism .......................................................................................... 40
   2.4.4 ER application ......................................................................................... 42
   2.4.5 ER properties ............................................................................................ 43
2.5 Electrospinning Technology .............................................................................. 44
   2.5.1 Development of electrospinning ............................................................... 48
   2.5.2 Key parameters of electrospinning ............................................................ 52
   2.5.3 Potential applications for electrospun fibers .......................................... 59
2.6 Rolling resistance test method in industry ....................................................... 65
2.7 Summary and considerations of research plan .............................................. 68

III. A STUDY OF ROLLING RESISTANCE OF ELECTROSPUN POLYMER FABRICS ........................................................... 71

3.1 Objectives ......................................................................................................... 71
3.2 Introduction ....................................................................................................... 71
3.3 Experiment ....................................................................................................... 73
   3.3.1 Materials .................................................................................................. 73
   3.3.2 Preparation of the electrospun membranes ............................................. 76
   3.3.3 Characterization of electrospun fibers ..................................................... 78
3.4 Summary and discussion .................................................................................. 83
   3.4.1 Effect of polymer properties to fiber diameter and morphology ............ 83
3.4.2 Effect of polymer type on mechanical property by tensile test.........85
3.4.3 Effect of substrate type on rolling resistance..................................88
3.4.4 Effect of substrate type on non-dimensional damping factor ..........90
3.5 Industry process design in new tire generation (Wong 2013).............93
3.6 Conclusions.............................................................................................102

IV. TUNABLE ROLLING RESISTANCE FOR ELECTRORHEOLOGICAL FLUID REINFORCED SILICON RUBBER COMPOSITES..............................103
4.1 Objectives ................................................................................................103
4.2 Experiment..................................................................................................104
  4.2.1 Materials ..............................................................................................104
  4.2.2 Preparation of the silicon rubber/ERF composites .........................105
  4.2.3 Characterization of silicon rubber/ERF composites .......................106
4.3 Results and discussion ............................................................................111
  4.3.1 Effect of ER Fluid in silicon rubber on the morphology ...............111
  4.3.2 Mechanical properties of ER fluid reinforced rubber ....................117
  4.3.3 Constitutive model of ERF reinforced silicon rubber composite ......123
  4.3.4 Rolling resistance of ER fluid reinforced rubber .........................131
4.4 Conclusion ................................................................................................135

V. TUNABLE ROLLING RESISTANCE OF ELECTROSPUN FABRIC/ELECTRORHEOLOGICAL FLUID SMART COMPOSITES SYSTEM ............137
5.1 Objectives ................................................................................................137
5.2 Experiment................................................................................................137
  5.2.1 Materials ..............................................................................................138
5.2.2 Preparation of ERF/electrospun membranes by co-electrospinning... 138
5.2.3 SEM Characterization................................................................. 141
5.2.4 EDS Characterization................................................................. 141
5.2.5 Rolling resistance measurement ................................................. 141
5.3 Results and Discussion ................................................................. 142
  5.3.1 Effect of ER Fluid on the morphology of ERF/fabrics membranes ... 143
  5.3.2 Effect of ER Fluid on the rolling resistance of ERF/fabrics membranes ................................................................. 146
5.4 Conclusions.................................................................................. 150

VI. SUMMARY AND FUTURE WORK..................................................... 152
  6.1 Conclusions.................................................................................. 152
  6.2 Suggestion for future work .......................................................... 155

REFERENCES ..................................................................................... 157
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic diagram of an ensemble of linear polymer chains being crosslinked into an infinite network (Shaw, Montgomery T, 2005)</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic modulus-temperature curve showing various regions of viscoelastic behavior (Deniz KAYA, 2012)</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>A cross-section of a tire showing ply orientations (Philips)</td>
<td>11</td>
</tr>
<tr>
<td>2.4</td>
<td>Friction, rolling resistance and drag on different road types (part20 webpage)</td>
<td>15</td>
</tr>
<tr>
<td>2.5</td>
<td>Scheme of tire wet grip on road surface</td>
<td>16</td>
</tr>
<tr>
<td>2.6</td>
<td>Young’s modulus of rubbers containing MT carbon black as a function of contration. (Mullins, La 1965)</td>
<td>19</td>
</tr>
<tr>
<td>2.7</td>
<td>Stress-softening of natural rubber filled with MPC carbon black (Mullins effect). Numerals indicate the stress-strain cycles. (Bueche, F. 1960)</td>
<td>21</td>
</tr>
<tr>
<td>2.8</td>
<td>Three typical chains attached to two adjacent filler particle. (Bueche, F. 1960)</td>
<td>21</td>
</tr>
<tr>
<td>2.9</td>
<td>Classification of fillers based on the size of the primary filler particle (Klüppel 1997)</td>
<td>22</td>
</tr>
<tr>
<td>2.10</td>
<td>Relevant dimensions in rubber-filler interactions (Leblanc 2002)</td>
<td>23</td>
</tr>
<tr>
<td>2.11</td>
<td>Parameters contributing to shear modulus (a) Carbon black filled rubber; (b) Silica filled rubber (Coran, A. Y. 1992)</td>
<td>24</td>
</tr>
<tr>
<td>2.12</td>
<td>The principle of “chemical reinforcement” by coupling agent in rubber</td>
<td>26</td>
</tr>
<tr>
<td>2.13</td>
<td>Schematic illustration of the rubber -based strain sensor</td>
<td>37</td>
</tr>
</tbody>
</table>
2.14 The structural evolution of dielectric microspheres under an increasing electric field, from (a) no field, to (b) a moderate field of 500 V mm\(^{-1}\), to (c) a strong field of 900 V mm\(^{-1}\). Here the ER fluid consists of 1.5 micron glass spheres suspended in silicone oil (Wen 2008). ................................................................. 39

2.15 (a) A schematic of electrospinning station; (b) polymer nonwoven produced by electrospinning. .................................................. 46

2.16 Instability region in an electrified PEO-water jet (left); A trace of the jet in the entire instability region (right). (Shin, Y. M. 2001) ............ 47

2.17 Experimental setup used for co-electrospinning of compound core-shell nanofibers (left) and TEM of co-electrospun PEO as shell and PDT as core (right) (Sun Zaicheng 2003) ................................. 48

2.18 Schematic of co-electrospinning of PMMA/PNA using a single nozzle (left up); Optical appearance of as-spun core-shell microfibers (left bottom); Optical image of PMMA/PAN emulsion (right up); The issuance of a jet containing multiple stretched PMMA/DMF droplets in PAN/DMA matrix(right bottom) ................................. 49

2.19 Schematic of setup for electrospinning used to generate uniaxially aligned nanofibers (left); The orientation of PVP nanofibers on a collector containing a gap in middle (right) ...................... 50

2.20 Schematic electrospinning setup for collection continuous aligned fibers (left up); A yarn of fibers is formed between the needles and a rotating aluminum shaft (left bottom); Well-aligned PVA fibers collected on a Teflon tube with different surface velocity 1.3 m/s (right up) and 2.3 m/s (right bottom). ........................................ 51

2.21 Experimental setup for electrospinning with a collector can be moved linearly parallel (left); SEM pictures of aligned polystyrene fibers are parallel to each other with distance with stable range (right). ........... 51

2.22 Apparatus for rotating the copper wire drum (left upper); Electrospun fibers collected on the copper wires (right upper); SEM images of axially aligned fibers (bottom) .................................................. 52

2.23 Variation of beaded fibers as net charge density changes due to the addition of NaCl (Fong H. 1999) ................................. 54

2.24 SEM images of PDLA membranes fabricated by electrospinning of a 30 wt% solution at voltage of 20 kV, feeding rate of 20 μm/min and with 1 wt% of (A) KH\(_2\)PO\(_4\); (B)NaH\(_2\)PO\(_4\). .................................................. 55

2.25 SEM micrographs of porous PLLA fibers obtained via electrospinning of a solution of PLLA in dichloromethane............. 56
2.26 Mean diameter of electrospun type I collagen as a function of (a) collagen concentration and (b) voltage

2.27 SEM micrographs of electrospun PVC fibers as a function of the tip-to-collector distance: (a) 6, (b) 10, and (c) 15cm.

2.28 Wicking experiment of PVDF/PVA microtubule with silicone oil. The schematic of wicking test (bottom left) shows one end of the PVDF/PVA microtubule soaked into silicone oil and the other end in open air. Optical micrograph shows the meniscus (arrows) of the silicone oil rises (top half) due to capillary action. The wicking process is recorded as a function of time (s) (bottom right plot).

2.29 FESEM micrographs of PVDF membrane: (a) before separation, (b) after 10 μm, (c) after 5 μm, and (d) after 1 μm separation.

2.30 Surface modification techniques of electrospun nanofibers. (A) Plasma treatment or wet chemical method. (B) Surface graft polymerization. (C) Co-electrospinning.

2.31 A schematic representation of the generated thread (left); Characteristic photomicrographs of collected cells cultured over an incubation period of 9 days (right).

2.32 Potential applications of electrospun polymer nanofibers. (Huang Zheng-Ming 2003)

2.33 Typical test configuration for rolling resistance measurement (NHTSA, 2006)

2.34 Force method rolling resistance test method (NHTSA, 2006)

2.35 Schematic of rolling resistance test

3.1 Repeat unit of Polyvinylidene fluoride

3.2 Repeat unit in PCL structure

3.3 Nylon 6 structure

3.4 Electrospinning setup in laboratory

3.5 Scanning electron microscope

3.6 Mechanical property of electrospun fabrics is performed by Instron 5582 machine equipped with a 500 N load cell

3.7 The shape of each sample used for tensile test in research

3.8 Rolling resistance measurement setup

3.9 Collection data from Figure 3.8
| 3.10 | Rolling resistant test on different substrate | 82 |
| 3.11 | SEM micrographs of electrospun PCL fibers at 0.16g/ml solution concentration | 83 |
| 3.12 | SEM micrographs of electrospun PVDF fibers at solutions concentration of (a) 0.15 g/ml as PVDF1 (b) 0.17 g/ml as PVDF2... | 84 |
| 3.13 | SEM micrographs of electrospun nylon 6 fibers at 0.4g/ml solution concentration | 84 |
| 3.14 | Fiber diameter distributions of electrospun PCL (a), PVDF1 (b), PVDF2 (c) and nylon 6 (d) nonwoven mats from SEM images | 85 |
| 3.15 | Representatives stress-strain curves of electrospun polymer membranes | 85 |
| 3.16 | SEM of electrospun membrane PCL (a1, a2), PVDF1 (b1, b2), PVDF2 (c1, c2) and nylon 6 (d1, d2) before and after the tensile test... | 87 |
| 3.17 | Rolling resistance coefficient | 89 |
| 3.18 | The effect of elastic modulus to the rolling resistance coefficient in polymer electrospun membrane on different substrate | 90 |
| 3.19 | Damped oscillations of pendulum | 91 |
| 3.20 | Non-dimensional damping | 92 |
| 3.21 | Non-dimensional damping and natural frequency | 93 |
| 3.22 | A general schematic of an exemplary method of creating a polymeric article in accordance, employing a fabric to receive electrorheological fluid | 95 |
| 3.23 | A general schematic of an exemplary method of creating | 96 |
| 3.24 | A general schematic of an exemplary method of creating a polymeric article in employing chopped fibers to be immersed in electrorheological fluid | 97 |
| 3.25 | The polymer fibers made by melt spinning will be guided into ERF bath, then ERF impregnated polymer fiber will be wound into a tow... | 98 |
| 3.26 | A general schematic representation of the application of this invention in a tire | 99 |
| 3.27 | Piezoelectric materials and electrorheological composites | 101 |
| 4.1 | A schematic of hardness test for rubber/ERF composite under the various voltage applied | 108 |
| 4.2 | Rolling resistance test system with wood roller | 110 |
4.3 Scheme of rolling resistance test under high electrical voltage

4.4 AFM imaging of smart composite SRE5-5

4.5 AFM imaging of smart composite SRE5-25

4.6 Relationship between testing electric voltage and hardness of silicon rubber/ERF composite curved under 5 kV and 25 kV

4.7 Scanning electron microscope image of the morphology of the ERF/silicon rubber composite

4.8 SEM micrographs of surface morphology of (a) silicon rubber and (b) ERF reinforced silicon rubber composites SER5-5

4.9 EDX of surface morphology of (a) silicon rubber and (b) ERF reinforced silicon rubber composites SER5-5

4.10 Schematic of particles arrangement inside silicon rubber/ERF composite cured under electric field

4.11 Schematic of samples prepared in transverse direction (a) and axial direction (b) for tensile test

4.12 True stress vs. true strain curves for ERF reinforced silicon rubber composites with different ERF concentrations (0, 5% and 10% by weight)

4.13 True stress vs. true strain curves for ERF reinforced silicon rubber composites with 5% ERF concentrations vulcanized at different voltage (0, 10 kV, 15 kV and 25 kV)

4.14 Plot of curing voltage vs. maximum tensile stress

4.15 Comparison of true stress vs. true strain responses in axial and transverse directions for ERF reinforced silicon rubber composite with ERF concentration 5% vulcanized under (a) 0 kV, (b) 10 kV, and (c) 25 kV

4.16 Comparison between experimental and modeling curves for axial tensile properties of ERF reinforced silicone rubber composites

4.17 Comparison between experimental and modeling curves for transverse tensile properties of ERF reinforced silicone rubber composites

4.18 The relationship of axial small-strain elastic modulus against vulcanization voltage for ERF reinforced silicon rubber composite with a concentration of ERF (5% by weight)
The relationship of transverse small-strain elastic modulus against vulcanization voltage for ERF reinforced silicon rubber composite with a concentration of ERF (5% by weight)…… 130

The rolling resistance of ERF reinforced silicon rubber composite with different ERF concentrations prepared under vulcanization voltage of zero…………………………………… 131

The rolling resistance of ERF reinforced silicon rubber composite with ERF concentration of 5% prepared under different vulcanization voltages…………………………………… 133

The relationship between rolling resistance and elastic tensile modulus for the studied smart composite system SRE5 vulcanized under different voltages…………………………………… 134

A schematic of coaxial electrospinning station…………………… 139

The electrospinning station to collect aligned fabrics……………… 140

The ERF/electrospun membranes collected on the surface of rotating disc collector.…………………………………………………………………………………………………… 141

The lateral view of a modified pendulum-acoustic emission device to test the rolling resistance of ERF/electrospun membranes……………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………..
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Features of general purpose elastomers for use in tires (Blow 1971)…</td>
<td>8</td>
</tr>
<tr>
<td>2.2</td>
<td>Summary of dependence of the final cross-sectional jet radius on input parameters (Thompson, C. J. 2007)</td>
<td>53</td>
</tr>
<tr>
<td>3.1</td>
<td>Variation of elastic modulus and ultimate strength of electrospun polymer membranes</td>
<td>86</td>
</tr>
<tr>
<td>4.1</td>
<td>ERF reinforced silicon rubber vulcanized under different voltages</td>
<td>105</td>
</tr>
<tr>
<td>4.2</td>
<td>Empirical material parameters fitted in Mooney-Rivlin model</td>
<td>127</td>
</tr>
<tr>
<td>4.3</td>
<td>Empirical material parameters fitted in Ogden model</td>
<td>128</td>
</tr>
<tr>
<td>4.4</td>
<td>Summary of elastic modulus of studied tensile specimens calculated by Equation 10</td>
<td>129</td>
</tr>
</tbody>
</table>
CHAPTER I
INTRODUCTION

1.1 Background

The environmental impacts on humans with respect to the use of gasoline use are profound (Dunn 2002, Lutsey 2005, and Heavenrich 2005). With millions of passenger cars and light trucks on the road, burning billions of gallons per year, the fuel use continues to rise about 3% annually, propelled by continued increase in total number of vehicles on road, rising average distance driven per car, and falling average fuel economy (Pearce 2007). It is evident that reducing the fuel consumption will eventually improve the quality of environment and hence the concomitant effects (Hobson 2003 and Jingguang 2003). So saving energy and improving environmental quality is the first and most important object through reduced fuel usage (Schaefer, 2006).

One of the most promising opportunities for fuel savings across the entire fleet of existing vehicles is to reduce rolling resistance of tires instead of standard replacement models. Rolling resistance contributes to 6-10% of the overall fuel consumption of vehicles. This change improves the inherent efficiency of the vehicle, automatically saving fuel over a typical 30,000 to 50,000 mile lifetime of a set of tires.
According to the National Academy of Sciences, about 80 to 88% of the energy in a vehicle’s gasoline tank is wasted in various thermal, frictional, and standby losses of the engine and exhaust system. Only about 12 to 20% of the energy is left for actually vehicle motion (Schuring 1990, Menzies Jr 2006, Sandberg 2011 and McAllister 1983).

So lower fuel consumption of next generation vehicles and tire design is the primary driving force behind an understanding of rolling resistance of materials and tires. Furthermore, to enable future smart tire technology, rolling resistance needs to be fine tuned in response to environmental conditions. For example, when a vehicle is climbing uphill a higher rolling resistance is desired to give a greater torque for push. When the vehicle is running on a highway, a significantly reduced rolling resistance is essential to reduce fuel consumption. Understanding of how one can control rolling resistance in materials and tires design is thus essential.

The electrorheological (ER) fluid is typically a suspension of micro-sized porous particles (0.01~10um) dispersed in dielectric carrier liquids (Liu 2012, Wen 2008, Leng 1995, and Choi 2001). As dispersed particles one can select such materials as silica, aluminum silicate and polymer semiconductor. Transformer oil, silicone oil and other organic solvents can be used as carrier Liquids. ER fluid exhibit large reversible changes in their rheological properties when they are subjected to an external electric field. These changes are of high response (~10-3s) (Dassanayake 2000, Wei 2011 and Oh 2013). The Urea–coated barium titanyl oxalate BaTi (C₂O₄)₂ nanoparticles were the ER fluid materials with giant electrorheological effect. Field stress at 2kV/mm is up to 104Pa (Davis 1992, Tian 2002 and Yeh 2004).
The most significant change in the properties of material with ER fluid is the change of material stiffness, yield stress and damping, which varies with the electrical field intensity imposed upon ER fluid (Davis 1992, Tian 2002, Yeh 2004 and Youngs 1985). This methodology is used to realize the adjustment of rolling resistance by incorporating ER fluid into rubber matrix.

1.2 Introduction

In this research, a pendulum-acoustic emission device is adopted to evaluate the rolling resistance of different type materials. The laboratory-scale rolling resistance device was developed by Gent (2002). This apparatus for measuring the rolling resistance of a substrate comprises a rolling means for rolling contact with a surface to be measured. To our knowledge, we made the first attempt to measure the rolling resistance of electrospun membranes, silicone rubber/electrospun fabrics composites.

Since ER fluid can be controlled by external factor, we also tried to incorporate ER fluid into silicone rubber matrix or electrospun polymer membrane, and investigate the reversible changes in their rheological properties when they are subjected to an electric field influence as a function of rolling resistance of silicone rubber composites.

These experimentally data produce useful insights in coupling proper substrate materials with polymer fabrics for understanding the control of rolling resistance for future tires.
CHAPTER II
LITERATURE REVIEW

2.1 Tire history and structure

As early as 1826 Faraday found an empirical formula of $C_5H_8$ for natural rubber, and Greville Williams (1860) recognized that rubber was a polymer of isoprene. In 1910 Pickles put forward the straight-chain polymer structure for the rubber hydrocarbon, which is accepted universally now.

$$\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{CH} \quad \text{(CH}_2)_2 \quad \text{CH} \quad \text{(CH}_2)_2 \quad \text{CH} \quad \text{CH} \quad \text{CH}_2
\end{align*}$$

The elucidation of the structure of natural rubber paved the way for the development of synthetic rubbers.

