INCORPORATION OF DEVULCANIZED RUBBER IN A TIRE RUBBER COMPOUND

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Outline

• Introduction
  Recycled Tires/ Rubber Crumb/
  Vulcanization & Devulcanization
  Background and Objectives

• Experimental
  Process/ Materials/Characterization

• Results and Discussion

• Concluding Remarks

• Current Efforts
Introduction

• Annual generation of Scrap tires:
  - World: 1.6 billions
  - USA: 299 millions
  - Canada: 30 millions

References:
• “Scrap Tire Market in The United States”, Rubber Manufacturer Association, Nov 2006, page 15
• Schnekenburger, Michael, Tire Recycling in Canada-1999, Rubber Division, ACS, Paper No.166, Set.21-24, 1999
Introduction

Tire Recycling

- Statistics in 2005 for the USA show that nearly 87% of scrap tires in the U.S. were used in end use market.
- Statistics show that there is an eight-fold increase in percentage of consuming of scrap tires by end use market annually since 1990.
Introduction

- TDF (tire derived fuel) application consumed about 52% of total scrap tire in U.S.
- Civil engineering market is another big consumer of scrap tires in U.S (16%)
- 12% is consumed by ground rubber products.
Introduction

**Ground Rubber : Production Methods**

- Ambient grinding process
- Cryogenic grinding process
- Wet grinding process
- Extrusion
Introduction

- **Rubber Crumb Applications**
  - Sport Surfaces
  - Geotechnical/Asphalt Applications
  - Rubber and Plastic Products
  - Automotive Industry
  - Adhesives and Sealants
  - Construction
  - Shock Absorption and Safety Products
Rubber Vulcanization

- Raw rubber is soft and sticky material with a low tensile strength and elasticity.
- Atomic bridges composed of sulphur or carbon-carbon bonds link the polymer chains together.
- First discovered by Charles Goodyear in 1839.
- The vulcanized rubber is a thermoset material.
Introduction

Rubber Devulcanization

- Devulcanization refers to a process in which the crosslink bonds in the vulcanized rubber cleave totally or partially.

- The devulcanized rubber is able to be re-vulcanized and utilized again like a virgin rubber.
Advantages of breaking the 3D network:

(Devulcanized Rubber)

- Re - Compoundable
- Re – Processable
- Re - Vulcanizeable
Introduction

**Devulcanization Methods**

- Mechanical
- Ultrasonic
- Chemical
- Microwaves
- Microorganisms
Introduction

Thermo-Mechanical Devulcanization Process with Supercritical CO$_2$

- A continuous devulcanization process which is carried out in a twin screw extruder
- No chemical agents
- scCO$_2$ acts as a plastisizer and facilitates the process
- US patent 7,189,762
**Introduction**

**Devulcanization Mechanism**

- ScCO2 diffuses and swells the rubber network
- Elastic constant (k) for S-S bonds is about 1/30 that for C-C bonds
- Selective cleavage of S-S bonds occurs
Experimental

Feeder

Control Panel

Valve

Syringe Pump

Valve

CO₂ Cylinder

Gear box

Extruder

Thermocouples

Pressure Transducers

50 rpm 200 C
50 mm twin screw extruder (American Leistritz, NJ)
Experimental

Screw configuration

- In the first zone the crumb rubber is heated to the devulcanization temperature
- Kneading elements after injection of CO2 give the CO2 and rubber crumb a good mixing and enough shearing and stretching
Experimental

• Rubber Crumb (Edge Rubber co.)
  
  Particle size:
  60 mesh

• scCO$_2$ (Praxair)
Experimental

Typical devulcanized samples:

a) Samples of devulcanized rubber in strand shape
b) Devulcanized rubber ribbons exiting the die;
c) Samples of devulcanized rubber in ribbon shape
**Intruduction : Tire tread**

**Tire Tread :**
- Tread is the wear resistance component of the tire in contact with the road.
- It must provide traction, wet skid, and also minimum noise generation and low heat buildup.
- A blend of natural rubber, polybutadiene (BR), and styrene–butadiene rubber (SBR), compounded with carbon black, silica, oils, and vulcanizing chemicals.

