Developments in Recycling and Re-use of Waste Rubber

Martin Forrest
MPG – Rubber Seminar
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Contents of Presentation

- Overview of rubber recycling
- Use of rubber crumb
- Devulcanisation of rubber
- Other recycling techniques
- Future developments
- Conclusions
Waste rubber always re-used by rubber industry
- “Reclaim” processes developed in 19\textsuperscript{th} Century

Legislation has increased pressure to recycle
- Landfill Directive (1999/31/EC)
  - Ban on tyre waste in July 2006
  - 95\% target for recycling of car components
- European Parliament vote in 2017
  - Increase overall recycling rate to 70\% by 2030

Other pressures – e.g. Landfill taxes in UK
- UK recycling rates increased 7\% to \sim 50\% (1996 to 2017)
Activity over Last 20 Years

- Increased funding made available for recycling
  - Government - EU and National European (e.g. WRAP in UK)
  - Corporate initiatives (e.g. Ford)
- Most research carried out on recycling tyres
  - Regulations, ease of collection, tonnage etc
- Strong research activity in number of areas:
  - Devulcanisation processes
  - Use of rubber crumb
  - Recovery of materials, e.g. carbon black
- LCA studies for recycling tyres
- New standards and protocol’s for use of rubber crumb
Rubber Industry Data - Background

• Global annual rubber consumption
  • Tyres = ~11 million tonnes
  • GRG = ~10 million tonnes

• Global annual tyre statistics (ref: G.B. Sekhar)
  • 1.7 billion new tyres
  • 1.0 billion waste tyres

• Waste tyres in UK (0.5 million tonnes – ref: WRAP)
  • >95% recycled in total
    • 8.5% - re-treaded
    • 45.1% - reprocessed into materials and products
    • 24% - energy recovery
    • 22.4% - exported or other end-uses
Life Cycle Analysis – Recycling End of Life Tyres

• Data from “Institute for Environmental Research and Education” Report (2009)

<table>
<thead>
<tr>
<th>Recycling Route</th>
<th>Carbon Footprint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber Crumb in Road Surfaces</td>
<td>33% less than using asphalt</td>
</tr>
<tr>
<td>Rubber Crumb in Plastic</td>
<td>25% less than using virgin plastic</td>
</tr>
<tr>
<td>Energy Recovery</td>
<td>20% less than using coal</td>
</tr>
</tbody>
</table>

**Report’s Conclusion**: Re-use of tyre rubber make’s substantial contribution to reducing carbon emissions
## Generation of Waste – Different Industrial Processes

<table>
<thead>
<tr>
<th>Activity</th>
<th>Amount of Waste Rubber*</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Flash” produced in injection moulding</td>
<td>30 – 50%</td>
</tr>
<tr>
<td>Stamping out gaskets from cured sheet</td>
<td>20 – 40%</td>
</tr>
<tr>
<td>Extrusion processes</td>
<td>5 – 15%</td>
</tr>
<tr>
<td>All activities with a rubber factory</td>
<td>2 – 5%</td>
</tr>
</tbody>
</table>

*ref : D. Brown, Proceedings of “Recycling Rubber” Seminar
## World Overview – Fate of Waste Rubber Products

<table>
<thead>
<tr>
<th>Fate of Waste Rubber Products</th>
<th>Proportion*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recycled into New Rubber Products</td>
<td>3 – 15%</td>
</tr>
<tr>
<td>Recycled into any Product</td>
<td>5 – 23%</td>
</tr>
<tr>
<td>Used for Energy Recovery</td>
<td>25 – 60%</td>
</tr>
<tr>
<td>Sent to Landfill or Stockpiled</td>
<td>20 – 30%</td>
</tr>
</tbody>
</table>

*ref : D. Brown, Proceedings of “Recycling Rubber” Seminar
Production of Rubber Crumb
Production of Rubber Crumb – Starting Material for Many Recycling Processes