2.1.1 The history of natural rubber

Most synthetic rubbers are produced in two main stages: first, the production of the monomer or monomers, then the polymerization to form a rubber. The most significant early discovery in the polymerization process was achieved when Matthews and Strange (1910) patented the use of metallic sodium.

During the war of 1914-1918 methyl rubber was made in German on a commercial scale. In the rubber manufacturing industry, the production process is
defined into three stages: mixing, forming, and vulcanizing. At first, the polymers, fillers, processing aids, vulcanizing ingredients, and other additives have to be mixed together. The quality of the final product in the mixing step has uniform and high level of dispersion and consistent rheological properties.

The second production stage is the forming of the material into the shape required. The variety of methods is basically only four: spreading on fabric from solution, extrusion through a die, calendaring between rolling or bowls, and moulding. The final step is vulcanizing. The most important issue in the industry technology is the control of the chemical reactions leading to crosslinking, to bonding to metal and fabrics, and to polymer breakdown (Ten Brinke 2002).

2.1.2 Rubber Elasticity

Rubber is a viscoelastic material: when it deforms, a fraction of the energy is stored elastically, and the rest of energy is transferred into heat. These losses as well as aerodynamic drag and friction contact with road are unrecoverable losses for a moving vehicle (Heinrich G 2002).

From the standpoint of polymer structure, a vulcanized rubber consists of a three-dimensional network composed of very long rubber molecules laterally attached to one another at occasional points along their lengths. The cross-linkages may consist of primary valence bonds connecting the chains directly, or of an intermediate group or atom such as sulfur which is bonded to each of the two chains.
In process of cross-linking (vulcanization), the original long polymer molecules can be considered to lose their identity, and there emerges a single giant network structure, the basic elements of which are the portions of the molecules reaching from one cross-linkage to the next. When deformation occurs, the cross-linkages are shifted to new positions relative to one another in a manner paralleling the macroscopic deformation (Flory, Paul J. 1943).

![Figure 2.1 Schematic diagram of an ensemble of linear polymer chains being crosslinked into an infinite network (Shaw, Montgomery T, 2005)](image)
Polymer viscoelasticity refers to the time-dependent nature of deformation under an applied stress. Figure 2.2 shows idealized modulus-temperature curves for typical linear and crosslinked amorphous polymers. Four regions of viscoelastic behavior are defined in the plot. At low temperature, the polymer is hard and brittle, which is glassy region. With increasing temperature, the polymer is at the glass transition temperature where the brittle glass becomes resilient leather. As the temperature is further increased, the modulus again reaches a rubbery plateau. At this region, the crosslinks consisting of chemical bonds remain intact, preventing the chains from translating relative to one another. But for linear polymer, increasing temperature causes molecular motions to become more and more large-scale. If temperature is increased still further, barring chemical reaction the sample will become a viscous liquid. (Shaw, Montgomery T., 2005)

Figure 2.2 Schematic modulus-temperature curve showing various regions of viscoelastic behavior (Deniz KAYA, 2012)
But the temperature rate is still important for investing polymer viscoelastic behavior. When a polymer is deformed at a rapid rate there is not enough time for the polymer chains to untangle and thus the polymer behaves in a brittle manner with low fracture toughness. If stress is applied over a long period of time then viscous flow occurs and the polymer exhibits large amounts of strain or creep (Deniz KAYA, 2012).

2.1.3 Rubber in tire application

The most important usage of nature rubber is for vehicle tires. More than half of the natural rubber and synthetic rubbers produced in the world are consumed in the tire industry. The raw polymers used are nature rubber (NR), styrene-butadiene rubber (SBR), isobutylene-isoprene rubber (IIR), polybutadiene rubber (BR) and polyisoprene rubber (IR). The differences in their properties in relation to their use in tires are show in Table 2.1.

Table 2.1 Features of general purpose elastomers for use in tires (Blow 1971)

<table>
<thead>
<tr>
<th>Property</th>
<th>NR</th>
<th>IR</th>
<th>SBR</th>
<th>BR</th>
<th>IIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wear resistance</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Road holding</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Low heat build-up</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Tear resistance</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Gas and vapor impermeability</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Ageing resistance</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Ozone resistance</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
</tbody>
</table>

Ratings: 1, poor; 2, good; 3, very good; 4, excellent.
The world’s first pneumatic tires are invented by Robert William Thomson in 1845. They consisted of rubber tubes filled with air protected by a canvas cover with leather treads. The pneumatic tire is continually developed by Dunlop (1888). The first commercially available pneumatic tires consisted of an inner-tube surrounded by a “cover” made up of several layers of woven canvas-type fabric, held together by rubber bonding. These “covers” were coated with rubber, which was thickened in the tread area and were locked onto the rim in various ways (C. M. Blow 1982 and J. L. White 1995).

In the development of tire technology, polyester, glass fiber and more recently aramid and steel have been added to the reinforcing materials available to the tire designer. The introduction of carbon black and silica as a reinforcement strongly increases tread wear resistance and provides or enhances good physical properties for the cured rubber compound. But the difference between them is silica is used without a coupling agent. Nowadays pneumatic tires are conventionally prepared with a rubber tread, which is typically reinforced with various reinforcing fillers (Wolff 1996).

2.1.4 Tire Structure

As the pneumatic tire is so important for vehicle design, the tire structure is faced with an impossible task in trying to satisfy all the needs of the vehicle manufacturer (Clifton 1969).
A tire is a much more complex object than it looks. A tire is a circle geometrically, a flexible-membrane pressure container mechanically, a high-performance composite structurally, and materials made up by long chain macromolecules chemically (Mark 1994). Tires are the only contact between the car and the road and affect both the fuel economy and the safe operation of any vehicle.

A tire is composed of several parts: the tread, bead, sidewall, shoulder, and ply. The tread is the part that comes in contact with the road surface. High performance tires have small void ratios to provide more rubber in contact with the road for higher traction, but may be compounded with softer rubber that provides better traction, but wears quickly. The tread pattern is characterized by the geometrical shape of the grooves, lugs, voids and sipes.

Grooves are a design element of the tread arranged to channel water away from the footprint. Lugs are that tread portion that contacts the road surface. Tread voids provide space for the lug to flex and deform as it enters and exits the footprint. Low void areas have high contact area and therefore higher traction on clean, dry pavement. Sipes are valleys cut across the tire, which allow the water from the grooves to escape to the sides.

The bead is the part of the tire that contacts the rim on the wheel. The bead is typically reinforced with steel wire and compounded of high strength, low flexibility rubber. The sidewall is rubber reinforced with fabric or steel cords that provide for tensile strength and flexibility. The shoulder is that part of the tire at the edge of the tread.
Plies are layers of relatively cords embedded in the rubber to hold its shape by preventing the rubber from stretching in response to the internal pressure. The orientations of the plies play a large role in the performance.

Internal structure comprises two or four layers of cords. (see Figure 2.3) Each layer of rubber cord is known as a ply. Individual cords are evenly tensioned in the finished product, in order to obtain the optimum structural performance and achieve an acceptable level of uniform.

Radial-ply tires are equipped in most cars today. In a radial-ply tire, the reinforcing cords are aligned with the radius of the outer diameter radial-ply construction reduces rolling resistance, lengthen tread life, and improves the handling qualities of the vehicle.

Figure 2.3 A cross-section of a tire showing ply orientations (Philips)
2.1.5 Tire functions

A good tire should satisfy the following requirements: (a) generate the highest possible traction force between tire and road; (b) exactly and predictable steering characteristics under all handling situations; (c) the lowest possible rolling resistance and (d) the highest possible mileage.

From these considerations, the functions of a tire can be considered in relation to three basic roles: performance, vehicle mobility, and comfort. Performance, including driving, braking torque and rolling resistance, transfers forces or moments in forward direction. Vehicle mobility, including cornering, steering response, and abrasion, acts in the lateral direction, and the forces involved in comfort act (J. E. Mark 1994).

Out of all these qualifications, three main performance criteria stand out: rolling resistance, traction and wear resistance. These three properties are called “magic triangle”, which means that a balance must be found between these properties. These requirements are conflicting, as it is impossible to improve all three characteristics at the same time (Engehausen 2001).

2.1.6 Magic triangle in tire performance

The balance of three parts in magic triangle can be achieved using "green tire" technology. The rolling resistance of tire depends on the loss modulus of tread compound largely and its thermal conductivity.
The tire traction is determined by the friction properties of the tread compound. The tread plays a major role, as the friction coefficient of the tread determines the traction level of the tire. The mileage depend on the abrasion resistance of the tread compound, a complex property which itself depends on strength, fatigue and resistance to the effects of aging (K. A. Grosch 1996).

A major problem facing tire designers need to solve the compromise between low rolling resistance, high wet grip and high wear resistance. Rolling resistance is the amount of energy a tire absorbs as it revolves and deflects. The lower the rolling resistance the less fuel is required to propel the vehicle forward. Lowering the rolling resistance, however, commonly results in a reduction in wet grip performance, which of course is unacceptable (Freund 1995). A major step in solving this problem can be achieved by the replacement of carbon black by silica in the tire’s tread compound. This has enabled manufacturers to produce tires which provide improved wet grip properties, better winter performance and lower rolling resistance all at the same time.

A tire must deliver high traction and cornering forces on wet and dry roads, also called wet and dry grip. Grip is best served by rubber compounds, which absorb high levels of energy to avoid slippage. Traction depends on three main tire features: the tire construction; the tire tread compound and tread profile design; the road conditions. In addition, low wear and good durability and give a satisfactory driving comfort are still the tire requirement; the resistance to abrasion should be as high as possible to create a high mileage.
2.1.6.1 Rolling resistance

Reducing energy consumption is a national goal for many reasons, from economy and environment to improve air quality and reducing greenhouse gas emissions. Tire rolling resistance is defined by Hall and Moreland (2001) as “the energy consumed per unit distance of travel as a tire rolls under load”. A vehicle’s fuel economy is affected by tire rolling resistance, therefore, fuel saving could be achieved by reducing tire rolling resistance. Therefore, the rolling resistance of replacement tires could have a significant impact on the fuel economy.

Low rolling resistance requires compounds, which absorb low quantities of energy. By use of proper tread compounds, the hysteresis characteristics can be controlled, thereby providing lower rolling resistance without affecting wet grip and wear resistance (Loganathan 2000).

Silica improves rolling resistance by about 25%, and fuel consumption fell by about 5%. When compared to tires without silica, rolling resistance drops by about 38%. Fuel consumption falls by 3 to 8%, depending on the basis of comparison. The prior studies, tire producers have put much emphasis on reduction of the tire rolling resistance, while simultaneously improving other aspects of tire performance (Hall 2001).
By use of proper tread compounds, it is possible to reduce lower rolling resistance without affecting wet grip and wear resistance (Matthan 1998). Rolling resistance plays a surprisingly large role in fuel consumption: for passenger cars and light trucks, a decrease in rolling resistance with minimum 10% can yield fuel consumption improvements ranging from 0.5 to 1.5%; and for heavy trucks, an improvement of 10% can yield fuel savings of 1.5 to 3.0% (Schuring 1980).

Figure 2.4 Friction, rolling resistance and drag on different road types (part20 webpage)

2.1.6.2 Wet traction property

Wet traction is the tire's traction, or grip, under wet conditions. Traction is the force used to generate motion between a body and a surface. Wet traction is improved by the tread design's ability to channel water out of the tire footprint and reduce hydroplaning.
Tires play a major role in the balance of driving fun and safety demands especially on wet road surfaces. Though the scientific basics of the wet braking phenomenon are still under investigation, the introduction of silica system led to an immediate improvement of wet grip. Contacts to the road surface can be guaranteed even under wet conditions (Wet grip webpage).

Figure 2.5 Scheme of tire wet grip on road surface

2.1.6.3 Wear resistance

The abrasion of an automobile tire is a cyclic process. During the contact with the road, abrasion occurred and part of the energy was consumed. After this process, recovery take place partly, at the next contact, energy dissipation can occur again. The rate of recovery is dependent on the elastomer network.

For use at higher speeds, shorter time cycle is left for recovery and tire wears increases rapidly. Under these conditions, filler with a more active surface is wanted. In many cases, more active surfaces are present in carbon blacks having higher structure.
In filler reinforcement rubber, there are high energetic bonds which are coupling the filler and the rubber. A simple chipping of the silica applies into application, and then abrasion resistance is improved.

Stacey et al. (1975) have shown that aggregate size distribution influences the relation between hysteresis and reinforcement. At the same surface area, blacks with a wider aggregate size distribution imparted lower hysteresis than blacks with a narrow size distribution.

2.2 Filler reinforcement rubber in tire application

Natural rubber (NR) is known to exhibit numerous outstanding properties such as good oil resistance, low gas permeability, improved wet grip and rolling resistance, coupled with high strength; having properties resembling those of synthetic rubbers (Pal, Kaushik 2010). But for some specific application, most usage of elastomers would be impossible without the reinforcing character of certain fillers. In tire technology, reinforcement is usually defined by Medalia (1994) as the “improvement in abrasion, tear, cutting and rupture resistance, in stiffness and hardness of vulcanized compounds through the incorporation of finely divided particles”. A wide variety of fillers are commonly employed, such as carbon black, zinc oxide, carbonates and silicates of calcium and magnesium. Generally there are two types of fillers: reinforcing and nonreinforcing. The filler is reinforcing if it can increase the rubber stiffness without impact its strength and lose rubbery character. (Shaw, Montgomery T, 2005)
By the incorporation of particulate fillers, such as carbon black and silica (Payne 1962, Kraus 1971), this is the most common and easy way to improve the rubber properties. Further, such reinforcements induce agglomerate structure (Bokobza 2002, Rodgers 2004 and Wang 2002) and the rubber/filler interactions (Choi 2002, Wolff 1996).

The Guth-Smallwood equation is commonly used for describing the fillers effect in rubber system on elastic modulus. (Guth 1936, 1945 and Smallwood 1944)

\[
\frac{E_f}{E_0} = 1 + 2.5V_f + 14.1V_f^2
\]

where \(V_f\) is the volume fraction of fillers, and subscripts f and 0 refer to the filled and unfilled rubbers respectively. This equation is valid for the system up to a value about 0.3, which is used for an elasticity of filled rubbers. Mullins, La’s (1965) research about carbon black reinforced rubber had a good agreement with experimental date, which is illustrated in Figure 2.6.
In the filler-rubber system, the fillers are considered as rigid solid particles with high modulus. When the system is deformed, since the fillers are so much more rigid than the rubber, they essentially remain undeformed. Thus all the strain must be suffered by the rubbery phase of the sample. The actual strain can be rewritten as the following equation:

$$\Lambda = 1 + \varepsilon (1 + 2.5V_f + 14.1V_f^2)$$

where $\epsilon$ is the applied strain on the filled system, and $\Lambda$ is Mooney-Rivlin parameter. (Mullins, La 1965)
From the experiments made by Mullins La (1965), the data has an excellent agreement with equation for rubbers filled up to 8%, but it is poorer for higher filled contents. The elastic properties of rubber itself are unaffected by the presence of these fillers.

Figure 2.7 (Bueche, F. 1960) represents three rubber chains attached to two filler particles before a force applied to rubber. These three type chains will rupture separately when the force becomes large gradually. The chain may merely pull loose from the filler surface, so the rubber will appear softer after the applied force is removed. This is another important filler effect in rubber system, which is called stress-softening or the Mullins effect (Govindjee, Sanjay 1991). From the Figure 2.8 of Bueche, F’s research (1965), after remove the strain of a filled sample was stretched for the first time to 100%, the sample can be restretched to 200%. If we repeat that stress-strain in a third cycle, a softening up to 200% can be achieved. Some of the chains may be relaxed, but others are already relatively extended. Upon stretching, the prestrained chains will reach maximum extension first and either will become detached from the fillers or will be broken. In the second cycle, these broken chains no longer support the stress, thus giving rise to the observed softening in stress. If the stress-strain cycle repeats several times, the process will keep repeating every time.
Figure 2.7 Stress-softening of natural rubber filled with MPC carbon black (Mullins effect). Numerals indicate the stress-strain cycles. (Bueche, F. 1960)

Figure 2.8 Three typical chains attached to two adjacent filler particle. (Bueche, F. 1960)
2.2.1 Classification of filler as reinforcement

There are a large variety of powdered minerals can be compounded with elastomers but not all have reinforcing capabilities, and carbon blacks and high-structure silica have been found to offer significant reinforcing effects. Other kinds of reinforcing fillers are still under research, which is discussed in the proposal later.

Many investigations on carbon blacks, silica, and organosilane coupling agents not only improve the mechanism of reinforcement, but also provided better performance for the development of tire compounds and tires (Wolff 1996). The fillers can be classified on basis of their chemical composition and influence on rubber properties (Blume 2002). The classification of fillers depends on the size of the filler particles as shown in Figure 2.9.

![Figure 2.9 Classification of fillers based on the size of the primary filler particle (Klüppel 1997)]
Particles around 1 micron do not have much reinforcing capabilities. Reinforcement is readily obtained with sizes smaller than 0.1 micron but particle structure appears as a more decisive factor. The nano-scale particles interact with each other and have a strong filler-filler-network, so filler aggregation and agglomeration happened very often (Kraus 1978).

Figure 2.10 Relevant dimensions in rubber-filler interactions (Leblanc 2002)

In graphite or silica filler-rubber system, Figure 2.10 highlights this comparison; using typical dimensions of filler that can be considered reinforce rubber often. Boxes in the figure indicate rubber-filler interactions likely.
In general, carbon black and silica are used to reinforce elastomers often. For carbon black filled rubber, physical bonding between carbon black and polymer plays an important role in rubber reinforcement. On the other hand, for silica-filled rubber, the interaction between silica and polymer interaction, filler-filler interaction affects the material characteristics as described by Payne. (1961) The “Payne effect” (Figure 2.11, Coran, A. Y. 1992) describe that the shear modulus contributions in rubber reinforcement, such as the hydrodynamic effect, the polymer network contribution and the filler-polymer interaction, and the strain-dependent filler-filler interaction (Mihara 2009).

2.2.1.1 Carbon black filler

The use of carbon black is the most popular and widely reinforcing filler in the history of tires.
Organoclay nano particles separate in the substrate, in order to obtain very large surface areas (Bowden 1966). Hence, reinforcement is primarily the enhancement of strength and strength-related properties, such as abrasion resistance, hardness, and modulus, reduction in material costs and improvements in processing (Kragelskii 1982, Buckley 1981 and V.A. Bely 1982).

Kraus (1977) found the reinforcement effect of elastomers by carbon black is governed by the morphology of the black and its physical and chemical interactions with the polymer. The latter are strongly affected by graphitization and surface oxidation, which mechanical properties of reinforced rubbers depend on.

2.2.1.2 Silica reinforce rubber

In order to expand the magic triangle, the compounds prepared with silica makes it possible to completely improved better wet grip, reduced rolling resistance with a wear resistance similar to that of carbon black compounds and also a decrease in the rolling noise (Localli JL 1999). Silica filled rubber systems are suitable for the investigation of chain scission of rubber molecules during the deformation.

In the rubber compounding technology, the rubber/filler interactions can be controlled by the introduction of coupling agent (Goerl 1997, Yatsuyanagi 2001, and Kim K-J 2002). To achieve the desired reinforcement of a silica-filled rubber, a chemical linkage between silica and polymer matrix is needed. The principle of this “chemical reinforcement” by coupling agent is displayed in the Figure below (Reinforcement webpage).
The silica-active site provides the coupling of the silane to the silica surface during the mixing process. The rubber-active site reacts with the polymer during vulcanization and therefore couples the silica chemically to the rubber.

The morphological structure of silica plays an important role in the physical properties of filled rubber. The particles aggregate easily, since an interaction between the primary particles have take place (Wolff 1996).

