Innovations in Rubber Design

4 Hamilton Pl, London W1J 7BQ, UK
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Continuous rubber recycling
using a co-rotating twin screw extruder

Dr. Alessandro GALLO
1. About Maris company and CTSE
2. Continuous rubber recycling using a c-TSE
3. Conclusions
Established in 1962, Maris is a leading force in the production of Co-Rotating Twin-Screw Extruders. Its 50-year know-how is ensured by a full “in-house” process that involves all levels of the production: design and engineering, manufacturing and assembling.

The company boasts a state-of-the-art Technological Center, dedicated to both the development of innovative processes and applications, as well as running trials for the most diverse materials and compounds.

Maris is a Customer oriented company, experienced in providing global solutions as well as turn-key projects, with the ultimate goal of exceeding the Customers’ expectations and creating a long term cooperation and trust.
1. Maris Company profile

**In house activities**

**In-house production activities:**

- CAD engineering for new lines design, and innovation
- Organization of working cycles
- Gear-box parts machining as gear cutters, grinders, etc (automatic working centers)
- Barrels manufacturing (automatic working centers)
- Screw elements production (automatic working centers)
- Robotized welding center
- Software customizing
- Quality control
- Complete line assembling
- Test of complete line before delivery of the extruders
1. Maris Company profile

Different kinds of Extruder

- Single-Screw
- Twin-Screw
- Multiple-screw

- Co-rotating
  - Intermeshing
  - Non-intermeshing

- Counter-rotating

- Rotating center shaft
- Static center shaft
Co-Rotating Twin-Screw Extruder features: $D_o/D_i$ ratio

Channel depth:

$$H = D_o - a = \frac{D_o}{2} \left( 1 - \frac{D_i}{D_o} \right)$$

Shear rate in the channel:

$$\gamma = \frac{\pi \cdot D \cdot \nu}{H} = \frac{2\pi \cdot \nu}{1 - D_i / D_o}$$

$\nu$ = screws speed (s⁻¹)
MARIS is capable of providing Co-rotating Twin-screw extruders with three different $D_o/D_i$ ratios:

<table>
<thead>
<tr>
<th>TM series</th>
<th>M/HT</th>
<th>HS</th>
<th>VM</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_o/D_i$</td>
<td>1.55</td>
<td>1.65</td>
<td>1.78</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feature</th>
<th>M/HT</th>
<th>HS</th>
<th>VM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel depth (H)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Free volume</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shear rate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shear stress</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residence time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Capacity</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1. Maris Company profile

Co-Rotating Twin-Screw Extruder features: **screw elements**

<table>
<thead>
<tr>
<th>Screw conveying block</th>
<th>screw channels:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Lengthwise open</td>
<td></td>
</tr>
<tr>
<td>- Crosswise closed</td>
<td></td>
</tr>
<tr>
<td>- No material exchange between channels</td>
<td></td>
</tr>
<tr>
<td>- No backflow along the screw</td>
<td></td>
</tr>
<tr>
<td>- No calender effect, the flow does not pass through the screws</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Screw kneading block</th>
<th>screw channels:</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Lengthwise open</td>
<td></td>
</tr>
<tr>
<td>- Crosswise closed</td>
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<tr>
<td>- Material exchange between channels</td>
<td></td>
</tr>
<tr>
<td>- Backflow along the screw</td>
<td></td>
</tr>
</tbody>
</table>
1. Maris Company profile

Co-Rotating Twin-Screw Extruder features: **screw elements**

- **CONVEYING ELEMENT**
  - Right Hand
  - Left Hand

- **KNEADING ELEMENT**
  - Right Hand
  - Left Hand

**Screw 1**

**Screw 2**

no communication through the channels

**Screw 1**

**Screw 2**

communication through the channels

Backflow
1. About Maris company and CTSE
2. Continuous rubber recycling using a c-TSE
3. Conclusions
2. Continuous Rubber Recycling

Vulcanized rubber: chemical structure

Plastomer

Entanglement (Physical interaction)

Elastomer

Crosslink (Chemical Bond)
2. Continuous Rubber Recycling

Vulcanized rubber: chemical structure

Crosslinking:  
- physical - chemical:
  - heat
  - UV
- chemical: heat + curing agent:  
  - peroxide
  - sulfur

<table>
<thead>
<tr>
<th>Bond</th>
<th>$E_{\text{bond}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>370</td>
</tr>
<tr>
<td>C-S</td>
<td>310</td>
</tr>
<tr>
<td>S-S</td>
<td>270</td>
</tr>
</tbody>
</table>

Network

Thermal treatment

Material degradation
2. Continuous Rubber Recycling

Vulcanized rubber reuse

Post consumer waste, waste products, scraps ...