- **Rubber crumb - types**
  - Whole tyre (possible fabric/metal contamination)
  - Tyre tread only (very low contamination - premium product)
  - Other crumb rubbers commercially available – Nitrile, EPDM, FKM etc

- **Grinding technologies**
  - Cryogenic grinding (<150 mesh)
  - Water jet grinding (<150 mesh)
  - Ambient grinding (down to ~100 mesh)
  - Specialist systems (e.g. semi-cryogenic)

- **Sieving stage - after grinding**
  - Grades crumb into particle sizes
    - e.g. 40 mesh (~400 µm)
Particle Shape – Ambient and Cryogenic Crumb

Ambient Crumb

Cryogenic Crumb
Rubber Crumb – Quality Standards

- WRAP Quality Protocol (2009)
  - Defines what point rubber fully recovered and no longer waste
  - Defines categories based on size
- BSI PAS 107:2007 (ambient crumb only)
  - Collection of raw material, e.g. tread tyre buffing's
  - Storage of raw material, manufacture and storage of final product
- General properties of crumb
  - ASTM D-5603-2008 (grades 1 to 6 - mesh size, bulk density etc)
- Particle size and particle size distribution
  - ASTM D-5644-2008 (Ro-tap sieve test method)
- Chemical properties
  - ASTM D-297-2006 (sulphur level, ash composition)
Uses of Rubber Crumb
Uses of Rubber Crumb

- Plastic products
  - Wide range of plastics investigated – PE/PP, Nylon, Polystyrene etc
  - Properties dependent on – level, type of compatibiliser etc

- Rubber products
  - Up to 50% reported if activated/small particle size used
  - EPDM compounds, Large tyres etc

- Other products
  - Wood/crumb blends - sound insulation products
    - Better than pure wood products
  - Concrete – for construction products
  - Bitumen and aggregate – road and path surfacing materials
  - Gypsum plaster - improves elastic behaviour stops cracking
  - Adhesives – improves elasticity
Rubber Crumb - Construction Products

Synthetic Roof Slate

Concrete Building Blocks
Bridleways and Footpaths  Soil Improver & Turf Protector
Rubber Crumb – Adhesive and Underlay

Tile-on-Wood Adhesive

Carpet Underlay
Rubber Crumb –
Barrier Products and Large Tyres

Moulded Barrier Products – crumb and shred

Earthmover Tyre - activated crumb (to 50%)
Cryosintering using Rubber Crumb

- Cryosinter process to manufacture products
  - High pressure sintering of crumb directly into products
    - e.g. Shoe soles
  - Surface of crumb activated to improve interfacial adhesion
  - Quality of end product very dependent upon:
    - quality of crumb and effectiveness of surface treatment
  - Tensile strengths above 10 MPa are possible

- Active area for Research
  - EU funded Cryosinter project (2006 to 2008)
  - Workers at Universities (e.g. Massachusetts and Florida)
Devulcanisation of Rubber
## Properties of Chemical Bonds in Sulphur-cured Rubber

### Bond Energies (ref: E. Finazzi et al)

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Energies (kJ mol)</th>
<th>Location in Rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-S</td>
<td>270</td>
<td>Di- and polysulphidic crosslinks</td>
</tr>
<tr>
<td>C-S</td>
<td>310</td>
<td>Monosulphidic crosslinks</td>
</tr>
<tr>
<td>C-C</td>
<td>370</td>
<td>Main-chain bonds in rubber molecules</td>
</tr>
</tbody>
</table>

### Elastic Constants of Bonds (ref: E. Finazzi et al)

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Elastic constant</th>
<th>Location in Rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-S</td>
<td>~3</td>
<td>Di- and polysulphidic crosslinks</td>
</tr>
<tr>
<td>C-S</td>
<td>Intermediate value</td>
<td>Monosulphidic crosslinks</td>
</tr>
<tr>
<td>C-C</td>
<td>~100</td>
<td>Main-chain bonds in rubber molecules</td>
</tr>
</tbody>
</table>
1. Bond energies
   - C-S and S-S bonds lower dissociation energies than C-C bonds – break upon heating