The use of silica can result in a 20% reduction in rolling resistance corresponds to a 5% fuel saving and more relative to carbon black. The use of silica can also improve wet skid performance. In addition, wet skid performance can be improved by as much as 15%, substantially improving braking distances at the same time (Mihara 2009).

2.2.2. Filler reinforce rubber mechanisms

The use of fillers in rubber technology has paramount meaning. Reinforcement is primarily the enhancement of strength and strength-related properties, abrasion resistance, hardness and modulus (Choi S-S 2003 and Heinrich G 2002).
It is now generally agreed that in many cases the polymer is attached to the surface of effective filler (Bueche 1957).

Epoxidized natural rubber (ENR)-layered silicate composites were produced by melt compounding and sulfur curing in Varghese’s (2003) research. Intercalation/exfoliation of the silicates was best displayed in stiffness- and strength-related mechanical parameters and reflected in the glass transition.

Ideal materials giving a low $\text{tg}\delta$ at medium temperature (50-70 °C) can reduce the rolling resistance and a high $\text{tg}\delta$ a low temperature (0-10 °C) can obtain high wet grip (Donnet 2003). The filler networking seems to be a dominant factor (Gerspacher 1999) in the hysteretic behavior of vulcanized compounds.

Fröhlich J. etc (2005) studied the mechanism of reinforcement, such as specific surface area, structure and surface activity on the Payne-effect, and get a better understanding of filler-polymer interaction.

Filled rubber compounds are complex polymer systems that exhibit a number of singular flow properties, which play an important role induced strong interactions arising between the elastomer and the filler particles. Leblanc (2002) discusses that dimensional aspects offer the most likely key to understand the relationships between bound rubber and flow properties.

Bokobza (2002) demonstrated that carbon black- and silica-filled natural rubber exhibit increases in the cross-linking density ascribed to filler-polymer links, whereas a large decrease in the orientation level.
In Suzuki’s study (2005), effect of rubber/filler interactions on the stress-strain behavior for silica filled styrene-butadiene rubber (SBR) vulcanizes were studied in relation to the chain scissions of rubber molecules during deformation. At a given strain, the tensile stress increased with increasing the interfacial interactions between rubber molecules and silica surface, and the degree of chain scission was closely related to the mechanical energy applied to the vulcanizes.

Mélé (2002) showed that the filler content has a relationship with shear modulus then related to either the reinforcement effect induced by fillers or the development of specific additional interactions between phases.

2.2.2.1 Effect of coupling agent in filler/rubber composite

The properties of filler/rubber composite are determined by the network between filler and substrate largely. By using coupling agent in this system, the network will be improved in order to increase the composite property.

Ansarifar (2005) obtained synthetic silica to reinforce natural rubber with the coupling agent bis (3-triethoxysilylpropyl-) tetrasulphane (TESPT). The silica was perfectly dispersed in the rubber, which can improve the composite properties.

Ou (1994) evaluated that the extent of reinforcement in NR vulcanizes is reduced when the silica are alkylated.

2.2.3 Improvement the tire rubber properties by adding fillers

Any tire rubber modification contributes to reduce the fuel consumption which can be brought a huge signification to economy and environment. Many research have been done to improve tire rubber performance.
The fuel energy is consumed by the contact between tire surface and road. Friction is a very common phenomenon in daily life and industry, which is governed by the processes occurring in the surfaces layers of body in moving contact. The two main components used in studies of friction are adhesion and deformation (Fuller 1981). The changes in surface layer arise from mechanical stresses, temperature and chemical reactions. Polymers due to their specific structure and mechanical behavior are more sensitive to these factors (Myshkin 2006).

2.2.3.1 Rolling resistance

Increasing pressure to improve vehicle fuel economy and decrease emissions has driven the tire and rubber industries to reduce tire rolling resistance. But rolling resistance behavior is a quite complex operating condition. Combined with accurate dynamic material property measurements, finite element models used in some research have provided designers with a tool to understand the behavior of each rubber product and optimize tire construction and material properties to minimize rolling resistance. However, with the current level of understanding and optimization of rolling resistance, material development and tire construction are still needed to achieve further rolling resistance reductions (David E 2001).

In Evans’ (1954) paper, rolling friction in the elastic range is primarily due to elastic hysteresis losses of a wheel with a solid rubber tire.
Hess (1983) focus on the effect carbon black type and loading on the rolling resistance of SBR/BR radial passenger tire treads. The rolling loss variations showed a good correlation with either tan δ or resilience. Reduced black loading lowers rolling resistance without much effect on traction. Increasing black fineness raises both rolling resistance and traction.

González (1996) used the compound p-aminobenzenesulfonyl azide to develop as a new type of carbon black to rubber coupling agent. Its addition to rubber compounds increases resilience and module while reducing abrasion loss. Rubber compositions containing this coupling agent may be used in tire treads to reduce rolling resistance and improve wet skid resistance.

Precipitated silica is used in the treads of vehicles tires improve tear strength, cut-growth resistance and resistance to ozone aging and reduce the rolling resistance and increase the wet traction of the tire (Waddell 1996).

Rattanasom (2007) use silica/carbon black blends enhance the mechanical and dynamic properties of natural rubber vulcanizates. The results reveal that silica/ carbon black hybrid filler exhibit the better overall mechanical properties, such as tensile strength, tear strength, abrasion resistance, crack growth resistance, heat buildup resistance and rolling resistance. This is because the higher amount of carbon black is incorporated into natural rubber more easily than silica at the initial stage of mixing.
In Prasertsi’s (2011) research, a well-dispersed silica suspension is used for preparing silica/natural rubber. The composite without silane exhibited comparable abrasion resistance, rolling resistance and heat build-up to those of the silane filled conventional composite.

2.2.3.2 Wet grip

From the prior work, two accepted theories are used for the development of improved wet grip tire tread compounds: reducing the tread compound resilience; and increasing the tread polymer glass transition temperature (Tabor 1960, Bulgin 1962 and Bond 1984).

Gonzalez (1996) used the compound $p$-aminobenzenesulfonyl azide as a new type of carbon black to rubber coupling agent. This rubber compounds increases resilience and moduli while reducing abrasion loss and the rubber Tg is shifted to higher temperatures. Rubber compositions containing this coupling agent may be used in tire treads to reduce rolling resistance and improve wet skid resistance.

Wu (2008) investigated the influence of in situ modification of silica with bis-(3-(triethoxysilyl)-propyl)-tetrasulfide (TESPT) filled solution SBR compound. The compound with in situ modification of silica exhibited higher tan $\delta$ in the temperature range of -30 to 10°C.

Peng (2010) prepared natural rubber/multi-walled carbon nanotube composites. The composites showed a remarkable increase in the tensile strength of and, glass transition temperature is higher and thermal stability is better, which due to the strong interfacial adhesion between natural rubber phase and filler.
2.2.3.3 Abrasion property

Zhou (2001) treated Zinc oxide whisker with a coupling agent, which was mixed into natural rubber. The results showed that tensile strength and wear-resistance of the composites progressively increases with an increased amount of the related whisker.

The blends of high styrene rubber (HSR) and natural rubber (NR) with nano silica were mixed with carbon black by Pal, Kaushik (2010). Blends of carbon black/HSR showed the maximum optimum cure time, higher abrasion resistance a. The NR-HSR blends with addition of nano silica have very good abrasion properties.

Pal, Kaushik (2010) blended high styrene rubber (HSR) and natural rubber (NR) with nitrile blended PVC and nanosilica mixed with carbon black. Blends containing with PVC shows high abrasion resistant properties.

Zhou (2005) used polyurethane matrix composites reinforced with aluminum oxide (Al$_2$O$_3$) particles were. This composite has an improvement at wear resistance in erosion conditions. In addition, the hardness increased gradually.

The effect of fillers on morphology and wear characteristics are studied in butadiene rubber/high styrene rubber/natural rubber blends with carbon black. Blends containing carbon blacks show high abrasion resistant properties (Pal, Kaushik 2010).

2.2.3.4 Mechanical properties

For mechanical properties, Ikeda (1997) concluded that tensile tests were normalized by the following equation:

\[
\text{Reinforcement index (RI)} = \frac{N_1}{N_2}/(\text{Silica content/100})
\]
where \( N1 \) and \( N2 \) are nominal values obtained by mechanical measurements of the samples with and without silica, respectively.

Mixing the filler with high tensile stress into rubber, there will be an improvement in mechanical properties. But the situation of filler suspension in substrate is still a problem determine the composite property.

Boonstra (1975) used solated silanol groups to improve strength but lower modulus for hydroxyl-terminated silicone rubber.

Ikeda (1997) used tetraethoxysilane (TEOS) reinforce styrene–butadiene rubber by a sol–gel process using. The method using only TEOS was found to have better performance than the mixture system in tensile tests, dynamic mechanical measurements. In addition, the large the in situ silica particles, the better the mechanical properties found.

From Ramorino’s (2009) work, it gets better performance in mechanical behavior of natural rubber/organo-modified montmorillonite vulcanisates. Such a viscoelastic behavior associated to filler network contributes to support the hypothesis that in filled rubbers the mechanisms of filler networking.

The effects of different particle shapes of ultrafine silica used as filler on the properties of natural rubber compounds were investigated in Idrus’ study (2011). Three shapes of filler are cubical, elongated and irregular. Because of better filler–rubber interaction, irregular shaped fillers showed the highest tensile strength, elongation at break and hardness compared with the other shapes.
Beside silica and carbon black as the wide use in filler reinforces the rubber, there still have some filler used to modify the rubber properties. Fiber reinforcement is well-known filler to improve the stiffness, strength, and the high temperature performance of polymeric materials (Folkes 1992 and Li 1993). The mechanical properties of the resulting glass fiber reinforced composite material depend heavily on the nature of the fiber–matrix interface.

Laura (2002) used nylon 6 and its blends with ethylene–propylene rubber (EPR-g-MA) plus glass fibers. Both octyl and anhydride treated glass fibers improve the heat distortion temperature.

Shanmugharaj (2007) considered the surface functionalization of multiwalled carbon nanotubes, which is carried out by acid treatment followed by reaction with multifunctional silane, 3-aminopropyltriethoxysilane. Modulus and tensile strength increase due to higher polymer-filler interaction between the carbon nanotube and NR vulcanizates.

Arroyo (2007) blended epoxidized natural rubber and filler treatment on the morphology. This homogeneous morphology gives rise to a sensible increase in physical and mechanical properties of the nanocomposite.

Rajasekar (2009) prepared epoxidized natural rubber/modified nanoclay composites. The compounds showed enhancement in mechanical properties, higher swelling resistance in oil.
De Falco (2007) produced cured styrene–butadiene rubber (SBR)/multi-walled carbon nanotubes composites with a sulphur/accelerator system at 150 °C. Significant improvement in Young’s modulus and tensile strength were achieved without sacrificing SBR elastomer high elongation at break because of the homogeneous dispersion of filler throughout matrix and strong interfacial adhesion between them.

Kim (2005) used natural rubber filled with carbon black with different particle diameters. Based on his test data, it was noticed that the fatigue life, the hysteresis, the small-scale roughness and the critical J-value have high ranked when the natural rubber compound filled with small diameters carbon black.

Reinforcement of natural rubber was achieved using carboxylated multiwalled carbon nanotubes dispersed with sodium dodecyl sulfate in Bhattacharyya’s (2008) work. The tests demonstrated a strong enhancement in the Young’s modulus, tensile strength and storage modulus at low-strain.

Cai Han-Hai (2003) used ultrafine calcium carbonate to reinforce natural rubber latex film. The results showed that tear strength, tensile strength, and modulus were improved.

2.3 Smart tire

In recently research, advanced tire sensor system is under developing as “smart tire” which is equipped with a sensor to monitor strain, air pressure, temperature inside car and truck tires, to improve automobile safely. The aim is both to prevent accidents caused by a tire burst and to provide an economical advantage through a reduction of fuel consumption and a longer tire lifetime (J. Yi 2002).
The Government of the United States of America has passed a new Transportation, Recall, Enhancement, Accountability and Documentation (TREAD) Act, which states that new automobiles must be equipped with a tire pressure monitoring system (TPMS) to inform the driver when the air pressure in their car's tires is low (Title 49 US Code 30101). To improve reliability of automobile tires and anti-lock braking system (ABS), intelligent tires that measure strain of tires are increasingly demanded (F. Gustafsson 1997).

There are two kinds of measurement to monitor tire condition: indirect and direct measurement. A simple method is based on indirect measurement using wheel speed sensors and electronic control unit of antilock braking system (N. Persson 1991 and F. Gustafsson 2001). The indirect measurement, however, depends on the type of the tire and needs calibration which causes low reliability. Direct measurement has been developed using clamp-on-rim sensors by SmarTire System Inc. or valve-attached sensors by Schrader Electronics Ltd. Although these methods have high accuracy and reliability for the pressure monitoring, they need battery to activate the sensors. For a battery-less method, D.S. Snyder (1985) proposed piezoelectric reed included in a tire sensor unit. The wheel movements cause the piezoelectric reed to bend and generate electricity.
In R. Matsuzaki’s studies (2005 and 2007), strain sensors based on flexible epoxy and polyimide substrates using changes in capacitance is developed. However there is still a difference in stiffness between the tire surface and sensor, which is called interface edge (Y.Y. Yang 1997). The ways using for power these sensors are photovoltaic, thermoelectric and vibration based power sources.

Matsuzaki (2008) proposes a rubber-based capacitive strain sensor fabricated using photolithography. The sensor is attached to the inner surface of a commercially available radial tire, and found to successfully measure the strain of the tire. (See Figure 2.13)

Figure 2.13 Schematic illustration of the rubber-based strain sensor

As a direct method for tire strain monitoring, A. Pohl (1999) proposed surface acoustic wave sensors, and M.E. Palmer (2002) proposed optical fiber sensors to monitor strain of the tire. Intelligent tires also offer beneficial effects for the other advanced active safety systems such as traction control systems (TCSs) and vehicle stability assist (VSA).
The piezoelectric polymer–PZT composite materials manufactured in van den Ende’s (2012) study are to be considered as serious candidates for direct strain energy harvesting from tire deformations.

Matsuzaki (2006) measured the strain precisely, multiple power spectrum features of the sensor output to estimate the strain with a statistical method. The method is effective for the passive wireless strain monitoring of actual radial tires.

A pressure-measurement system based on surface-acoustic-wave (SAW) sensors is presented in Schimetta’s (2000) paper. With a new way of matching the sensor impedance to the SAW reflector impedance, both a high signal-to-noise ratio and a high signal dynamic are achieved, which supports accurate signal evaluation.

In Matsuzaki’s (2007) paper, they proposed a patch-type flexible sensor which is composed of flexible substrates and ultra-flexible resin, and the stiffness of the sensor is low while its elongation is high, allowing it to be applied to the strain measurement of automobile tires.

In Yi’s (2008) paper, they present polyvinylidene fluoride (PVDF)-based sensors embed on the inner tread surface to measure the tire rubber tread deformation for understanding and estimation of wheel/ground interactions for mobile robots and vehicles.

Understanding the tire/road interactions is however challenging. In Zhang Yizhai’s (2012) paper, a pressure-sensitive, electric conductive rubber sensor is embedded inside the tire rubber layer to measure the force distributions.
2.4 ER fluids

Winslow (1949) is the first one to introduce the electrorheological behaviors in his paper. Since then, researchers have been developed many electrorheological (ER) fluid (Figure 2.14).

Figure 2.14 The structural evolution of dielectric microspheres under an increasing electric field, from (a) no field, to (b) a moderate field of 500 V mm\(^{-1}\), to (c) a strong field of 900 V mm\(^{-1}\). Here the ER fluid consists of 1.5 micron glass spheres suspended in silicone oil (Wen 2008).

2.4.1 ER fluids concept

ER fluids are commonly polarizable particles suspend in a nonconducting dielectric liquid (Block 1988, Jordan 1989 and Halsey 1990). The polarizable particles form one-dimensional solid lines along the electrical field at first, and these lines then slowly aggregate to form columns. Rheological properties of ER fluids are changed drastically by an applied electric field (Halsey 1990).

This structure is changed very rapidly by the ER effect. When the field is removed the polarization of the particles disappears and the viscosity quickly returns to its original value (Hao T 2001 and Zhao X P 2002). Therefore, ER fluids can be adjusted and controlled by external factors, which is considered as smart material systems.
2.4.2 ER preparation

Most ER fluid are made of solid particles suspense into insulate liquid. The particle material includes inorganic non-metallic, organic and polymeric semi-conductive materials. Silicone oil, vegetable oil, mineral oil, paraffin and chlorinated hydrocarbon oils, etc are used as liquid phase, which have a low conductivity and high breakdown strength (Hao 2002).

The size effect has been reported by Cho et al (2003). The spherical, monodisperse polymer microshperes (PAPMMAs) consisting of a poly(methyl methacrylate) core and a polyaniline (PANI) shell were prepared and adopted as dispersed materials for ER fluids, in which electrical conductivity was originated primarily from the surface coated conducting PANI layer. The performances of PAPMMA-based ER fluids were enhanced with increasing core particle size.

Shen (2006) demonstrate the wetting characteristic of barium titanyl oxalate coated with urea suspended in either silicone oil or hydrocarbon oil. By adding a controlled, small amount of surfactant additive to the hydrocarbon oil suspension, the consistency can change drastically to resemble that of the silicone oil suspension.

2.4.3 ER mechanism

Block (1990) believed there was no obvious mechanism for power consumption related to the structure formation which is responsible for solidification unless the maintenance of that structure against the disruptive action of shear stress.
Parthasarathy (1996) reviewed the ER physical mechanisms proposed: electrostatic polarization, interelectrode circulation, double-layer overlap, and water bridging. But both the double-layer overlap and water bridging mechanisms lost their physical basis when they applied into anhydrous ER fluids. The polarization mechanism is accepted by most researchers.

Concerning the mechanism of electrorheology, it was quite natural that the dielectric polarization theory (Chen, Y. 1991) appeared, because the electrorheological behavior was closely related to dielectric phenomena.

In Halsey’s (1992) paper, they postulated a microscopic mechanism for the shear thinning in ER fluids.

Hao (1998) investigated a possible ER mechanism is proposed as follows: a large interfacial polarization would facilitate the particle to attain a large amount of charges on the surface, then leading to the turn of particle along the direction of an electric field to form a fibrillation structure; the strength of fibrillation chains is thus determined by the particle polarization force, i.e., the particle dielectric constant.

Gehin (2004) investigated the role of interaction forces on the ER response of an ER fluid, in terms of microstructure and flow behavior. The equilibrium structure depends on the balance of van der Waals force, electrostatic repulsion, thermal energy, and field-induced dipole attraction. The polarization forces are the main parameters in determining the electric-field-induced aggregation. The silica water content has enormous influence on the ER properties of these suspensions.
By control the colloid’s flow properties through an electric field, Wen (2008 and 2004, Huang 2006) found giant electrorheological effect, owing its origin to molecular dipoles, which was described and contrasted with the conventional ER effect that arises from induced polarization effects.

2.4.4 ER application

According dispersed phase, the ER fluid can be divided into type: inorganic oxide materials (Winslow 1953), non-oxide inorganic (Carlson 1988) and organic and polymeric materials (Stangroom 1980).

Because of the ER fluid effect, it could be used as a mechanical-electronic interface for transferring and controlling mechanical movement, such as damping devices, clutches, brakes, actuators, and robotic controlling systems.

Electronic control of stress transfer has applications in devices such as active shock absorbers and engine mounts, clutches and brakes, actuators, control valves, and artificial joints (Brooks 1992).

Bullough (1978) used the ER fluid in vibration control when both Coulomb and viscous damping was achieved by means of an ER valve-operated vibration damper.

Industrial robots are operated either by electric motors or by fluid power in Stangroom’s (1983) paper. An electric motor can be controlled by the magnetic linkage between the rotor and stator.