- combustion
  - energy

- thermal cracking
  - hydrocarbons
  - carbon black

- grinding

- devulcanization

- fillers
  (rubber mats, ..)

- rubber recycling
2. Continuous Rubber Recycling

Devulcanization target: selective break of crosslink bonds
(Typically C-S and S-S bonds)

Physical methods:
- ultrasonic
- microwave
- mechanical stress

Chemical methods:
use of a Devulcanization Agent (DVA) to:
- break crosslinks
- stabilize fragments

Chemical – physical methods: synergic action of:
- mechanical stress
- DVA
Only a small percentage of rubber waste is recycled by devulcanization at present time.

Commonly used industrial processes are based on:

- Chemical methods:  
  - in surge tank  
  - solvents, DVA

- Chemical – mechanical methods:  
  - DVA  
  - Mixing device (e.g. a two-roll mill)

Critical aspects:

- In general, batch or time consuming
- Use of solvents and chemicals
- Harmful for environment
- Difficult to manage
- Downstream equipment need
- Vulcanized rubber in powder form
2. Continuous Rubber Recycling

Why using a co-rotating twin screw extruder?

<table>
<thead>
<tr>
<th></th>
<th>C-C</th>
<th>C-S</th>
<th>S-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{bond}$ (kJ/mol)</td>
<td>370</td>
<td>310</td>
<td>270</td>
</tr>
<tr>
<td>$k$ (N/m)</td>
<td>$k_{cc} \approx 100$</td>
<td>$k_{cs}$</td>
<td>$k_{ss} \approx 3$</td>
</tr>
</tbody>
</table>

Thermal excitation:

- Applying mechanical stress, energy localizes mainly in S-S bonds
- High shear strain needed: at low strain, entropic effects dominate elasticity

(See K. Fukumori and M. Matsushita, R&D Review of Toyota CRDL Vol. 38 No. 1)
Describing in the easiest possible way a covalent chemical bond as an electrostatic interaction between atoms, we can say that at 0 K it has some particular features such as its Energy (Eb) and its length (xb). Over this Energetic level (for example increasing the temperature) the bond shows a behaviour like a spring, balancing the attractive and the repulsive forces between the atoms. The two extremes of this situation are the proximity of the atoms (contrasted by repulsive forces) and the non-bond, the rupture of the chemical bond obtaining again two separate atoms.
2. Continuous Rubber Recycling

The potential well in a covalent chemical bond

Thanks to the high-temperature effects and in the first part of extruder it is possible to excite atoms which produce the contraction/enlargement of the spring. When all the bond are excited the shear force attacks mainly bond with the lowest konstant elastic of the bond, the polysulfonic ones, preserving the others chemical's species.

Thanks to the chemical resonance theory it is possible to explain in which way the process should be selective also for the peroxide-cured compounds.
2. Continuous Rubber Recycling

- Chemical modification
- Rheological Properties
- Mechanical Properties
Characterization of the devulcanized rubber: some significant results

Rubber types discussed: NR, SBR, NBR, EPDM

Analysis performed:

- $^{13}$C NMR
- extraction with solvent
- MDR rheometry
- mechanical properties
  (Modulus, tensile strength, elongation, hardness, …)
2. Continuous Rubber Recycling

**Characterization** of the devulcanized rubber: $^{13}$C NMR monitoring of the cis / trans poli-isoprene conversion

Poly-isoprene

Two stereoisomers for the C=C double bond:

- Most frequent
- Very small percentage

(with stereo-selective polymerization (Ziegler-Natta))

Percentage of trans isomer: index of chemical / mechanical stress undergone
2. Continuous Rubber Recycling