2. Elastic constants
   - S-S bonds much “stiffer” – break upon application of shear force

3. Chemical properties
   - Can target S-S and C-S bonds using “chemical bullets”

Processes often use more than one mechanism
Ideally a commercial process should:

- Be continuous - economies of scale/higher efficiency
- Use standard processing equipment with minimal modification - lower capital investment
- Devulcanise different types of rubber
- Have no additional H&S concerns - use industry approved substances
- Produce devulcanised rubber with:
  - good processing characteristics - scorch and cure times, good rheological properties etc
  - good physical properties upon re-vulcanisation – tensile strength, elongation, compression set etc
<table>
<thead>
<tr>
<th>Technology</th>
<th>Basis of Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal*</td>
<td>Heat-induced cross-link scission</td>
</tr>
<tr>
<td>Thermal with Chemicals*</td>
<td>Targeted chemical reactions at elevated temperature</td>
</tr>
<tr>
<td>Mechanical**</td>
<td>Shear-induced cross-link scission</td>
</tr>
<tr>
<td>Mechanical with Chemicals**</td>
<td>Shear/chemical devulcanisation</td>
</tr>
<tr>
<td>Ultrasonic</td>
<td>Ultrasound energy</td>
</tr>
<tr>
<td>Microwave</td>
<td>Energy generated by microwaves</td>
</tr>
<tr>
<td>Microbiological</td>
<td>Microorganisms</td>
</tr>
</tbody>
</table>

*Not commercialised – used for research

** Either operated near ambient or heat introduced, e.g. by heated extruder
Thermo-Mechanical Processes

- Technology
  - Use shear or combination of heat and shear forces to break x-links
  - Can be carried out in intermixer (batch), extruder (continuous) or specialist equipment (e.g. HSM process)

- Advantages
  - No chemicals involved – cheaper, environmentally friendly
  - Standard processing equipment can be used – modifications possible (e.g. use of CO₂ as process aid)

- Disadvantages
  - Some chain scission can occur
  - Can work better with heat resistant rubbers, e.g. EPDM and Butyl rubber

- Commercialisation, e.g.:
  - HSM Process – now owned by Rep
  - H.S. Polymer Reprocessing – HSP Process
  - Rubber Resources
Thermo-mechanical System – Using CO2
(Zhang et al - University of Waterloo)
Thermo-mechanical System - Watson-Brown HSM Process

Stator/Rotor Parts

Complete Assembly
Thermo-mechanical Processes – With Devulcanisation Chemicals

- **Technology**
  - Combination of heat, shear and chemical reactions to break x-links
  - Intermixer (batch process) or extruder (continuous) possible
  - Can be assisted by liquid CO2 as carrier/swelling agent – e.g. in extruder

- **Advantages**
  - Flexible with good control over process
  - Lower temperatures can be used – reduces degradation
  - Some systems do not require rubber re-compounding for re-curing

- **Examples of chemicals used**
  - Thiophilic compounds – De-Link system
  - Urea compound and a Difunctional acid compound - Levgum system
  - Hexadecyclamine – sulphur cured EPDM

- **Commercialisation, e.g:**
  - De-link – developed in mid-1990’s
  - Levgum
Ultrasonic Process

- Technology
  - Developed since 1980’s at Akron University by Dr Isayev
  - Ultrasound used to selectively break x-links
  - Extrusion based systems developed
    - twin screw and single screw

- Advantages
  - Works with a range of rubber types:
    - NR, SBR, Butyl and BR
    - Well characterised

- Commercialisation
  - Akron University
  - Ultramer, Redwood Rubber, Rubberworks International - all in USA
Ultrasonic Devulcanisation Systems – provided by Dr Isayev (Akron University)
Characterisation of Devulcanised Rubber