Many researchers are considered to use ER fluid with vibration control in large-scale commercial exploitation, in which the fluids can provide damping forces whose magnitude is a function of the electrical stimulus.
Williams (1993) concerned mathematical modeling of electrorheological fluids when used in oscillating squeeze-flow mode; in a prototype automotive engine mount.

The ER fluid device is operated in the squeeze flow mode, where exhibit sufficient field-induced damping forces were shown when subjected to various mechanical and electrical inputs and hence, they are capable of providing adaptable fixing characteristics for blast resistant and structural members such as blast walls on offshore platforms (El Wahed 2002).

Lou (1994) demonstrated the suitability of ER technology was used to create an automotive suspension damper whose resistive force is readily controlled by an external electrical signal. The device was applied in a semi-active suspension system for the Army's high mobility multipurpose wheeled vehicle. In the future, more ER device will be developed.

2.4.5 ER properties

A good ER fluid should have: (a) high yield stress preferably equal to or larger than 5 kPa under an electric field of 2 kV/mm; (b) low current density passing through the ER fluid preferably less than 20 μA/cm²; (c) a wide working temperature range. A good ER fluid should give a strong ER effect within the temperature range -30 to 120°C; (d) a short response time. The response time of an ER fluid scales at 10⁻³ s. For some specific purposes, an even faster response is required; and (e) high stability. The ER fluid should be chemically and physically stable. (Hao, Tian, 2002)
The ER effect can be determined by the applied electric field strength and the frequency, particle conductivity, particle dielectric properties, particle volume fraction, etc.

In microstructural model, Bonnecaze (1992) described that the static yield stress increases with the dielectric constant ratio and dynamic yield stress dominated the rheology of the ER fluid at large electric field strengths.

Ikazaki (1998) studied the effect of dielectric properties both at hydrous and anhydrous ER fluids system which have a high ER effect. This effect increased with increasing difference between the dielectric constants below and above the relaxation frequency.

Zhang’s (2007) research is ER effect of Barium titanate nano-powders modified by coating with urea suspended in methyl-silicone oil. This ER fluid shows Bingham characteristics and the static shearing stress increases with an increase of the electric field strength.

Some researchers have reported that an ER suspension of urea coated BaTiO(C₂O₄)₂ particles can increase the static yield stress up to about 20 times (Wen 2003 and Hou 2006).

2.5 Electrospinning Technology

Electrospinning process is an efficient technique to generate the nano-scale fibers from polymer solution. (Huang Zheng-Ming 2003, Reneker, Darrell H 1996 and Greiner Andreas 2007)
Electrospinning is a simple technique, which uses high static voltage to electrically charge the polymer solution for producing ultra-fine fibers (Baji, Avinash 2001). The unique properties of electrospun nanofibers is the high surface area to mass ratio which make them attractive for many applications.

An electrospinning setup usually consists of a syringe filled with polymer solutions, which be charged with high voltage source, and electrospun fibers are collected by a grounded conductive collector. A custom made electrospinning station is shown in Figure 2.15 (a). A metering syringe pump is used to control the flow rate of polymer solution. The types of collector could be different, in order to meet different fiber collection requirement. Figure 2.15 (b) shows a SEM image of electrospun nonwoven ultrafine fibers.
In a typical process, the polymer solution is extruded from a needle to form a droplet under electric field effect. When high voltage is applied, the droplet will overcome the surface tension to induce the formation of a liquid jet that is subsequently accelerated toward a grounded collector. The droplet elongated into conical shapes, which is named “Taylor cone” (see Figure 2.16). As the solvent is evaporating, this liquid jet is stretched to many times its original length to produce continuous, ultrathin fibers of the polymer (Reneker, Darrell H. 2000 and Shin, Y. M. 2001). Under the usage of syringe pump, continuous feeding mode will exist, which many ultrathin fibers can be obtained in short time.
When the liquid jet is extremely elongated by high voltage, its structure characterization will have a change. Electrospinning fibers display different crystal structures compared to bulk polymer materials. Because of a high ratio of stretching, polymer molecules have an alignment along the fiber axis and a high degree of molecular orientations. During the fiber formation process, a fraction of the chains crystallizes to form lamellae consisting of small crystals and the remaining fraction forms the amorphous phase (Kongkhlang 2008, Lim 2008 and Baji 2008). Both the shape and the morphology of electrospun fibers are important to their applications.
2.5.1 Development of electrospinning

Although some polymers cannot electrospinning, but Sun Zaicheng (2003) described a process of core-shell nano-/meso-fibers by co-electrospinning of two materials (Figure 2.17). He found that co-electrospinning is of particular method for these core materials that will not form fibers via electrospinning by themselves.

Figure 2.17 Experimental setup used for co-electrospinning of compound core-shell nanofibers (left) and TEM of co-electrospun PEO as shell and PDT as core (right) (Sun Zaicheng 2003)

Co-electrospinning requires relatively coannular nozzles widely. Bazilevsky Alexander V. (2007) demonstrated a single-nozzle co-electrospinning technique to get core-shell structure polymer fibers similar to that attained via coannular nozzles using blends of PMMA/PAN solutions in DMF (Figure 2.18). In this mixing solution, the PMMA solution droplets trapped at the base of the Taylor cone issuing the PAN solution jet from its tip. By this way, the outer shell flow is sufficiently strong to stretch the inner droplet into the Taylor cone, thus forming a core-shell jet.
The electrospun fibers are often collected as randomly oriented structures in the form of nonwoven mats which can be used in many fields, but in others application, aligned and ordered structures are required.

By change the type of collector in order to control and improve the orientation of electrospun fibers, some researchers have much success. Li Dan (2003) reported a simple method that generated aligned nanofibers by introducing a gap into the conventional collector. Under this method, the nano-fibers were stretched across the gap to form a parallel array (Figure 2.19).
Pan Huan (2003) used a cylinder collector rotating at a high speed, which fibers can combine in a yarn. In this method, continuous, well-aligned and large area fabrics can be formed. Pan also conceded the influences of the concentration of the solution and proved that the fiber alignment becomes better at increasing take-up velocity; and fibers of more concentrated solutions can be collected continuously at higher velocity.
Figure 2.20 Schematic electrospinning setup for collection continuous aligned fibers (left up); A yarn of fibers is formed between the needles and a rotating aluminum shaft (left bottom); Well-aligned PVA fibers collected on a Teflon tube with different surface velocity 1.3 m/s (right up) and 2.3 m/s (right bottom).

Figure 2.21 Experimental setup for electrospinning with a collector can be moved linearly parallel (left); SEM pictures of aligned polystyrene fibers are parallel to each other with distance with stable range (right).

Sundaray, Bibekananda (2004) reported the formation of aligned polymer fibers with separation between the fibers in the range of 5–100 mm (Figure 2.21). This achievement is an important step toward the exploitation of these fibers in applications.
Katta (2004) reported a simple and successful method for spinning sheets with one centimeter wide strips of aligned nanofibers (see Figure 2.22). Katta used copper wires spaced parallel to form a circular drum. In some applications there is interest in the structure of parallel alignment nanofibers have unique properties, which can be used in electrical or optical applications.

2.5.2 Key parameters of electrospinning

The electrospinning parameters are used to control the shape, dimension, and morphology of electrospun fibers. Thompson, C. J. (2007) summarized the parameters affected to final cross-sectional radius of electrospun fibers which is shown in Table 2.2.
Table 2.2 Summary of dependence of the final cross-sectional jet radius on input parameters (Thompson, C. J. 2007)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Regression</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Parameters with strong effect</strong></td>
<td></td>
</tr>
<tr>
<td>Initial jet radius</td>
<td>Linear</td>
</tr>
<tr>
<td>Volumetric charge density</td>
<td>Linear</td>
</tr>
<tr>
<td>Distance from nozzle to collector</td>
<td>Power-law</td>
</tr>
<tr>
<td>Initial elongational viscosity</td>
<td>Linear</td>
</tr>
<tr>
<td>Relaxation time</td>
<td>Power-law</td>
</tr>
<tr>
<td><strong>Parameters with moderate effect</strong></td>
<td></td>
</tr>
<tr>
<td>Initial polymer concentration</td>
<td>Linear</td>
</tr>
<tr>
<td>Perturbation frequency</td>
<td>Linear</td>
</tr>
<tr>
<td>Solvent vapor Pressure</td>
<td>Linear</td>
</tr>
<tr>
<td>Solution density</td>
<td>Linear</td>
</tr>
<tr>
<td>Electric potential</td>
<td>Linear</td>
</tr>
<tr>
<td><strong>Parameters with minor effect</strong></td>
<td></td>
</tr>
<tr>
<td>Vapor diffusivity</td>
<td>Power-law</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>Linear</td>
</tr>
<tr>
<td>Surface tension</td>
<td>Linear</td>
</tr>
</tbody>
</table>
These mainly factors which affect the production of electrospun fibers during the electrospinning process can conclude into three parts: (a) The polymer solution properties, such as viscosity, elasticity, conductivity, and surface tension; (b) The process parameters, such as the gap distance between the capillary tip and the collector applied voltage, and hydrostatic pressure in the solution container; and (c) The environmental effects, such as temperature, humidity and air flow.

2.5.2.1 Solution concentration

The formation of electrospun fibers is primarily based on the viscosity and surface tension of the polymer solution. Different polymers require different solution concentrations to be electrospun.

![Figure 2.23 Variation of beaded fibers as net charge density changes due to the addition of NaCl (Fong H. 1999)](image)

It has been found that the polymer concentration also effects the formation of the beads. Figure 2.23 shows the representative images of beads and beaded fibers for solutions with a range of viscosity. The shape of the beads gradually changes from spherical to spindle-like, when the polymer concentration varied from low to high levels (Fong H. 1999).
2.5.2.2 Conductivity

The charge ions in the polymer solution greatly influence fiber formation. As the charges carried by the jet increase, higher elongation forces are imposed to the jet under the electrical field, resulting in smaller bead and thinner fiber diameters. Zong (2002) reported that relationship between the charge ions and fiber diameter. In Figure 2.24, different salts have different effects on the final fiber diameter. Because of the density of the charges carried by the jet, the size of the ions has an important impact on the resulting fiber diameter. Ions with smaller atomic radius have a higher charge density and thus a higher mobility under an external electric field (Zong 2002).

Figure 2.24 SEM images of PDLA membranes fabricated by electrospinning of a 30 wt% solution at voltage of 20 kV, feeding rate of 20 μm/min and with 1 wt% of (A) KH2PO4; (B) NaH2PO4.

2.5.2.3 Evaporation of solvent

During the electrospinning process, the solvent evaporates rate leads to the rapid solidification of electrospinning jet and results in the imperfect crystallites in electrospun fibers, then the morphology of electrospun fibers (Huang, Zheng-Ming 2003).
Bognitzki (2001) used highly volatile solvents to produce PLLA fibers and obtained electrospun fibers with a regular pore structure being oriented along the fiber axis (see Figure 2.25). This regular phase morphology is generated by rapid phase separation during the electrospinning process. The solvent rich regions are apparently transformed into pores. Lee (2002) studied the effect of volume rate of the solvent on the fiber diameter and morphology of PVC fibers. They found that as the amount of DMF in the THF/DMF mixed solvent increased, the average fiber diameter decreased.

![SEM micrographs of porous PLLA fibers obtained via electrospinning of a solution of PLLA in dichloromethane](image)

Figure 2.25 SEM micrographs of porous PLLA fibers obtained via electrospinning of a solution of PLLA in dichloromethane

2.5.2.4 Applied voltage

In general, applied high voltage will cause high deposition rate due to large amount of mass flow from the needle tip. Deitzel (2001) found that the fiber morphology changed from a defect free fiber at 5.5 kV to a highly beaded structure at 9.0 kV in polyethylene oxide-water system.
Megelski (2002) determined the dependence of the fiber diameter of polystyrene fibers on voltage, and showed that the fiber size decreased from 20 mm to 10 mm when the voltage was increased from 5 kV to 12 kV. Kidoaki, Satoru (2005) considered the effect of polymer concentration and Voltage (see Figure 2.26). An increase in concentration resulted in a significant increase in fiber diameter; an increase in voltage from 9.2 kV to 25 kV did not induce a significant change in the mean diameter of the fibers, but still have some effect.

Figure 2.26 Mean diameter of electrospun type I collagen as a function of (a) collagen concentration and (b) voltage.

2.5.2.5 Capillary tip-to-collector distance

When tip and collector are closer to each other, the effect of fiber deposition time, evaporation rate, and instability interval will enlarge, subsequently fiber characteristics will have a change.
Megelski (2002) demonstrated that the morphology changed from round to flat shape when the nozzle-collector distance is decreased. Lee, Keun Hyung (2002) also showed the effect of the tip-to-collector distance (Figure 2.27). A 15 wt % PVC solution dissolved in THF/DMF with a 50/50 volume ratio was used for the electrospinning. From the image, we can found the average fiber diameter decreased with an increasing tip-to-collector distance,

![SEM micrographs of electrospun PVC fibers as a function of the tip-to-collector distance: (a) 6, (b) 10, and (c) 15cm.](image)

2.5.2.6 Flow rate

Megelski (2002) found that the flow rate of polymer solution affects the jet velocity and the material transfer rate with enhanced pore and fiber sizes and beaded structures, as well with an increase in the polymer flow rate in case of polystyrene fibers. Many experiment data shows a power law relationship between electric current and solution flow rate under the condition of fixed voltage. In addition, He (2005) got that the charged jet can be considered as one-dimensional flow, conservation of mass gives

\[ \pi r^2 u \rho = Q \]

where \( Q \) is the mass flow rate, \( r \) is radius of the jet, \( u \) is the velocity, \( \rho \) is density.
2.5.3 Potential applications for electrospun fibers

Since the properties of electrospinning technology and electrospun fibers: the diversity of electrospinnable materials and the unique features associated with electrospun fibers, there are lots of possibilities in various applications (Doshi Jayesh 1993, Fang Jian 2008 and Huang Zheng-Ming 2003).

Na (2012) produced PVDF/PVA microtubes by coaxial electrospinning. This uniform hollow structure could be utilized as responsive fibers that can be controlled by mechano-electric coupling. The silicone oil can be modified as magneto-rheological and/or electro-rheological fluids whereby mechanical deformation can be activated by electrical signals and vice versa. Such a design in materials integration will lead to numerous industrial applications such as actuators made of polymer fibers (Figure 2.28).

Figure 2.28 Wicking experiment of PVDF/PVA microtubule with silicone oil. The schematic of wicking test (bottom left) shows one end of the PVDF/PVA microtubule soaked into silicone oil and the other end in open air. Optical micrograph shows the meniscus (arrows) of the silicone oil rises (top half) due to capillary action. The wicking process is recorded as a function of time (s) (bottom right plot).
Gopal (2006) use PVDF electrospun nanofibrous microfiltration membrane to remove micro-particles in the range of 5-10 μm effectively without any damage to the membrane (Figure 2.29). There is a potential of using these membranes as pre-filters prior to ultrafiltration or nanofiltration to minimize the possibility of fouling and contamination from micro-organisms or micro-particles and also to separate cells.

Since electrospun nanofibers with a high surface area to volume ratio, their potential applications received much attention in biomedical devices, tissue engineering scaffolds, and drug delivery carriers.
Synthetic polymers can be controlled easier by electrospinning compare with natural polymers. Yoo (2009) summarized surface modification strategies of electrospun polymeric nanofibers for controlled drug delivery and tissue engineering. Surface modification of nanofibers includes plasma treatment, wet chemical method, surface graft polymerization, and co-electrospinning of surface active agents and polymers. A variety of bioactive molecules including anti-cancer drugs, enzymes, cytokines, and polysaccharides were entrapped within the interior or physically immobilized on the surface for controlled drug delivery. Surfaces of electrospun nanofibers were also chemically modified with immobilizing cell specific bioactive ligands to enhance cell adhesion, proliferation, and differentiation by mimicking morphology and biological functions of extracellular matrix.

The electrospun nanofiber mesh possesses highly interconnected open nanoporous structure with a high specific surface area, offering an ideal condition for sustained and local drug delivery. Various surface modification techniques for applying synthetic polymer nanofibers to tissue engineering and drug delivery are presented in Figure 2.30.
Figure 2.30 Surface modification techniques of electrospun nanofibers. (A) Plasma treatment or wet chemical method. (B) Surface graft polymerization. (C) Co-electrospinning.
Townsend-Nicholson (2006) used coaxial electrospinning technology for the generation of scaffolds comprised of living cells. This way deposit active biological threads and scaffolds. Figure 2.31 (left) showed coaxial needle arrangement where a concentrated living biosuspension inside and a medicalgrade poly(dimethylsiloxane) (PDMS) medium outside. Using this technique, they got the finest cell-bearing composite microthreads (Figure 2.31 right). And from collected cells, there is no evidence of having incurred any cellular damage during the bionanofabrication process. This study demonstrated the feasibility of using coaxial electrospinning technology for biological and biomedical applications requiring the deposition of living cells as composite microthreads for forming active biological scaffolds.

Figure 2.31 A schematic representation of the generated thread (left); Characteristic photomicrographs of collected cells cultured over an incubation period of 9 days (right).
Most researchers have studied the modification of the electrospinning conditions and apparatus for obtaining fibers with different sizes, shapes, morphologies, structures, alignments (Demir Mustafa Muammer 2002, Bognitzki Michael 2001 and Casper Cheryl L. 2004). The applications of electrospun nanofibers have a broad range of fields, such as filtration (Gopal Renuga 2006, Gibson Phillip 2001), composite reinforcement, smart textiles, biomedical applications including drug delivery (Zeng Jing 2003), scaffold (Li Wan-Ju 2002), tissue engineering (Sill Travis J. 2008 and Li Mengyan 2006), and wound dressing, functional materials (Ko Frank 2003), energy and electronics such as batteries/cells (Kim Chan 2006), sensors and catalysts (Lu Ping 2008).

Figure 2.32 Potential applications of electrospun polymer nanofibers. (Huang Zheng-Ming 2003)
These application fields based on electrospun polymer nanofibers have been steadily extended especially in recent years. A distribution of patents based on the field of electrospun fiber applications is urgently increased in recent years. Huang Zheng-Ming (2003) summarized e perspective application areas shown in Figure 2.32. Although most of these applications have not reached industry level and still stay at a laboratory research and development stage, their promising potential attracted attentions and investments from academia, governments, and industry all over the world.

2.6 Rolling resistance test method in industry

In industry, the basic principle of tire rolling resistance measured in a laboratory is in that a tire is mounted on a free-rolling spindle, loaded against a large-diameter powered test drum, turned by the drum to simulate on-road rolling operation, and rolling loss evaluated (Evans 2009). The concept of rolling resistance in the book The Pneumatic Tire (LaClair, 2006):

“Rolling resistance is the effort required to keep a given tire rolling. Its magnitude depends on the tire used, the nature of the surface on which it rolls, and the operating conditions - inflation pressure, load and speed.”

In laboratory test, rolling resistance (energy loss) is calculated by measuring the amount of additional force, torque, or power necessary to keep the tire rolling at the test conditions.

A picture of a laboratory rolling resistance test using a force method can be seen in Figure 2.33.
During the test, the loaded radius ($r_L$) of the tire is measured during the steady-state conditions. According to ISO 28580 the Rolling Resistance ($F_r$) at the tire/drum interface is calculated by the following equation:

$$F_r = F_t \left[1 + \left(\frac{r_L}{R}\right)\right] - F_{pl}$$

$F_t$ is spindle force, $r_L$ is ratio of the loaded tire radius, $R$ is wheel radius, $F_{pl}$ is the skim load.
There is another test method used a torque method machine. The torque method measures the torque required to maintain the rotation of the drum. The drum is connected to the motor through a “torque cell”.