**Why devulcanized rubber incorporation ?**
- Lowering the cost of raw material.
- Recycling of scrap tires.
Introduction: Tire tread

Cross-section of a high-performance passenger tire
Experimental

Compounding recipe for samples

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Control</th>
<th>10%</th>
<th>20%</th>
<th>30%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tread MB</td>
<td>194 phr</td>
<td>174 phr</td>
<td>155 phr</td>
<td>135 phr</td>
</tr>
<tr>
<td>Devulcanized rubber</td>
<td>-</td>
<td>20 phr</td>
<td>39 phr</td>
<td>59 phr</td>
</tr>
<tr>
<td>OBTS</td>
<td>1.25 phr</td>
<td>1.25 phr</td>
<td>1.25 phr</td>
<td>1.25 phr</td>
</tr>
<tr>
<td>PVI</td>
<td>0.3 phr</td>
<td>0.3 phr</td>
<td>0.3 phr</td>
<td>0.3 phr</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.95 phr</td>
<td>1.95 phr</td>
<td>1.95 phr</td>
<td>1.95 phr</td>
</tr>
</tbody>
</table>

• Tire tread MB is a compound of NR and BR plus carbon black, oil, anti ozonant, and etc.

• Tire tread MB was replaced by Devulcanized rubber in order to lower the cost of compound
Experimental

Sample preparation

• The virgin tire compound and devulcanized rubber were first mixed in a Banbury mixer

• Then curing chemicals were added during milling the compound on a two roll mill

• Appropriate curing time was determined using the MDR test data

• Samples were pressed and cured into standard testing specimens using a hot press
Experimental Characterization

- Mooney viscosity
- Curing Properties (MH, Ts₂, T₉₀)
- Tensile properties (Tensile strength, Elongation at break, Modulus)
- Tear strength
- Hardness (shore A)
- Heat aging (72 hr @ 70 °C)
- Hysteresis (heat build up)
- Cut and chip (% of mass loss)
A slight increase for Mooney viscosity can be observed when the percent of devulcanized rubber in virgin rubber compound increases.

Presence of remained cross-link bonds could be the reason for the Mooney viscosity increasing.
Results & Discussion

Curing characteristics ($T_{s2}$ & $T_{c90}$)

- **Scorch time** ($T_{s2}$) and **optimum cure time** ($T_{c90}$) do not change by incorporation of devulcanized rubber into a tire tread compound up to **30%**.
Results & Discussion

Curing characteristics (MH)

- A very slight increase at the beginning can be observed for the $M_H$ value and then it starts to decrease.

- The difference is very low so one can say the $M_H$ value remains almost constant.
Results & Discussion

Tensile strength

- **Tensile strength decreases as devulcanized rubber content increases**

- **Sample with 30% devulcanized rubber shows an 83% retention of tensile strength**
**Results & Discussion**

**Elongation at break**

- *Elongation at break decreases as devulcanized rubber content increases*

- *Sample with 30% devulcanized rubber shows an 80.4% retention of elongation at break*
• Modulus increases as the content of devulcanized rubber increases in the tire tread compound
• **Tear strength increases by 7% at the beginning (when 10 % devulcanized rubber is added) and then starts to decrease**

• **Compound containing 30% devulcanized rubber shows around 95 % retention of tear strength**
Results & Discussion

Hardness

- Addition of devulcanized rubber does not change the hardness of tire tread compound
Results & Discussion

Heat aging (72 hr @ 70 °C)

- Tensile strength increases around 10% after aging for the control compound, this value for the compounds having devulcanized rubber is around 3%.
- Elongation at break decreases by 8% for control compound while for samples 10 & 20 this value is 16%. For sample having 30% devulcanized rubber elongation decreases by 18% after aging process.
Results & Discussion

Damping and Hysteresis

- Specimens were subjected to a dynamic load for 25 min at 148 °C using a flexometer
- Hysteresis (heat build up under dynamic stress) decreases as content of devulcanized rubber increases in tire tread compound
- Tan δ (damping) does not show a distinguishable trend and fluctuates from 0.332 to 0.408
Results & Discussion

Mass loss in cut & chip test

- This test shows the service performance of tire treads
- Percent of mass loss in a cut and chip test increases as the percent of devulcanized rubber increases in a tire tread compound
Concluding remarks

- Devulcanization of ground tire rubber crumbs under stress in the twin screw extruder with supercritical CO2 is a continuous, cost-effective, and environmentally friendly process.
- A reasonably high throughput of devulcanized rubber has been obtained in the devulcanization process in a twin screw extruder, which is stable.
- Devulcanized rubber obtained from our devulcanization process was incorporated in a virgin tire compound and the results show that by addition up to 30% of devulcanized rubber the Mooney viscosity, Hardness, tear strength and curing properties does not change significantly. Tensile strength and elongation at break decrease up to 15% and 20%, and heat build up improves.
- These results show that devulcanized rubber can be incorporated in a tire compound in order to lower the price without significant deterioration of compound properties. However, additional experiments are required to further optimize the tire compound properties.
Current Efforts

• Optimization the properties of the tire tread and devulcanized rubber compound

• Incorporation of devulcanized rubber in a conveyor belt compound

• Devulcanization of EPDM scrap rubber

• Preparation of TPV material by using the devulcanized rubber
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