• Chemical Analysis Methods
  • Solvent extraction to indicate degree of devulcanisation
  • Molecular weight by Gel Permeation Chromatography (GPC)
    • Determines molecular weight – shows if chain scission has occurred

• Physical Testing Methods
  • Residual x-links by equilibrium swelling – gives x-link density
  • Viscosity and Modulus – effected by residual x-links

• Processibility
  • Cure characteristics, extrusion and moulding performance etc

• Physical Properties
  • Hardness, tensile strength of final product
Uses of Devulcanised Rubber

- Manufacture of new products
  - Tyre rubber into General Rubber Goods
    - Gaskets, seals, anti-vibration mounts etc
- End-of-life product back into new product
  - Part replacement of compound
    - Tyre treads – e.g. OTR tyres
    - EPDM Weather strip
    - Industrial mats
- Re-use of in-house manufacturing scrap
  - Where tonnages allow
- Blends with thermoplastics
  - Thermoplastic rubbers
Products Manufactured from Devulcanised Rubber

Retreaded Tyres (up to 30%)  GRG (up to 50%)
Other Routes for Recycling Waste Rubber
Other Routes for Recycling Waste Rubber
– Summary List

• Reclaiming Processes
  • Produce process aids and cost reduction additives
• Incineration to generate electricity
• Pyrolysis to yield products
  • Manufacture of Hydrocarbon Products/Fuel Oils
  • Recovery of Carbon Black and other fillers (e.g. silica)
• Retreading of truck tyres – form of recycling
  • Truck tyres retreaded up to six times – re-use of carcass etc
• General
  • Use in Civil Engineering Projects
    • e.g. shred as “lightweight fill” in bridges
  • Landfill engineering
    • e.g. shred for leachate collection
Incineration - Energy Recovery

- Comparative Energy Content (N. Ishizawa)

<table>
<thead>
<tr>
<th>Product</th>
<th>Energy Content (kcal/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>6,000</td>
</tr>
<tr>
<td>Tyres</td>
<td>8,000</td>
</tr>
<tr>
<td>Heavy Oil</td>
<td>9,000</td>
</tr>
</tbody>
</table>

- Geographical Data – Proportion of waste tyres incinerated
  - 70% Japan and Brazil
  - 53% in USA and 41% Europe
  - 22% Australia
  - 0% Mexico and New Zealand

- Incineration in Cement Kilns – Salts and oxides useful in cement
  - High temps (~2,000 °C) covert steel to iron oxide
  - Calcium sulphate generated (CaO in cement + SO\textsubscript{2} from breakdown of rubber)
### Pyrolysis of Tyres – Products

<table>
<thead>
<tr>
<th>Product</th>
<th>Approximate Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Gas</td>
<td>10-12</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>40-45</td>
</tr>
<tr>
<td>Carbon Black*</td>
<td>30-35</td>
</tr>
<tr>
<td>Steel Wire</td>
<td>10-15</td>
</tr>
<tr>
<td>Inorganic Material</td>
<td>&gt;15</td>
</tr>
</tbody>
</table>

- Recovered Carbon Black - Research findings:
  - Particle size, distribution and structure different to original black
  - Around ~80% carbon due to inorganics on surface
  - Similar properties to SRF N774
Future Developments and Conclusions
Future Developments

• Pressure to recycle continue to increase
  • EU may ban landfilling of all materials by 2025
• Use of rubber crumb continue to grow
  • e.g. construction products
• Further improvements in devulcanisation processes
  • Goal to retain 100% of properties
  • Reduction in costs
• More recycling of GRG’s
• Increase in use of recovered black
Conclusions

- Range of options for recycling rubber
- Devulcanisation can be very effective
- Rubber crumb used successfully in many different products
- Good quality new products possible in many cases
- Level of rubber recycling will increase
Thank You
and Any Questions?

For further information : mforrest@smithers.com