In order to improve elastomeric products, we need to measure the rolling resistance of tire components. Most prior researchers use apparatus and methods to measure hysteresis or modulus to get the rolling resistance. From these parameters, we can obtain an approximation of rolling resistance. These indoor rolling resistance test methods simulate the real road condition, and calculate energy loss during rolling. But for research of new tire materials, it’s impossible to take a huge amount to do these tests. Gent (2007) invented a laboratory method to directly test the rolling resistance which a small amount of materials are needed. (Figure 2.35) This apparatus comprises a roller for rolling contact with a substrate to be measured, an arm attached to the roller and extending downward from said roller to free space below the roller, a swing weight integral with or attached to the arm distal from the roller.

The apparatus may further comprise a lever attached to the roller for controlling the initial amplitude of the swing weight when a rolling resistance measurement is taken.
In the illustrated embodiment, the roller is a cylinder, and the arm extends at substantially 90° horizontally outward from the mass center of the roller, and is further directed downward to a location below the roller. An acoustic emission device is used to measure and collect data.

2.7 Summary and considerations of research plan

Tire plays an important role in the total fuel consumption of a passenger car. The balance of magic triangle can be achieved by "green tire" technology. Two important tire requirements are rolling resistance (fuel consumption) and wet grip (safety) for economy and environment. A new rubber composite to be developed which allows the tire rolling resistance to be reduced while improving the wet grip performance.
Filler reinforced rubber is an easy but effective technology to modify rubber, which is still in development. From the existing research work indicate that future studies are necessary to understand the interactions in filler-rubber network systems, especially under the external effect.

Carbon black and silica both are the common fillers to modify the rubber performance. Rubber/carbon black or silica composite provides better grip and braking, lower rolling resistance compare with pure nature rubber in tire compounds and tire application. In summary, carbon black filler will increase the rolling resistance and wet grip but reduce wear resistance; whereas the silica filler plays an opposite impact in some part. Especially, in rubber/carbon black composite has an enhancement of strength and strength-related properties. But these particles aggregating in the rubber need to solve urgently, which reduce the composite properties. Moreover, the rolling resistance property of composite is stable cannot be tuned in recently studies.

ER fluids are commonly polarizable particles suspense in a non-conducting dielectric liquid. These particles inside can form columns along the electrical field, and became disorder immediately when the electrical field is disappeared. ER fluid has high yield stress, shearing stress, wide working temperature and short response time under electrical field. BaTi (C₂O₄)₂ nanoparticles coated with urea suspense in silicone oil has a giant electrorheological effect, which will be used in my work. This adjustable fluid compound with rubber will be a new concept for smart tire.
From the previous research, the smart tire is only limited in using sensor to monitor tire strain to improve the tire reliability. The fuel saving is urgent to solve in the new generation of tire industry.

In order to enable future smart tire technology, rolling resistance needs to be responsible to environmental conditions. In this work, smart materials with adjustable coefficient of rolling resistance will be prepared by mixing silicone rubber with ER fluid. The ER fluid in composites can be polarized under electric field easily, which will induce the change of rubber properties. In this way, rolling resistance will be controlled by external factors.

Rubber composite with smart property needs to be developed urgently. A pendulum-acoustic emission device is adopted to evaluate the rolling resistance of different type materials in our lab. In this study, BaTi (C₂O₄)₂ nanoparticles coated with urea suspense in silicone oil is used as ER fluid. The effect of external electrical field will be investigated throughout the experimental study. Influence of ER fluid content and configuration in rubber will also be addressed in the study. Through this work, the smart composites would gain more knowledge in mechanisms and knowledge and will find applications in tire and other field.
CHAPTER III

A STUDY OF ROLLING RESISTANCE OF ELECTROSPUN POLYMER FABRICS

3.1 Objectives

The rolling resistance is found to depend on viscoelastic properties, adhesion and surface characteristics. In this topic, we evaluated the rolling resistance using a free oscillation of a pendulum. Different substrate materials such as asphalt, rubber, wood, high-density polyethylene (HDPE), nylon, polycaprolactone (PCL) and poly(vinylidene fluoride) (PVDF) were tested by a laboratory fabricated pendulum steel roller. The damping factor is examined using an envelope analysis technique based on Hilbert transform methodology.

3.2 Introduction

Rolling resistance, which consists of a hysteresis loss due to viscoelastic deformation and surface characteristics such as adhesion, friction and drag, is an important parameter for tires design and development. Currently, the development of tire materials is based on a correlation between rolling resistance and the viscoelastic properties of the rubber compounds, particularly the loss factor, tanδ. Surface and sub-
surface phenomena are not taken into account. A change in bending stiffness of fibrous structures critically influences the ability of fibers to meander through surface asperities, thus altering the adhesion and rolling resistance of materials.

Lower fuel consumption of next generation vehicle and tires designs is a primary driving force behind an understanding of rolling resistance in materials and tires. Furthermore, to enable future smart tires technology, rolling resistance needs to be fine tuned in response to environmental conditions. For example, when a vehicle is climbing uphill a higher rolling resistance is desired to give a greater torque for push. When the vehicle is running on a highway, a significantly reduced rolling resistance is essential to fuel consumption. Understandings of how one can control rolling resistance in materials and tires design are thus essential.

Rolling resistance is a complex phenomenon due to its dependency on various factors such as: contact geometry, materials, frequency of stressing, surface conditions, load and temperature. The elastic hysteresis considers that rolling resistance, \( F \), of elastic bodies in terms of a hysteresis loss factor \( (\alpha) \), defined as the fraction of the input energy (or the elastic work of compression) per unit distance rolled \( (\Phi) \) which is dissipated by internal friction.
The importance of differentiating contributions of contributing factors like adhesion, slipping, and viscoelastic energy loss due to cyclic deformation of contacting roller and substrate. In this study, the elastic-plastic behavior and adhesion energy of three kinds of polymers electrospun membranes are studied. The rolling resistances of different polymer membranes are measured on different substrates. A simple interdependent relationship between adhesion energy and rolling resistance is evident.

3.3 Experiment

 Electrospinning method is used to prepared nano-scale electrospun membrane, high-density polyethylene (HDPE), nylon, polycaprolactone (PCL) and poly(vinylidene fluoride) (PVDF) will be used as polymer fabrics. And we evaluated the rolling resistance using a free oscillation of a pendulum.

3.3.1 Materials

 PVDF (Kynar761) was supplied by Arkema Incorporation. Polycaprolactone (PCL) (CAS 24980-41-4) and Nylon 6 (CAS 25038-54-4) with a molecular weight of 244 g/mol were purchased from Sigma-Aldrich.

 PVDF (Figure 3.1) is a specialty plastic material in the fluoropolymer family; it is used generally in applications requiring the highest purity, strength, and resistance to solvents, acids, bases and heat and low smoke generation during a fire event. It has a low melting point of around 177 °C (Wikipedia Polyvinylidene fluoride).
Piezoelectric property is a unique and important property for PVDF, which is commonly used as insulation on electrical wires, because of its combination of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance. Electrospinning of PVDF polymer is widely studied by researchers (Choi 2003, Yee 2007, Zhao Zhizhen 2005, Na 2012, and Baji 2012). Their research focuses on controlling internal parameters, and determines the physical properties.

Figure 3.1 Repeat unit of Polyvinylidene fluoride

Polycaprolactone (PCL) is a biodegradable polyester with a low melting point of around 60°C and a glass transition temperature of about -60 °C (Figure 3.2). The most common use of polycaprolactone is in the manufacture of speciality polyurethanes. Polycaprolactones impart good water, oil, solvent and chlorine resistance to the polyurethane produced (Wikipedia Polycaprolactone).

PCL as aliphatic polyester and its copolymers are biodegradable polymers that have been used in biomedical and industrial application due to their biodegradability. PCL has crystallizable rubbery properties so has been widely utilized for improving elasticity (Lee 2003).
It has physical properties of a very tough, nylon-like plastic that melts, and easily achieved by immersing in hot water. PCL's specific heat and conductivity are low enough that it is not hard to handle at this temperature. This makes it ideal for small-scale modeling, part fabrication, repair of plastic objects, and rapid prototyping where heat resistance is not needed.

![Repeat unit in PCL structure](image)

Figure 3.2 Repeat unit in PCL structure

Electrospinning PCL fiber is well development by researchers these years. They change the polymer solution properties, process parameters to effect the morphology and physical properties (Zhang YZ 2005, Yoshimoto H 2003, Wong 2008, Baji 2007 and Shi 2010).

Nylon 6 (Figure 3.3) is a semicrystalline polyamide. Unlike most other nylons, nylon 6 is not a condensation polymer, but instead is formed by ring-opening polymerization; this makes it a special case in the comparison between condensation and addition polymers. Its melting point is 219.9°C. Nylon 6 fibers are tough, possessing high tensile strength, as well as elasticity and luster. They are wrinkle-proof and highly resistant to abrasion and chemicals such as acids and alkalis. The fibers can absorb up to 2.4% of water, although this lowers tensile strength. The glass transition temperature of Nylon 6 is 47 °C (Wikipedia Nylon 6).
Since its high strength property, it is widely used for gears, fittings, and bearings, in automotive industry for under-the-hood parts, and as a material for power tools housings. Nylon 6 is used as thread in bristles for toothbrushes, surgical sutures, and strings for acoustic and classical musical instruments, including guitars, sitars, violins, violas, and cellos. It is also used in the manufacture of a large variety of threads, ropes, filaments, nets, and tire cords, as well as hosiery and knitted garments. It can also be used in gun frames (Fong 2002, Jose 2007, and Baji 2010).

![Figure 3.3 Nylon 6 structure](image)

Some researchers (Liu 2007, Dong 2008, Li Lei 2006, Ryu 2003 and Baji 2011) are compound nylon 6 with other materials in order to get a composite with better physical properties. Recent work has been focused on trying to prepare ultra-fine fibers with excellent mechanical properties and smooth fibers like skin.

- N, N-Dimethylformamide (DMF) and acetone from Fisher Scientific, dichloromethane (DCM) from BMD Chemicals Inc., and formic acid from EMD Corporation are used as fiber precursors. Rubber gaskets, wood, copper, steel are from Home Depot and asphalt came from Ohio department of transportation.

3.3.2 Preparation of the electrospun membranes

Two concentrations of PVDF solutions (0.15 g/ml and 0.17 g/ml) are prepared by dissolving PVDF in DMF and acetone with a volume ratio of 7:3 at 40-50°C for 2h.
The conditions for electronspinning are 0.3mL/h solution rate and applied voltage 10kV. PVDF 1 and PVDF 2 are prepared with different solution concentrations, respectively.

DMF and dichloromethane with a volume ratio of 1:2 are used to dissolve PCL at 25°C for 3h. 0.16g/ml PCL solutions are prepared to electrospin PCL fibers with solution feed rate 0.5mL/h, and applied voltage 10kV.

Nylon 6 is dissolved in formic acid at room temperature for 4h. Nylon 6 fibers are fabricated using 0.4 g/ml solution with solution feed rate 0.24 mL/h and an applied voltage 25kV.

These three polymer solutions are electrospun into nonwovens membrane by using a single syringe setup (Figure 3.4) under specific voltage and the needle is positioned 15 cm from the collector. After 10 h, the sample membranes are collected on aluminum foil and dried in vacuum oven at 50°C for 12 h.
Figure 3.4 Electrospinning setup in laboratory

3.3.3 Characterization of electrospun fibers

SEM characterization, mechanical testing (tensile test) and rolling resistance test will be used to characterize the property of electrospun fibers.

3.3.3.1 SEM characterization

Morphology and the average fiber diameter of electrospun membranes are examined by scanning electron microscope (SEM, JEOL JSM-6510LV, Figure 3.5), which uses second electrons and back-scattered electrons.
Before scanning, all samples are coated with silver by sputter coater (K757x, Emitech) for 90 seconds at 55A. Average fiber diameter is determined from SEM micrographs by software Image J. For each sample, more than 200 fibers from at least 5 images were measured for calculation.

Figure 3.5 Scanning electron microscope

3.3.3.2 Mechanical testing

The tensile test is used to understand materials’ mechanical properties. From the test, we will know the elastic modulus, yield strength, strain-hardening, etc.

Tensile test is using 500 N load cell in Instron 5582 machine (Figure 3.6) at room temperature, and is repeated five times for each sample (shape as Figure 3.7) and strain rate is 5 mm/min. The thickness of each sample is tested 5 times to get an average value.
Figure 3.6 Mechanical property of electrospun fabrics is performed by Instron 5582 machine equipped with a 500 N load cell

Figure 3.7 The shape of each sample used for tensile test in research

3.3.3.3 Rolling resistance measurement

In this paper, we adopt Gent’s (2007) method to directly test the rolling resistance which a small amount of materials are needed.

A pendulum-acoustic emission device (Figure 3.8) is used to evaluate the rolling resistance of different type materials in our lab. The Go! Motion sensor was purchased from Vernier Software & Technology. Each sample is cut to square of 10 cm by 6 cm for measurement. Figure 3.9 shows a date collection from rolling resistance test.
Figure 3.8 Rolling resistance measurement setup

Figure 3.9 Collection data from Figure 3.8
According to ISO28580, rolling resistance ($F_r$) is the lost per distance covered and calculated by the following equation:

$$F_r = mgL(\cos\theta_{eval} - \cos\theta_{st})/d_C$$

Where $\theta_{eval}$ is the angular position of the pendulum bar after N oscillations; $\theta_{st}$ is the angle when pendulum bar is released; $d_C$ is the distance covered within N cycles.

Test substrates are wood, copper, electrospun nonwoven polymer membrane, asphalt, steel, rubber (see Figure 3.10).
3.4 Summary and discussion

Different substrate materials such as asphalt, rubber, wood, nylon 6, PCL and PVDF were tested by a laboratory fabricated pendulum steel roller. The damping factor is examined using an envelope analysis technique based on Hilbert transform methodology.

3.4.1 Effect of polymer properties to fiber diameter and morphology

By using different polymer solutions, the morphology and fiber diameter is changed, which affect the rolling resistance of polymer membrane.

Figure 3.11 SEM micrographs of electrospun PCL fibers at 0.16g/ml solution concentration
Figure 3.12 SEM micrographs of electrospun PVDF fibers at solutions concentration of (a) 0.15 g/ml as PVDF1 (b) 0.17 g/ml as PVDF2

Figure 3.13 SEM micrographs of electrospun nylon 6 fibers at 0.4g/ml solution concentration
From Figure 3.14, PCL fabrics have a largest wide range. Their fiber diameters are 529±228nm, 385±115nm, 689±196nm, 532±128nm.

3.4.2 Effect of polymer type on mechanical property by tensile test

In order to study the effect of polymer properties on their tensile test, the PCL, PVDF1, PVDF2 and nylon 6 fibers were subjected to tensile testing. Figure 3.15 shows the representative stress vs. strain curves.
Figure 3.15 shows the tensile stress-strain curves of four different electrospun polymer fibers. PCL gives rise to the highest rate of change of stress as strain increases whereas PVDF gives the lowest. The materials with higher modulus are found to have lower failure strains. The elastic modulus and tensile strength data are provided in Table 3.1. A preliminary observation of Table 3.1 shows that PCL specimen has higher elastic modulus in these four kind polymers.

Table 3.1 Variation of elastic modulus and ultimate strength of electrospun polymer membranes

<table>
<thead>
<tr>
<th></th>
<th>PCL</th>
<th>Nylon 6</th>
<th>PVDF1</th>
<th>PVDF2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus (MPa)</td>
<td>690</td>
<td>498.5</td>
<td>198.6</td>
<td>234.3</td>
</tr>
<tr>
<td>Ultimate strength (MPa)</td>
<td>98.7</td>
<td>119.9</td>
<td>79.54</td>
<td>114.4</td>
</tr>
</tbody>
</table>
From Figure 3.16, PCL electrospun membrane keeps almost same configuration as the image before test compared with other three polymers, which shows the highest elastic modulus. Both PVDF membrane changes a lot during the test, which show the lower elastic modulus and ultimate strength.
3.4.3 Effect of substrate type on rolling resistance

The rolling resistance \( (F_r) \) of electrospun polymer membranes was determined by rolling resistance testing. A pendulum rolling apparatus was used to assess the coefficients of rolling resistance and normalized damping factors of selected materials. The coefficient of rolling resistance \( (C_r) \) is the rolling force \( (F_r) \) normalized against the normal force \( (N) \) between the roller and the substrate.

\[
C_r = \frac{F_r}{N}
\]

Two substrate pairs were used such that the roller surface could be modified with electrospun polymer fabrics including nylon, PCL and PVDF, and rubber for contact with asphalt, rubber, steel, copper and wood. The steel roller was also tested without the upper substrate and it is denoted as "self" in Figure 3.17 and Figure 3.19.

Using rolling resistance measurement apparatus shown in Figure 3.8, the coefficients of rolling resistance for different substrates are found and the results are provided in Figure 3.17.
In Figure 3.17, the modeled substrates are asphalt (A), copper (C), HDPE (H), rubber (R), steel (S) and wood (W). Since asphalt exhibits the highest surface asperities relative to other substrates, the contribution of surface roughness against rolling is higher in the case of asphalt. On the other hand, the difference between the rolling resistance values for copper, steel, and rubber is mainly caused by the change in their hysteresis loss properties.

Placing different polymers and fabrics between the roller and the substrate increases adhesion and viscoelastic loss effect. It is evident that some fabrics exhibit lower rolling resistance relative to rubber. Compared to the main tested materials, asphalt consistently shows the relatively highest rolling resistance; rubber demonstrates the second highest in comparison.
Combined with Figure 3.15 and 3.17, we can get the Figure 3.18. In this figure, we can see that there is consistently positive correlation between elastic modulus and rolling resistance coefficient. But for different type of polymer electrospun membrane, the polymer property still has effect on both of them. For PVDF, the elastic modulus of same type polymer keeps consistency with fiber diameters. Comparing with the other two types polymer: PVDF and Nylon 6, the glass transition temperature of PCL is below zero degree, which effects the mechanical property and rolling resistance.

3.4.4 Effect of substrate type on non-dimensional damping factor

In signal processing, the Hilbert transform is used to derive the analytic representation of a time signal containing a rapidly-oscillating component.
With this method (N. Thrane, 1984), an exponentially decay “envelope” \( Y(t) \) is obtained. The envelope is the amplitude of a complex signal which its real part is the real valued signal \( y(t) \) and its imaginary part \( \tilde{y}(t) \) is a signal obtained by shifting the real valued signal phase by 90° (Hilbert Transformed signal of real valued time history \( y(t) \)).

![Figure 3.19 Damped oscillations of pendulum](image)

The following equation used to obtain the non-dimensional damping is

\[
\xi = \frac{\log \left( \frac{Y(t_i)}{Y(t_j)} \right)}{\Delta t \cdot \omega_0}
\]
where $\xi$ is the normalized damping of the system, $Y(t_i)$ the displacement envelope of the pendulum oscillations (Figure 3.19), $\omega_0$ the natural frequency of the pendulum evaluated transforming the oscillations in the frequency domain, $\Delta t$ is time change between time $t_j$ and $t_i$.

Non-dimensional damping of the pendulum oscillations is obtained using this equation and the result is shown in Figure 3.20. Asphalt has relatively higher damping factor than rubber while electrospun membranes appear the lower. Damping results correlate well with the coefficient of rolling resistance; materials against asphalt demonstrate the highest damping values. PVDF2, PVDF1 and PCL consistently show lower damping values than rubber. This result provides the potential possibility of electrospun membranes improve the rolling resistance in rubber composite.

![Figure 3.20 Non-dimensional damping](image-url)
Based on an analysis of the measured pendulum oscillations, it is evident that the pendulum oscillates with a frequency below 1Hz as in Figure 3.21. This result differs from the assumption that the swing amplitude fell at constant rate until it became small, when the rate of decay itself decreased (Gent, 2007). Evaluating the frequency of oscillations for different materials, electrospun membranes exhibit the longer damping time relative to asphalt.

Figure 3.21 Non-dimensional damping and natural frequency

3.5 Industry process design in new tire generation (Wong 2013)

Since rubber viscoelasticity is not generally variable in the end product, understanding that certain rubber may benefit from the ability to vary the elastic modulus, whether time-dependent or time-independent, thereof, this part seeks to provide methods for making them.
When rolling resistance of tires could be reduced by even a small percentage, fuel consumption could be significantly lowered. However, merely providing tires with significantly lower or higher rolling resistance is not an acceptable solution in new tire generation. For example, the condition on a highway would not the same as driving mountainous roads and lifting heavy loads which required higher torque, frictional force and traction in tires. Thus, there is a need in the art for rubber articles, and particularly tires, in which the elastic modulus and time-dependent elasticity thereof can be varied.

ER fluids are suspensions of extremely fine non-conducting particles (up to 50 micrometres diameter) in an electrically insulating fluid. The apparent viscosity of these fluid changes reversibly in response to an electric field. For example, a typical ER fluid can go from the consistency of a liquid to that of a gel or even solid, and back, with millisecond-scale response time. The effect is better described as an electric field dependent shear yield stress. Hence the resistance to motion of the fluid can be controlled by adjusting the applied electric field.

This part introduces some manufactory method to incorporate electrorheological fluid into the polymeric materials. In this way, ER fluid is responsive to the application of an electric field to change the apparent viscosity or elastic modulus of the polymeric part. In particular embodiments, the electrorheological fluid is introduced to the rubber article through composite processing, wherein the electrorheological fluid is incorporated into woven or non-woven fabrics, fiber performs or discreet chopped strands and discontinuous fibers on tows and prepregs.
In particular embodiments, the rubber articles are tires, and the incorporation of electrorheological fluid therein allows the elastic modulus and thereby viscoelasticity and rolling resistance of the tire to be modified by the application of electric field across the electrorheological fluid containing structures.

A way of incorporating a woven or non-woven fabric electrorheological composite into a ply of polymer is shown in Figure 3.22. A woven or non-woven fabric is fed from a roll to pinch rolls along with the polymer carrier mat fed from roll. The pinch rolls press the two components together to form a composite material. This composite material is fed over a roll to an electrorheological fluid bath. Rollers are positioned within the volume of ER fluid, and the composite must travel through the fluid around the succedent rollers. This creates an electrorheological composite of the woven or non-woven fabric type. This electrorheological composite and carrier mat is collected at a take-up roll after being guided from the electrorheological fluid bath by a roller. Optionally, the electrorheological composite might be further pinched at pinch rolls. The ply collected at take-up roll can then be used to form articles, such as tires.

Figure 3.22 A general schematic of an exemplary method of creating a polymeric article in accordance, employing a fabric to receive electrorheological fluid.
Another method of incorporating ER fluid onto a fiber is shown in Figure 3.23. Multiple tows are advanced from tensioners through an electrorheological fluid bath holding an ER fluid. As the ER fluid-coated fibers exit the bath, they advance together by a guide aperture onto a moving platform. The moving platform moves laterally relative to a rotating mandrel so as to efficiently wind the grouping of ER fluid-coated fibers (or tows) on the mandrel. These fibers or tows can then be used to create woven or non-woven fabrics in tire application.

Figure 3.23 A general schematic of an exemplary method of creating electrorheological fluid bearing tows for use in this invention.
Referring to Figure 3.24, another method is provided and designated. In this method, a carrier mat is advanced from a carrier mat roller underneath a sprayer for spraying chopped fibers onto the exposed surface of the carrier mat. The carrier mat with discrete fibers is passed through an electrorheological fluid bath holding ER fluid. This coats the discrete fibers with ER fluid, and the assembled carrier mat and discrete fibers can be employed to create polymeric articles in application, such as tires.

Figure 3.24 A general schematic of an exemplary method of creating a polymeric article in employing chopped fibers to be immersed in electrorheological fluid.

There is still a method used for produce the polymer fibers incorporate with electrorheological fluid (see Figure 3.25). Under the effect of pump, the polymer melt go into the filter, and flow through spinneret, where the fiber size melt become fibers with temperature change under cold air. The spinning tower will force together using a roller, and go through ER fluid bath. There is a roller to control the electrorheological fluid volume.
After that, melt spinning fibers with ER fluid composite collect in package. This method compound electrorheological fluid with polymer melt spinning fibers during the fiber process, which will induce a better combination between ER fluids with fibers.

Figure 3.25: The polymer fibers made by melt spinning will be guided into ERF bath, then ERF impregnated polymer fiber will be wound into a tow.

Different ER fluids will be suitable for different applications, and many ER fluids exist and it is expected that many will be developed in the future. The present work focuses upon methods for incorporating ER fluid into polymeric materials which can be made to change its viscoelastic modulus by application of electric field. Different ER fluids will have different field strengths to alter the viscoelastic modulus.
In a particularly tire application, and the ER fluid is provided either as ER fluid filling a pocket or as an electrically-responsive component (fabric, fiber, perform, prepreg) so that the rolling resistance of the tire can be altered by the application of an electric field across the tire body. This is generally represented in Figure 3.26, wherein a smart tire includes a tire having an ER fluid therein (the suspended particles are represented). An electric field can be generated across the ER fluid, a switch and an adjustable voltage source measured by a voltmeter. Upon the application of an electric field of suitable strength, the ER fluid responds through particle alignment along the direction of electric filed lines and the elastic modulus of the tire is affected, creating a stiffer tire.

Figure 3.26 A general schematic representation of the application of this invention in a tire.
Many different ways, which introduce the ER fluids to the polymeric article might be found preferably for a given purposed. The ER fluid is part of a composite fabrication incorporated into the polymeric article. These microspheres are named as “electrorheological microspheres”. The composite fabrication may take many forms, including fibers, fabrics, tows, fiber performs and fiber prepregs that are introduced into an ER fluid bath so as to be fully soaked with stable electrorheological suspensions.

The electrorheological composites and electrorheological microspheres are collectively understood as "electrically-responsive components.” In the application of vehicle tires, the application of electric field could be employed to selectively increase the elastic modulus of the tires when decreased rolling resistance is desired, as, for example, when travelling at higher speeds on smoother surfaces such as highways. When improved tire responsiveness is desired, the electric field could be removed to decrease the elastic modulus of the tires, to provide great traction and vehicle stability in the condition needs higher rolling resistance.

An electroactive polymer will exhibit a change in size when stimulated by an electrical field. Some electroactive polymers, known as piezoelectric polymers, also conversely generate an electrical field (or electric polarization), when mechanical stress (eg. pressure) is applied to the polymers. Suitable piezoelectric polymer may broadly be selected from any polymer exhibiting this property, whether currently existing or hereinafter discovered. It is noted that piezoelectric polymers are the focus of much research in present times such that other specific types of piezoelectric polymer will likely be developed.
The combination between piezoelectric polymers and electrorheological composites (Figure 3.27) has a huge potential application in new generation tire. When there is a stress applied to the piezoelectric materials, electrical field will be produced. Under the effect of electrical field, the electrorheological fluid in composites will have a structure change which induced the change of composite stiffness. In this way, the rolling resistance will have a change. This combination structure has ordinary skill in specify area, especially in tire.

Figure 3.27 Piezoelectric materials and electrorheological composites
In a particular embodiment, the composites or spheres herein are incorporated into the body ply of a tire. As such, the ER fluid may be incorporated into common fabrics or microspheres employed to manufacture tires, and the electrorheological composite or filled microsphere formed by adding the ER fluid to the fabric is commonly incorporated into the tire. That is, by incorporating the ER fluid into a common tire fabric, the typical manufacturing process of the tire can be followed, but with ER fluid beneficially present in the body ply.

3.6 Conclusions

A pendulum rolling apparatus was used to assess the coefficients of rolling resistance and normalized damping factors of selected materials. Two different substrates were used in pairs such that the roller surface could be modified with electrospun polymer fabrics including nylon 6, PCL and PVDF for contact with asphalt, rubber, steel, copper and wood. As substrates, asphalt consistently gives rise to the highest rolling resistance and the shortest damping time, while steel produces the lowest rolling resistance and the longest damping time. Electrospun polymer fabrics appeared to provide a tuning opportunity for changing the rolling resistance from the extremes of highly viscoelastic rubber and a time-independent steel roller.

And this part also introduces many different ways to process the ER fluids into the polymeric article in industry. These electrorheological composites may take many forms, including fibers, fabrics, tows, fiber performs and fiber prepregs. In this form, it will be easily used in manufacture, especially in tire application.
CHAPTER IV

TUNABLE ROLLING RESISTANCE FOR ELECTRORHEOLOGICAL FLUID REINFORCED SILICON RUBBER COMPOSITES

4.1 Objectives

The experimental results in previous chapter indicate that rolling resistance has certain dependency with the mechanical properties and surface characteristics of the material. In this chapter, in the purpose of designing a smart composite system that owns tunable rolling resistance, we adopt electrorheological fluids (ERF) as smart filler into silicon rubber. Also we improve the free oscillation of a pendulum to test rolling resistance when high voltage applied. The composites of silicone rubber with same concentration of ERF were vulcanized in different electric voltages. The effect of different ERF concentrations is investigated. The obtained smart ERF reinforced silicone rubber composites show tunable coefficients of rolling resistance against external electric field. We also study the mechanical properties and surface characteristics of smart composites under different vulcanized conditions. Two classical rubber constitutive models: Mooney-Rivlin model and Ogden model are adopted to understand the mechanical behavior of ERF reinforced rubber. The interaction of mechanical properties and rolling resistance of the studied smart composite system is discussed.
4.2 Experiment

In this chapter, in the purpose of designing a smart composite system that owns tunable rolling resistance, we adopt electrorheological fluids (ERF) as smart filler into silicon rubber.

4.2.1 Materials

Liquid silicone rubber (Two component, copyflex A and B ratio is 1:1) is ordered from YMOM Company. Part A is comprised of Vinyl dimethyl terminated polydimethylsiloxane (75%), silicon dioxide (25%) and Platinum dicarbonyl dichloride (0.01%), Part B is comprised of Vinyl dimethyl terminated polydimethylsiloxane (58.5%), Dimrthly siloxane fluid (13%), silicon dioxide (17.5%), Polymethyhydrogen siloxane (5%), Diatomaceous earth (5%) and Custom orange silicone pigment (%).

Traditional liquid silicones always have complicated mix steps and long time (24-36 hours) to cure. Even worse, its density is so thick and not easy to pour for experiments in laboratory. The silicon rubber we used is CopyFlex that was designed specifically for mold making. Using equal amounts of both components to combine to produce a silky and low viscosity liquid silicone rubber. After mixing, it needs 4-5 hours to cure at 70 degrees F.

ERF was purchased from Smart Materials Laboratory Ltd, Hong Kong. The ingredient is barium titanyl oxalate particles coated with urea suspended in silicone oil.
Table 4.1 ERF reinforced silicon rubber vulcanized under different voltages

<table>
<thead>
<tr>
<th>5% ERF weight content</th>
<th>Vulcanization Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRE5-0</td>
<td>0kV</td>
</tr>
<tr>
<td>SRE5-5</td>
<td>5kV</td>
</tr>
<tr>
<td>SRE5-10</td>
<td>10kV</td>
</tr>
<tr>
<td>SRE5-15</td>
<td>15kV</td>
</tr>
<tr>
<td>SRE5-20</td>
<td>20kV</td>
</tr>
<tr>
<td>SRE5-25</td>
<td>25kV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>10% ERF weight content</th>
<th>Vulcanization Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRE10-0</td>
<td>0kV</td>
</tr>
<tr>
<td>SRE10-25</td>
<td>25kV</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>0% ERF weight content</th>
<th>Vulcanization Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRE0-25</td>
<td>25kV</td>
</tr>
</tbody>
</table>

4.2.2 Preparation of the silicon rubber/ERF composites

First, combine Part A with ERF in a container and mix through ultrasound until the ER fluid distributed uniformly in Part A. Then scale out equal amount of Part B as Part A by weight, pour it into the mixture and mix thoroughly until the color is uniform. Pour the mixture out into a mold. The curing time is about 4-5 hours. A quick way to check if the rubber is completely cured is pressing the rubber surface and seeing if it leaves an imprint.
Table 4.1 summarizes the name and preparation conditions of studied smart ERF reinforced silicone rubber composites. 0%, 5% and 10% ERF by weight of the composites were chosen in this work and vulcanized under different voltages: 0kV, 5kV, 10kV, 15kV, 20kV and 25 kV.

4.2.3 Characterization of silicon rubber/ERF composites

SEM, AFM, Hardness measurements, tensile test and rolling resistance measurement will be used to characterized the properties of silicon rubber/ERF composites.

4.2.3.1 SEM characterization

SEM is one of the direct ways to observe the morphology of micro-size samples. Second electrons and back-scattered electrons are often used as the signals of SEM. In this chapter, morphology of silicon rubber/ERF composite is characterized by SEM (JEOL JSM-6510LV) by second electrons at an acceleration voltage of 20KV (see Figure 3.5). Before imaging, samples are coated with silver by sputter coater (K575x, Emitech) for 90 seconds at 55A to avoid charging. Fracture surfaces of the materials with different concentrations of ERF were examined.

4.2.3.2 AFM characterization

Atomic force micrographs (AFM) is a high resolution scanning probe microscope and be operated in numbers of modes. An AFM always consists of a cantilever with a tip, which will be tapping to examine the surface.
We will use contact mode in this chapter, the tip is statically snap-in and drag to scan the surface. The tip is oscillated near its resonant frequency with a few nanometers amplitude around 100-200nm.

AFM (Ntegra Spectra, NT-MDT) with a HA_NC/15 probe is used for this test. Images are taken with the scan size of 10×10 µm. AFM is used to examine the surface morphology of silicon rubber/ERF composite samples curing under different voltage. The set-point amplitude ratio was maintained at 0.6 minimize the deformation caused by the tip.

4.2.3.3 Hardness measurements

Hardness is a measure of how resistant solid matter is to various kinds of permanent shape change when a compressive force is applied. There are some measurements to test hardness, such as scratch hardness, indentation hardness and rebound hardness (Wikipedia for hardness). The hardness will reflect intermolecular bonds inside materials. The difference of hardness is dependent on stiffness, plasticity, strain, strength, viscoelasticity and so on.

The durometer is model EXP-A with serial No: 003518, which was purchased from gauge city. Each sample is tested for 50 times following ASTM D-2240, and calculated the average value to compare.
4.2.3.4 Tensile test

The uniaxial tensile test is used to understand materials’ mechanical properties and investigate the potential interaction between mechanical properties and rolling resistance performance. From the tests, we will know the constitutive behavior (elastoplastic, viscoelasticity and hyperelasticity etc.) and basic engineering constants (elastic modulus, yield stress and failure strain etc.). Tensile tests are conducted using an Instron 5582 machine at room temperature with a 500 N load cell. Five dog-bone style specimens of each type of sample are prepared with geometry shown in Figure 3.7.

The tensile specimen has a total length of 3.5 inch (88.9 mm). The gage section length is 1 inch (25.4 mm) and width is 0.25 inch (6.35 mm). The thickness of the specimen is around 2.5mm.
For the calculation of stress, the thickness of each specimen is measured 5 times and the average value is used. All specimens are tested at a constant displacement-controlled loading rate 5 mm/min. The displacement and force data were recorded at a sampling frequency of 5 Hz.

In tensile test, the force $F$ is pulling the sample with cross sectional area $A$ and original length $L_0$, then the stress is calculated by force over the cross-section area of the gage section, and the strain is calculated as the ratio of extension ($\Delta L$) over initial gage section length.

\[
\text{Stress } (\sigma) = \frac{F}{A} \\
\text{Strain } (\varepsilon) = \frac{\Delta L}{L_0}
\]

4.2.3.5 Rolling resistance measurement

Since we need to test the samples under high voltage, we need to modify the rolling resistance test system (Figure 3.8) from conductive to non-conductive for safety purpose. The new rolling resistance test device has the same shape as Figure 3.8, except changing the materials of roller from steel to wood. Also we reduce the size of sample through narrowing the roller’s diameter. In this way, we can obtain relatively higher electrical field when applying the same voltage. With this modified roller (see Figure 4.2), we use the same equation as Chapter 3.3.3.3 to calculate the rolling resistance ($F_r$).

\[
F_r = mgL(\cos\theta_{\text{eval}} - \cos\theta_{\text{st}})/d_C
\]
Where $\theta_{eval}$ is the angular position of the pendulum bar after $N$ oscillations; $\theta_{st}$ is the angle when pendulum bar is released; $d_c$ is the distance covered within $N$ cycles. Figure 4.3 shows the scheme of rolling resistance test under high electrical field. The voltage is applied through two copper plates that placed at two ends of the smart composite (ER fluid reinforced silicon rubber).

Figure 4.2 Rolling resistance test system with wood roller

Figure 4.3 Scheme of rolling resistance test under high electrical voltage
4.3 Results and discussion

The smart ERF reinforced silicone rubber composites show tunable coefficients of rolling resistance against external electric field. We also study the mechanical properties and surface characteristics of smart composites under different vulcanized conditions. Two classical rubber constitutive models: Mooney-Rivlin model and Ogden model are adopted to understand the mechanical behavior of ERF reinforced rubber.

4.3.1 Effect of ER Fluid in silicon rubber on the morphology

It is difficult for smart filler (ERF) to move freely in a vulcanized rubber due to constrain of polymer chain structure. So the ERF will have different alignment in the composites under different electric field during the vulcanization.

Figure 4.4 AFM imaging of smart composite SRE5-5

The surface structures of silicon rubber with 5% ERF composite vulcanized under electrical voltage of 5 KV and 25 KV (SRE5-5 and SRE5-25) are shown in Figure 4.4 and 4.5.
In Figure 4.5, it can be observed that there are particles aligning on the surface of SRE5-25 specimen along the high electrical field direction (white arrow). However, in Figure 4.4, the particle alignment on the surface is relatively random, due to the low electrical field. This indicates that the vulcanization voltage affect directly the surface morphology of ERF reinforced silicone rubber composites, which will influence the rolling resistance performance of the ERF composites.
Figure 4.6 Relationship between testing electric voltage and hardness of silicon rubber/ERF composite curved under 5 kV and 25 kV

Applying an electrical field (same direction as the vulcanization voltage) on the two ends of the cured composites, the aligning trend will be evident and the hardness also increases. The relationship of hardness against applied electrical field for SRE5-5 and SRE5-25 has been tested as shown in Figure 4.6, where the hardness of SRE5-5 increases with the increasing of electrical filed but reversely for SRE5-25. This is because the movement of ERF particle will become very difficult as a stable surface already formed when vulcanization voltage goes beyond a certain value.
Figure 4.7 Scanning electron microscope image of the morphology of the ERF/silicon rubber composite

The SEM image in Figure 4.7 shows that the particles (light color particles highlighted by red arrow in the figure) distributed very well and uniformly in the silicon rubbers, but there is still a few agglomerations existing in this composite. It is also found that the concentration of agglomeration is dependent on the filler concentration.

Figure 4.8 SEM micrographs of surface morphology of (a) silicon rubber and (b) ERF reinforced silicon rubber composites SER5-5

The SEM image in Figure 4.7 shows that the particles (light color particles highlighted by red arrow in the figure) distributed very well and uniformly in the silicon rubbers, but there is still a few agglomerations existing in this composite. It is also found that the concentration of agglomeration is dependent on the filler concentration.
Figure 4.9 EDX of surface morphology of (a) silicon rubber and (b) ERF reinforced silicon rubber composites SER5-5

Figure 4.8 compares the SEM micrographs of pure silicon rubber and ERF reinforced silicon rubber composite. From these pictures, the incorporation of ERF changes the surface morphology. The wrinkles of rubber surface evolve from line shaped to star shaped, which will then influence the hardness and rolling resistance properties. (Hanlon 1997, Johnson 1972, Ketterhagen 2010, Frank 1989 and Johnson 1989).
Energy dispersive X-ray spectroscopy (EDX) analysis is conducted for selected area (red box of Figure 4.8) of silicone rubber and ERF reinforced silicon rubber composite, as shown in Figure 4.9. The EDX results indicate that the ERF has been incorporated into the rubber very successfully. The element Ti is the characteristic component of ERF. The weight percentage and atomic content of Ti in spectrum1 (area) of SER5-5 is 0.33% and 0.11%, respectively. The weight percentage and atomic content of Ti in spectrum2 (red cross) of SER5-5 is 0.44% and 0.11%, respectively. The results suggest that the distribution of ERF is almost homogeneous.

Figure 4.10 Schematic of particles arrangement inside silicon rubber/ERF composite cured under electric field
Globally, we also observed a tendency that the ERF particles will gather toward the positive electrode (see scheme of Figure 4.10) resulting a relatively higher concentration of ERF particles nearby the positive electrode and creating a gradual concentration along the direction of electrical field. In this work, we consider this non-uniformity a minor defect and ignorable in the analysis of the following sections. However, there is great necessarily to improve the manufacture process in the future.

4.3.2 Mechanical properties of ER fluid reinforced rubber

As discussed in the previous section, there should be certain connection between the mechanical properties and rolling resistance of the studied material. In this part, uniaxial tensile tests are conducted for different type of specimens to investigate the effect of ERF concentration and vulcanization voltage on the mechanical properties. This will enable us to study the interaction between mechanical properties and rolling resistance.
Two types of specimens are tested, axial specimen and transverse specimen as shown in Figure 4.11. As mentioned in the previous section, there is a gradual changing of concentration along the direction of electrical field, however, since the effective region of tensile specimen is only the gage section where the variation of concentration is not that significant as from the images of Figure 4.11. We consider this non-uniformity ignorable for the mechanical tests, as the tensile responses are almost isotropic as will be shown in a later section.
4.3.2.1 Effect of ER fluid content on the tensile properties of ER fluid reinforced rubber

Figure 4.12 True stress vs. true strain curves for ERF reinforced silicon rubber composites with different ERF concentrations (0, 5% and 10% by weight)

Figure 4.12 shows the true stress vs. true strain curves of ERF reinforced silicon rubber composites with different ERF concentrations. Basically, the stress-strain responses of the composites with different concentrations are similar before fracture, showing a gradual stiffening behavior. This is mainly controlled by the hyperelastic feature of silicon rubber. It is also noticed that the stress-strain curve shows a typical hyperelasticity response (gradual stiffening slope) and can be divided into two stages: mild curvature (for strain level 0 to 0.5) and steep curvature (for strain level beyond 0.5). The stiffening effect is much more significant at the steep curvature stage (stage 2) than that at the mild curvature stage.
It is also noticed from Figure 4.12 that the addition of ERF increases significantly the failure stress/strain of the ERF reinforced silicon rubber composite. There is a 42% increment of ultimate failure stress followed by the increase of ERF concentration from 0 to 5%, and a 20% increment from 5% to 10%. This indicates that ERF particles can increase the toughness of the rubber, which is likely due to the rheology of ERF.

4.3.2.2 Effect of vulcanization voltage on tensile properties of ER fluid reinforced rubber

![Figure 4.13 True stress vs. true strain curves for ERF reinforced silicon rubber composites with 5% ERF concentrations vulcanized at different voltage (0, 10 kV, 15 kV and 25 kV)](image-url)
Due to the change of alignment of ERF under electrical field with different intensity, the vulcanization voltage will also influence the mechanical properties of ERF reinforced silicon rubber composites. Figure 4.13 compares the true stress against true strain curves for ERF reinforced silicon rubber composites with 5% ERF concentrations vulcanized at different voltage (0, 10 kV, 15 kV and 25 kV). The results from Figure 4.13 show a decrease of ultimate failure stress with the increase of vulcanization voltage. This is because under a higher vulcanization voltage the ERF particles tend to align in a more regular way almost linearly from positive electrode to negative electrode, which result in a relatively clearer boundary between silicon rubber and ERF than a lower vulcanization voltage (Adriani 1988, Parthasarathy 1996, and Block 1990).

In other works, under a higher vulcanization voltage, the ERF particles along the same line are connected together forming a large-size stiffer reinforcement. For this type of two-phase composites, damage/failure is very likely to initiate along the boundaries between rubber and ERF particles. And the larger the particle size or the stiffer the particle, the easier fracture occurs. Figure 4.14 plots the relationship of vulcanization voltage and ultimate tensile stress. A linear fitting curve could be used to describe the linear descending relationship. We note that even the ultimate failure stress does not affect directly the rolling resistance behavior of the smart composites. The knowledge of failure properties are necessary for structure design purpose.
4.3.2.3 Anisotropic effect of ERF reinforced silicon rubber composite

Due to the applying of vulcanization electrical field, the microstructure of ERF reinforced silicon rubber composite will show anisotropic feature as shown in Figure 4.11. Two types of specimens (axial and transverse specimens) are prepared to evaluate the anisotropic feature of tensile properties. As shown in Figure 4.15, the tensile properties have some difference in both axial and transverse directions. This indicates that the in-plane tensile properties ERF reinforced silicon rubber composite can be considered as anisotropic.
Figure 4.15 Comparison of true stress vs. true strain responses in axial and transverse directions for ERF reinforced silicon rubber composite with ERF concentration 5% vulcanized under (a) 0KV, (b) 10KV, and (c) 25KV

4.3.3 Constitutive model of ERF reinforced silicon rubber composite

To further understand the mechanical behavior of ERF reinforced rubber, constitutive behaviors of all tensile specimens are investigated. Two classical rubber constitutive models are adopted and then compared: Mooney-Rivlin model and Ogden model.

4.3.3.1. Mooney-Rivlin theory

According to Mooney (1940) and Rivlin (1997), the mechanical strain energy can be expressed as a sum of the invariants as follows:

\[ W = \sum_i \sum_j C_{ij} (I_1 - 3)^i (I_2 - 3)^j + D(J - 1)^2 \]  \hspace{1cm} (1)
where $W$ represents the strain energy potential, $C_{ij}$ and $D$ will be determined through curve fitting measured stress-strain curves to the derivative of the equation. $J$ is the volume ratio. $I_1$, $I_2$ and $I_3$ are three invariants of the deformation tensor, generally expressed as equations (2):

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$  \(2\)

$$I_2 = \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_1^2 \lambda_3^2$$  \(3\)

$$I_3 = \lambda_1^2 \lambda_2^2 \lambda_3^2$$  \(4\)

where $\lambda_1$, $\lambda_2$, $\lambda_3$ are the stretch ratio in three different directions. We note that $I_3$ is not a term in Equation (1) as it is a constant value, 1, according to constant volume. Consider a uniaxial loading case, the stretch ratio can be denoted as:

$$\lambda_1 = \lambda = 1 + \varepsilon_{en}, \lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}}$$  \(5\)

where $\varepsilon_{en}$ is the engineering tensile strain. Then the invariants can be simplified as:

$$I_1 = \lambda^2 + 2\lambda^{-1}, I_2 = \lambda^{-2} + 2\lambda$$  \(6\)

It is popular to choose the following three coefficient $C_{10}$, $C_{01}$ and $C_{20}$.

Substituting Equation (6) into Equation (1) and taking derivative, we can then obtain the relationship between stress and stretch ratio:

$$\sigma_1 = 2C_{10} \left( \lambda^2 - \frac{1}{\lambda} \right) + 2C_{01} \left( \lambda - \frac{1}{\lambda^2} \right) + 4C_{20} \left( \lambda^2 - \frac{1}{\lambda} \right) \left( \lambda^2 + \frac{2}{\lambda} - 3 \right)$$  \(7\)

We notice that the bulk modulus term is eliminated, this is achieved as assuming $\sigma_3=0$.

4.3.3.2 Ogden theory

There is another strain energy formulation was proposed by Ogden (1972) to describe the rubber-like polymers:
\[ W = \sum_{i=1}^{3} \sum_{j=1}^{n} \frac{u_j}{a_j} (\lambda_i^{a_j} - 1) + K(J - 1 - \ln J) \]  

(8)

where \( a_j \) is non-integer, \( J = \lambda_1 \lambda_2 \lambda_3 \); \( \lambda_i^* = \lambda_i J^{-1/3} \). Using \( \frac{\partial f}{\partial \lambda_i} = \lambda_j \lambda_k \), \( J=1 \) and \( \lambda_i^* = \lambda_i \), the constitutive model takes the form (Ogden 1972)

\[ \sigma = \sum_{j=1}^{n} u_j (\lambda^{a_j} + \lambda^{-a_j/2}) \]  

(9)

where \( u_j \) and \( a_j \) are empirical material parameters determined through curve fitting against experimental data.

After obtaining the material parameters \( u_j \) and \( a_j \), we can estimate the small strain Young’s modulus of the material using the equation below:

\[ E = \frac{3}{2} \sum \mu_n a_n \]  

(10)

Generally, \( n = 3 \) is sufficient to achieve a good fit of the experimental curves.

Curve fitting is conducted in MATLAB using the ‘fsolve’ function with the Levenberg-Marquardt algorithm, which is a standard technique for solving nonlinear least square problems. Figure 4.16 and 4.17 (experimental-model figures) show the comparison between experimental and models curves for both axial and transverse tensile responses, where we can observe a good correlation between all experimental and modeling curves. The parameters for Mooney-Rivlin and Ogden models are summarized in Table 4.2 and 4.3, respectively.
Figure 4.16 Comparison between experimental and modeling curves for axial tensile properties of ERF reinforced silicone rubber composites.
Figure 4.17 Comparison between experimental and modeling curves for transverse tensile properties of ERF reinforced silicone rubber composites.

Table 4.2 Empirical material parameters fitted in Ogden model

<table>
<thead>
<tr>
<th>Specimens</th>
<th>$\mu_1$</th>
<th>$\mu_2$</th>
<th>$\mu_3$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SRE5-0</td>
<td>2.2737</td>
<td>-6.2044</td>
<td>-6.2044</td>
<td>1.1837</td>
<td>0.1736</td>
<td>0.1664</td>
</tr>
<tr>
<td>SRE5-10</td>
<td>0.0037</td>
<td>0.2094</td>
<td>0.2094</td>
<td>5.8393</td>
<td>1.6908</td>
<td>1.6906</td>
</tr>
<tr>
<td>Axial</td>
<td>SRE5-15</td>
<td>0.0042</td>
<td>0.2327</td>
<td>0.2327</td>
<td>5.6146</td>
<td>1.6257</td>
</tr>
<tr>
<td>Specimens</td>
<td>SRE5-25</td>
<td>0.0021</td>
<td>0.263</td>
<td>0.2628</td>
<td>6.5205</td>
<td>1.4402</td>
</tr>
<tr>
<td>SRE0-0</td>
<td>8.4539</td>
<td>13.1647</td>
<td>13.1647</td>
<td>0.7494</td>
<td>0.2259</td>
<td>0.2235</td>
</tr>
<tr>
<td>SRE10-0</td>
<td>8.429</td>
<td>-13.235</td>
<td>-13.235</td>
<td>0.855</td>
<td>0.257</td>
<td>0.262</td>
</tr>
<tr>
<td>Transverse</td>
<td>SRE5-0</td>
<td>9.5732</td>
<td>15.1373</td>
<td>15.1372</td>
<td>0.7757</td>
<td>0.2466</td>
</tr>
<tr>
<td>Specimen</td>
<td>SRE5-10</td>
<td>5.3842</td>
<td>-8.0149</td>
<td>-8.0149</td>
<td>0.8923</td>
<td>0.2765</td>
</tr>
<tr>
<td></td>
<td>SRE5-25</td>
<td>0.002</td>
<td>0.2497</td>
<td>0.2498</td>
<td>6.6538</td>
<td>1.4833</td>
</tr>
</tbody>
</table>
Table 4.3 Empirical material parameters fitted in Mooney-Rivlin model

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>SRE5-0</th>
<th>SRE5-10</th>
<th>SRE5-15</th>
<th>SRE5-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial Specimens</td>
<td>0.2612</td>
<td>-0.1162</td>
<td>-0.0011</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1529</td>
<td>0.0312</td>
<td>0.0057</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.16</td>
<td>0.0368</td>
<td>0.0048</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1441</td>
<td>0.0524</td>
<td>0.0045</td>
<td></td>
</tr>
<tr>
<td>Transverse Specimen</td>
<td>0.368</td>
<td>-0.2748</td>
<td>-0.0123</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.4744</td>
<td>-0.4058</td>
<td>-0.0144</td>
<td></td>
</tr>
<tr>
<td>SRE10-0</td>
<td>0.4375</td>
<td>-0.3656</td>
<td>-0.0144</td>
<td></td>
</tr>
<tr>
<td>SRE5-10</td>
<td>0.311</td>
<td>-0.1791</td>
<td>-0.0054</td>
<td></td>
</tr>
<tr>
<td>SRE5-25</td>
<td>0.1411</td>
<td>0.0493</td>
<td>0.0049</td>
<td></td>
</tr>
</tbody>
</table>

In Figure 4.16 and 4.17, the modeling results match well with the experimental data, and Ogden model shows better correlation than Mooney-Rivlin model in simulating the tensile response of ERF reinforced silicon rubber composites. Therefore, it is safely to conclude that the presented Ogden model is more suitable to describe to constitutive behavior of ERF reinforced rubber. Now Equation 10 is recalled to analyze the effect of ERF on the elastic modulus. The calculated small-strain elastic modulus values for tested tensile specimens are summarized in Table 4.4.

128
Table 4.4 Summary of elastic modulus of studied tensile specimens calculated by Equation 10.

<table>
<thead>
<tr>
<th>Specimen Type</th>
<th>SRE5-0</th>
<th>SRE5-10</th>
<th>SRE5-15</th>
<th>SRE5-25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial Specimens</td>
<td>0.872824</td>
<td>1.094506</td>
<td>1.170238</td>
<td>1.164901</td>
</tr>
<tr>
<td></td>
<td>SRE0-0</td>
<td>0.628705</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SRE10-0</td>
<td>0.506745</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transverse</td>
<td>SRE5-0</td>
<td>0.517087</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specimen</td>
<td>SRE5-10</td>
<td>0.826221</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>SRE5-25</td>
<td>1.129263</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.18 The relationship of axial small-strain elastic modulus against vulcanization voltage for ERF reinforced silicon rubber composite with a concentration of ERF (5% by weight)
Figure 4.19 The relationship of transverse small-strain elastic modulus against vulcanization voltage for ERF reinforced silicon rubber composite with a concentration of ERF (5% by weight)

Figure 4.18 and 4.19 plot the relationship of elastic modulus against vulcanization voltage for ERF reinforced silicon rubber composite with 5% ERF. From the data and figures, we can find that the elastic modulus increases with the increase of vulcanization voltage for both axial and transverse directions. The axial tensile modulus increases 33% from 0.87 KPa to 1.16 KPa with the increase of voltage from 0 KV to 25 KV voltage; the transverse tensile modulus increases about 100% from 0.51 KPa to 1.12 KPa with the increase of voltage from 0 KV to 25 KV voltage. The particles inside the rubber will become a linear arrangement under electrical field, so the stiffness of the smart composites will increase with the increase of voltage.
4.3.4 Rolling resistance of ER fluid reinforced rubber

The main focus of this work is studying the tunable rolling resistance of the smart composite system. The rolling resistance of specimens listed in Table 4.1 are tested under different electrical voltage and analyzed in this section.

4.3.4.1 Effect of ER fluid content on the rolling resistance of rubber

Figure 4.20 The rolling resistance of ERF reinforced silicon rubber composite with different ERF concentrations prepared under vulcanization voltage of zero.

Figure 4.20 shows the rolling resistance against electrical voltage responses for ERF reinforced silicon rubber composites with different ERF concentrations. It is found that the rolling resistance coefficient $C_r$ decreases with the increase of electrical voltage. It is interesting that there is a slightly decreasing of rolling resistance even for pure silicon rubber (ERF concentration of 0).
This is mostly likely due to the conductivity of silicon rubber that under a high electrical voltage, the molecular structure may be changed slightly. It is also shown that SRE5-0 has the lowest Cr compared with ERF composites with concentration 0 and 10%. The results show that Cr of SRE5-0 decreases from 0.00071214 to 0.00066812 with the electric voltage from 0 to 20kV. SRE10-0 shows relatively larger Cr, but more significant decreasing tendency with the increase of electric voltage. The results show us that the composites exhibit tunable rolling resistance properties due to incorporation of ERF, where Cr can be adjusted through changing the electric field.

The possible reason of property changes is in part due to the change of surface morphology and mechanical property of composites. The reason that the smart composites with a ERF concentration of 10% shows higher rolling resistance is probably due to the worse surface morphology. This is because when the ERF concentration exceeds a certain critical value, there could be relatively more large aggregation under a high applied electrical voltage.

4.3.4.2 Effect of vulcanization voltage on the rolling resistance of ER fluid reinforced rubber

Figure 4.21 shows the effect of vulcanization voltage on the rolling resistance behavior of ERF reinforced silicon rubber composite with a concentration of 5%. Evidently, the rolling resistance of the smart composites vulcanized at all voltages decreases with the increasing applied testing voltage.
An interesting phenomena is found that when the rolling resistance decreases with the increase of vulcanization voltage for the voltage range from 0 KV to 15 KV, but reversely when the voltage goes beyond 20 KV.

![Diagram](image)

**Figure 4.21** The rolling resistance of ERF reinforced silicon rubber composite with ERF concentration of 5% prepared under different vulcanization voltages

Firstly, as have investigated in the previous sections, the increase of vulcanization voltage results in an increase of elastic modulus and hardness. However, when the vulcanization voltage is too high, the movement of ERF particles and silicon rubber itself will produce a relatively rougher surface morphology that will then cause a decreasing of the rolling resistance.
As from the results of Figure 4.20 and 4.21, the smart composite system (SRE5-15) with ERF concentration of 5% and vulcanization voltage 15 KV provides the best rolling resistance performance. Also it is found that SRE5-15 shows the maximum variation of rolling resistance under applied voltage, where the Cr decreases about 25% from 0.00067 to 0.00050.

4.3.4.3 Correlation of rolling resistance with mechanical properties

Figure 4.22 The relationship between rolling resistance and elastic tensile modulus for the studied smart composite system SRE5 vulcanized under different voltages.

As discussed in the previous sections, the rolling resistance depends on mainly the stiffness and surface morphology of the material. To further understand the relationship between rolling resistance and elastic modulus, a correlation analysis is conducted to reveal the dependency of rolling resistance on elastic modulus.
Figure 4.22 plots rolling resistance against elastic tensile modulus data for the studied smart composite system SER5 vulcanized under different voltages, where the dots indicate experimental values (the modulus are calculated using Ogden model as described in Section 4.3.3) and the line curves represent linear fitting of the data. Basically, the rolling resistance decreases with the increase of modulus consistent with previous conclusions. And the linear curve could in certain extend describing the relationship between rolling resistance and elastic modulus, although we still found that the data has a large dispersion, which is due to the dependency of rolling resistance on other properties (e.g. surface morphology).

4.4 Conclusion

In this chapter, we studied the tunable mechanical, morphology and rolling resistance properties of ERF reinforced silicon rubber composites. A series of smart composite specimens with different ERF concentrations and vulcanization voltages are prepared, studied and analyzed. A modified rolling resistance test system with wood pendulum and acoustic emission monitor was developed to evaluate the rolling resistance coefficients of ERF reinforced silicon rubber composites under high electric voltage. The rolling resistance coefficients of all composites were found to be decrease with the increase of test voltage, while the ERF concentration and vulcanization voltage show a more complicated relationship with rolling resistance coefficient. When the ERF concentration is 5% and vulcanization voltage is 15 KV, the composite exhibited a lowest rolling resistance compared with other preparation conditions, due to a combined impact of mechanical stiffness and surface morphology.
On the other hand, the mechanical properties and hardness show a monoclinic relationship with vulcanization voltage. The elastic modulus and hardness increases with the increase of vulcanization voltage. Hyperelastic constitutive models, Mooney-Rivlin model and Ogden model, are developed to describe the tensile behavior of ERF reinforced rubber, of which the Ogden model shows relatively better correlation with experimental data and is considered to be more suitable to describe to constitutive behavior of ERF reinforced rubber.

Overall, introducing ERF as smart filler into the silicon rubber, we successfully developed a smart composite material with adjustable rolling resistance coefficient under electrical field. The process of polarization shows certain impact on the rubber surface and mechanical property according to our controllable experiments. This smart composite system presents potential for new-generation tire material or other applications.
CHAPTER V

TUNABLE ROLLING RESISTANCE OF ELECTROSPUN FABRIC/
ELECTRORHEOLOGICAL FLUID SMART COMPOSITES SYSTEM

5.1 Objectives

In this chapter, an alternative smart composite system with tunable rolling resistance is studied. We propose a co-electrospinning technology to prepare electrorheological fluid (ERF)/fabrics membranes composite. A pendulum-acoustic emission device is used to evaluate the rolling resistance of ERF/fabrics membranes composite. Two different co-electrospinning smart composite systems are studied: ERF/PVDF and ERF/PCL. The tunable rolling resistance behavior of this smart composite system is studied through testing under different external electrical field. The surface morphology is also examined to further understand its interaction between rolling resistance.

5.2 Experiment

A co-electrospinning technology is used to prepare electrorheological fluid (ERF)/fabrics membranes composite. Two different co-electrospinning smart composite systems are studied: ERF/PVDF and ERF/PCL.
5.2.1 Materials

PVDF (Kynar761) was supplied by Arkema Incorporation. Polycaprolactone (PCL) (CAS 24980-41-4) was purchased from Sigma-Aldrich. PVDF is well known for its piezoelectric property, which is commonly used as insulation on electrical wires, because of its combination of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance and heat resistance.

PCL is a biodegradable polyester with a low melting point and glass transition temperature. It has good resistance to water, oil, solvent and chlorine.

ERF was purchased from Smart Materials Laboratory Ltd, Hong Kong. The ingredient is barium titanyl oxalate particles coated with urea suspended in silicone oil.

5.2.2 Preparation of ERF/electrospun membranes by co-electrospinning

For the polymer/ERF coaxial electrospinning fabrication, PVDF and PCL solution are fabricated into nano-fabrics membrane while the ERF is fabricated as the filling fluids inside the polymer membranes.

PVDF solution with 0.17 g/ml concentration is prepared by dissolving PVDF in DMF and acetone with a volume ratio of 7:3 at 40-50°C for 2h. The electrospinning is conducted with a solution feed rate of 0.3 mL/h under applied voltage 10 KV. DMF and dichloromethane with a volume ratio of 1:2 are used to dissolved PCL at 25 °C for 3h. The PCL solution of concentration 0.16 g/ml is utilized to electrospun PCL fibers with a solution feed rate of 0.5 mL/h under applied voltage 10 KV.
The co-electrospinning setup is shown in Figure 5.1, which includes two syringes to feed polymer solutions and ERF into the electrospin microtubules, independently. The co-axial configured tip was built by two concentric needles. Coaxial electrospinning is performed with varied core and shell feeding rates. The feeding rate of ERF is 1.5 mL/h, and PVDF shell feed rate is kept at 1.7 mL/h while PCL shell feed rate is 0.5 mL/h. A customized rotatable collector prepared by a rotating disc. The distance between spinneret and collector is 150 mm. The rotating disc collector has a diameter of 150 mm and electrospun fibers are collected at TUV of 20 m/s. Then aligned fiber will be collected on surface of rotating disc collector, as shown in Figure 5.2. All the experiments are operated at room temperature.

Figure 5.1 A schematic of coaxial electrospinning station
Figure 5.2 The electrospinning station to collect aligned fabrics
5.2.3 SEM Characterization

In this chapter, the in-situ morphology of electrospun membranes is characterized by SEM (JEOL JSM-6510LV). The samples were pre-coated with silver by sputter coater (K575x, Emitech) for 1.5 min at 55 A. Before the test, the ERF/fabrics membranes were dried in vacuum oven at 40 °C for 12 h. Due to the hydrophilic character, the ERF/fabrics membranes were stored in a dry box before the SEM testing.

5.2.4 EDS Characterization

Energy Dispersive Spectroscopy (EDS) use backscattered electron images from scan area of the SEM display to detect different atomic number elements and their relative proportions. EDS is one typical chemical analysis for characterizing the elemental composition of microscopic particles. With the attachment of the energy dispersive spectrometer, the elemental composition of materials can be obtained. The elements in samples were detected by X-act detector from Oxford Instruments.

5.2.5 Rolling resistance measurement

In this chapter, we adopt Gent’s method to directly test the rolling resistances using a small amount of materials.
The modified pendulum-acoustic emission device (Figure 5.4) developed in the previous chapter is utilized to evaluate the rolling resistance of the ERF/fabric membranes. The distance between two electrodes is 55 mm. The wood substrate is used to maintain the strength of the electric field.

![Figure 5.4 The lateral view of a modified pendulum-acoustic emission device to test the rolling resistance of ERF/electrospun membranes](image)

5.3 Results and Discussion

A pendulum-acoustic emission device is used to evaluate the rolling resistance of ERF/fabrics membranes composite. Two different co-electrospinning smart composite systems are studied: ERF/PVDF and ERF/PCL. The surface morphology is also examined to further understand its interaction between rolling resistance.
5.3.1 Effect of ER Fluid on the morphology of ERF/fabrics membranes

Figure 5.5 SEM micrographs of electrospun PCL membranes (a) with and (b) without ERF particles

Figure 5.5 SEM micrographs of electrospun PCL membranes (a) with and (b) without ERF particles
The *in-situ* morphologies of electrospun fabrics membrane and ERF/fabrics membrane are first studied as shown Figure 5.5. The PCL membranes present excellent alignment along one direction due to the usage of rotating disc collector in the electrospinning station. It is also observed in Figure 5.5 (a) the distribution of ERF particles among the aligned PCL fibers. The introduction of ERF into the fabrics membrane could change the surface morphology and lead to a change of effective elastic modulus and hardness of the membrane, which will affect the rolling resistance as discussed in the previous chapter.

Figure 5.6 SEM and EDX characterization of random ERF/PVDF fabrics membrane
The morphologies of random and aligned ERF/PVDF fabrics membranes are characterized using SEM and EDX as shown in Figure 5.6 and 5.7. In Figure 5.6, the fibers are aligning randomly directing to all different directions while in Figure 5.7 the most of PVDF fibers are aligning along the same direction. In both Figure 5.6 and 5.7, we can see clearly the presence of ERF particles.

From the SEM pictures, it can be seen that ERF particle incorporated into electrospun fibers successfully by coaxial electrospinning. The introduction of ERF changes the property of electrospun membranes, which effect the coefficient of rolling resistance. It implies that the influence of surface morphology is dominant with ERF concentration.

The EDX results further demonstrate the successful incorporation of ERF into electrospun fabrics. Figure 5.6 also presents the EDX results of the random ERF/PVDF fabrics membrane. The element Ti is the characteristic component of ERF. The weight ratio and atomic ratio of Ti in spectrum 1 (point) of random ERF/PVDF fabrics membranes is 4.98 % and 1.63 %, respectively. The weight ratio and atomic ratio of Ti in spectrum 2 (area) of random ERF/PVDF fabrics membranes is 2.93 % and 0.84 %, respectively. The results indicate that the distribution of ERF is almost homogeneous.

Figure 5.7 shows the EDX results of aligned ERF/PVDF fabrics membrane, in which the weight ratio and atomic ratio of element Ti in spectrum 1 (point) of ERF/PVDF fabrics membranes is 35.1 % and 33.34 % respectively. The weight % and atomic % of Ti in spectrum 2 (area) of ERF/PVDF fabrics membranes is 6.98 % and 2.35 % respectively.
Figure 5.7 SEM and EDX characterization of aligned ERF/PVDF fabrics membrane

5.3.2 Effect of ER Fluid on the rolling resistance of ERF/fabrics membranes

Figure 5.8 The rolling resistance-electric voltage relationship for ERF/PVDF fabrics membranes with random and aligned fabrics arrangement.
The rolling resistance behavior of ERF/fabrics membranes are tested under different electrical voltage based on the test procedure introduced in Chapter 3 and 4. Figure 5.8 shows the rolling resistance against electric voltage data of both random and aligned ERF/PVDF fabrics membranes. As from Figure 5.8, the aligned ERF/PVDF fabrics membrane shows lower rolling resistance compared to the random ERF/PVDF fabrics membrane. Also, the rolling resistance constant first decreases with the increasing of test voltage and then starts increasing when the voltage goes beyond a critical value: 20 KV for the random ERF/PVDF fabrics membrane and 30 kV for the aligned ERF/PVDF fabrics membrane. This is because under an applied electrical voltage the ERF will move and aligning along the electrical field direction. With the increase of electrical voltage, initially the movement of ERF will stretch the farbics membrane and increase the effective stiffness of the composite membrane. But once the voltage is too high, the fabrics could be over-stretched, result in a relatively rough surface and higher rolling resistance.

The maximum change of $Cr$ for the aligned ERF/PVDF fabrics is from 0.000936 to 0.000825. While for the random ERF/PVDF fabrics, the maximum change of rolling resistance is from 0.00097 to 0.000925. The change of rolling resistance of aligned ERF/PVDF fabrics membrane is more significant. This is due to the factor that the ERF particles have more space to move among the aligned fabrics.
Figure 5.9 The relationship between rolling resistance and test electric voltage for aligned electropun PCL fabrics with and without ERF.

The influence of ERF on the rolling resistance of PCL electrospun fabrics membranes is studied through testing the rolling resistance of aligned PCL fabrics membranes with and without ERF. Figure 5.9 shows the rolling resistance against electrical voltage data for aligned electropun PCL fabrics with and without ERF. It is evident that the aligned PCL/ERF fabrics membrane has relatively lower voltage than that of aligned PCL fabrics membrane under all voltage. It is interesting to find that the rolling resistance of the aligned PCL fabrics increases with the increase of electrical voltage; while the rolling resistance of aligned ERF/PCL fabrics membrane decreases first with the increase of electrical voltage and starts increase when the voltage goes beyond 20 KV. The sensitivity of PCL fabrics membrane to electrical field is due to its thin thickness and electrical permittivity that it is very easy to curl and stick with the wooden roller by electrostatic effect, which will then result in uneven surface and an increase of rolling resistance. And the introducing of ERF particles lowers the rolling resistance of the composite membrane significantly.
As from Figure 5.9, the maximum change of rolling resistance for aligned ERF/PCL fabrics membrane is from 0.000815 to 0.000755 and achieves the lowest at electrical voltage 20KV. The results suggest that the ERF/electrospun fabrics membrane exhibits great smart properties due to incorporation of ERF, where rolling resistance can be adjusted by changing the electric field.

To conclude, Figure 5.10 shows the schematic diagrams of ERF/fabrics membrane under electrical field. According to the structure and mechanism of polymer electrospun membranes, the particle inside fabric membranes will be aligned under the electrical field. Without electrical voltage, the ERF particles are separated randomly inside fabric membranes as shown in Figure 5.10. After applying the testing voltage, the state of fiber will be stretched tight with the influence of particle movement. The stiffness of ERF/electrospun membranes will be changed with the evolution of microstructure. This will then influence the rolling resistance accordingly as discussed in the previous sections. For the random ERF/PVDF electrospun membranes, the arrangement of fibers is still random, which will restrict the movement of particles. So the rolling resistance will not change too much. But the particle inside the aligned ERF/PVDF electrospun membranes will force the PVDF electrospun membranes to align in an orderly manner resulting a more significant impact of rolling resistance.
Figure 5.10 Schematic diagrams of ERF particle movement and its influence on polymer electrospun fibers in (a) random and (b) aligned arrangement under the effect of applied testing electrical voltage

5.4 Conclusions

The rolling resistance performance of a smart composite system, ERF reinforced electrospinning fabrics membrane, is studied. The coaxial electrospinning approach is utilized to fabric ERF/fabrics membranes.
The different smart composite systems are prepared: random ERF/fabrics membrane prepared using the regular station and aligned ERF/fabrics membrane prepared with a rotating disc collector. The modified wood-pendulum acoustic-emission device is utilized to measure the rolling resistance properties of the ERF/fabrics membranes. The effect of ERF reinforcement on the morphology and rolling resistance properties of the smart composite system is studied. The effect of electrical voltage on the rolling resistance performance is investigated as well.

The results indicate that the electrospun PVDF or PCL membranes with ERF reinforcement exhibited tunable rolling resistance with increasing test voltage. The minimums value of rolling resistance coefficient is found to be 0.000825 for the aligned ERF/PVDF membrane tested under an electric voltage of 30 kV, and 0.000755 for the aligned ERF/PCL membranes tested under an electric voltage of 20 kV. The morphology and EDS results confirm that the successful incorporation of ERF particles into the polymer electrospun fabric. It is found that the process of polarization affects the surface morphology of the composite membrane and the rolling resistance behavior, which results in the increase of rolling resistance when the voltage increases beyond certain critical value.
6.1 Conclusions

In this dissertation, we presented a series of studies on smart composite material systems with tunable rolling resistance properties. A pendulum rolling apparatus was designed and utilized to assess the coefficients of rolling resistance for selected materials, which is an effective method to characterize rolling resistance in laboratory level. Acoustic emission sensor was employed to collector the damping data, which is used to calculate the rolling resistance coefficients. Two different smart composite systems were studied: ERF reinforced silicon rubber and ERF reinforced polymer fabrics membrane. ER fluid studied in this work is known to have a giant electrorheological effect under high electrical voltage, showing controllable liquid-solid transitions. Specific fabrication processes for these smart composites were designed to introduce ER fluids into the polymeric articles.

Chapter 3, “A Study of Rolling Resistance of Electrospun Polymer Fabrics”, proposed the design of pendulum rolling apparatus and fabrication of smart composite system. The developed rolling resistance test system was utilized to evaluate the rolling resistance properties of different materials, including wood, copper, asphalt, rubber and
polymer fabrics et al. Specific attention was paid on the electrospun polymer fabrics which is known to be cheap and flexible in design. The test results suggest that the polymer fabrics system presents a great potential for the application of tunable rolling resistance, due to its porous structure and viscoelasticity. A specific design for ERF reinforced polymer fabrics system was presented, which is already patented.

Chapter 4, “Tunable Rolling Resistance for Electrorheological Fluid Reinforced Silicon Rubber Composites”, conducted a comprehensive study on the tunable rolling resistance of a smart ERF/rubber composite material using ERF as smart filler. We successfully prepared a series of smart composites, silicon rubber with different ERF concentrations and vulcanization voltages, with adjustable rolling resistance coefficient under electrical field. The tunable mechanical, morphology and rolling resistance properties of ERF reinforced silicon rubber composites were studied. The rolling resistance coefficients of ERF/silicon rubber composites were found to be decrease with the increase of test voltage, while the ERF concentration and vulcanization voltage show a more complicated relationship with rolling resistance coefficient. When the ERF concentration is 5 % and vulcanization voltage is 15 kV, the composite exhibited a lowest rolling resistance compared with other preparation conditions, due to a combined impact of mechanical stiffness and surface morphology.

Mechanical properties and hardness of the composite were also investigated. A monoclinic relationship with vulcanization voltage was found. The elastic modulus and hardness increases with the increase of vulcanization voltage.
Hyperelastic constitutive models, Mooney-Rivlin model and Ogden model, are developed to describe the tensile behavior of ERF reinforced rubber, of which the Ogden model shows relatively better correlation with experimental data and is considered to be more suitable to describe to constitutive behavior of ERF reinforced rubber.

Chapter 5, “Tunable Rolling Resistance of Electrorheological Fluid Reinforced Electrospun Fabric Membrane”, proposed a coaxial electrospinning method to prepare ERF reinforced electrospun fabric membrane. The aligned electrospun fabric was collected using a rotating disc collector. The morphology and EDS result confirms the successfully incorporation of ERF into the polymer electrospun fabric. A modified pendulum-acoustic emission device is used to test the rolling resistance of ERF/electrospun membranes. The minimums value of rolling resistance coefficient is found to be 0.000825 for the aligned ERF/PVDF membrane tested under an electric voltage of 30 kV, and 0.000755 for the aligned ERF/PCL membranes tested under an electric voltage of 20 kV. The morphology and EDS results confirm that the successful incorporation of ERF particles into the polymer electrospun fabric. It is found that the process of polarization affects the surface morphology of the composite membrane and the rolling resistance behavior, which results in the increase of rolling resistance when the voltage increases beyond certain critical value.
In general, the work presented provides a comprehensive understanding of the tunable rolling resistance of polymer materials with the incorporation of ER Fluid. The proposed manufacture and test methods are valuable in the design of new smart composite system and owns significant potential for industry application. The results demonstrate the great potential of ERF for preparing smart composite system. Through studying the rolling resistance properties of a series of material systems, we identified the impact of surface morphology, elastic properties and hardness on the rolling resistance coefficients. As a pilot work, this dissertation also opens a new path for improving the energy efficiency of vehicles through designing novel smart material systems for the tires.

6.2 Suggestion for future work

In future work, the theoretical modeling study should be developed at first. Although the Ogden model was chosen and completed to describe the tensile behavior of ERF reinforced rubber, no theory or mechanism to explain the relationship between rolling resistance and mechanical property for ERF/ polymer electrospun membrane. And extensive experimental works are needed to quantify and qualify the properties and mechanism of ERF/ polymer electrospun membrane.

Secondly, since the hollow fiber structure was fabricated successfully in our laboratory by Na (2012) and their potential application was patented by Wong (2012), the following research can be focused on filling ER fluid into electrospun hollow fibers, which could produce more controllable morphology.
On the other hand, piezoelectric polymer materials can also be introduced to fabricate electrospinning hollow fibers as wall structure. In this way, stretching or bend hollow fibers wall will result in electrical field along the fibers, which could initiate liquid-solid transitions for the ERF core. And more responsive materials, such as magneto-rheological fluid (Carlson 1996 and Ginder 1996), pressure responsive fluid (LaValley Sr 1991 and Brisco 1995), can be considered as smart filler for other applications.

At last, it is urgent to convert the research to industry application products. This smart composite system presents potential for new-generation tire material or other applications. These experimentally data produce useful insights in coupling proper substrate materials with ER fluid for understanding the control of rolling resistance for future smart tires technology.
REFERENCES


50. Dunlop, John Boyd. An Improvement in Tyres of Wheels for Bicycles, Tricycles, or Other Road Cars. HM Stationery Office, 1888.


208. Stangroom, J. E. "Improvements in or relating to electric field responsive fluids." UK Patent 1570234 (1980).


231. Wikipedia Polyvinylidene fluoride
http://en.wikipedia.org/wiki/Polyvinylidene_fluoride

232. Wikipedia Stress-strain curve
https://en.wikipedia.org/wiki/Stress%E2%80%93strain_curve

233. Wikipedia Young’s modulus https://en.wikipedia.org/wiki/Young%27s_modulus