**Characterization** of the devulcanized rubber: $^{13}$C NMR monitoring of the cis / trans poli-isoprene conversion

<table>
<thead>
<tr>
<th>Maris Thermo – Mechanical Process</th>
<th>Trans %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PI raw</td>
<td>1.2</td>
</tr>
<tr>
<td>PI compound (not vulcanized)</td>
<td>1.9</td>
</tr>
<tr>
<td>PI compound (vulcanized)</td>
<td>2.5</td>
</tr>
<tr>
<td>PI de-vulcanized by MARIS</td>
<td>5.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermo – Chemical process (*1)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NR compound (vulcanized)</td>
<td>3.0</td>
</tr>
<tr>
<td>NR devulcanized with Diphenyldisulphide (2.4 wt%)</td>
<td>19.0 ~6X</td>
</tr>
<tr>
<td>NR devulcanized with Diphenyldisulphide (10 wt%)</td>
<td>41.0 ~14X</td>
</tr>
</tbody>
</table>

*1: Rif.: “Mechanism involved in the recycling of NR and EPDM”; M.a.L. Verbrugen, L. Van Der Does, J.W.M. Noordermeer - RC&T Vol. 72, 731-740
### Characterization of the devulcanized rubber: solvent extraction

<table>
<thead>
<tr>
<th></th>
<th>PI compound NON vulcanized</th>
<th>PI compound vulcanized</th>
<th>PI compound de-vulcanized</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGA, total organic</td>
<td>69.06</td>
<td>69.9</td>
<td>63.9</td>
</tr>
<tr>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>extracted fraction,</td>
<td>-</td>
<td>10.8</td>
<td>46.7</td>
</tr>
<tr>
<td>in CHCl₃ (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>apparent crosslinking</td>
<td>-</td>
<td>4.43 E-5</td>
<td>9.67 E-6</td>
</tr>
<tr>
<td>(mol/g)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Apparent crosslinking computed by **Flory – Rhener model**:

\[
\nu = \frac{\ln(1-v_r) + v_r + \chi v_r^2}{V_s (0.5v_r - v_r^{1/3})}
\]

- \( \nu_r \): polymer volume fraction in swollen vulcanize
- \( \chi \): polymer-solvent interaction parameter
- \( V_s \): solvent molar volume
- \( v \): number of elastically active network chains per unit volume

Devulcanization yield: 70 – 80 %
2. Continuous Rubber Recycling

**Characterization** of the devulcanized rubber: **Rheometry**

<table>
<thead>
<tr>
<th></th>
<th>PI</th>
<th>PI</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>DE-vulc</td>
<td>Virgin</td>
<td>DE-vulc (40%)</td>
<td>Virgin (60%)</td>
</tr>
</tbody>
</table>

Cur: YES  YES  YES  NO

Mooney: 100.1 - 52.2

| M46 | 7.38 | 910.94 |
| M86 | 20.11 | 332.68 |
| ts20 | 0.64 | 0.51 |
| ts90 | 5.85 | 2.8 |

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**Legend:**
- red: vulcanizable
- blue: devulcanized

**Graph:**
- Torque vs. time
- Plot showing the comparison between vulcanizable and devulcanized rubber over time.
## 2. Continuous Rubber Recycling

**Characterization** of the devulcanized rubber: **Mechanical properties**

<table>
<thead>
<tr>
<th></th>
<th>PI virgin</th>
<th>PI DE-vulc (40 %)</th>
<th>PI Virgin (60 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus at 100% (M Pa)</td>
<td>0.95</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Modulus at 300% (M Pa)</td>
<td>1.78</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>Tensile strength (M Pa)</td>
<td>22.91</td>
<td>19.94</td>
<td></td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>891</td>
<td>835</td>
<td></td>
</tr>
<tr>
<td>IRHD Hardness</td>
<td>67.1</td>
<td>62.2</td>
<td></td>
</tr>
<tr>
<td>Elastic Yield</td>
<td>48.4</td>
<td>42.8</td>
<td></td>
</tr>
</tbody>
</table>
2. Continuous Rubber Recycling

The last question
2. Continuous Rubber Recycling

The investigation method

To better understand the process at 360° we decided to make an analytical investigation during an EPDM sulphur cured recycling. In particular we analysed fumes in the working area (1), in the aspiration on the head of the extruder (2), in the vacuum system (3a), and liquids in condensed in the vacuum system(3b).
2. Continuous Rubber Recycling

The analysis showed that processing this particular EPDM the sulphur was in every sampling point. Although in the working area there are no chemical risks to obtain this condition...

....It fundamental to suck up any gas and vapour by using the degassing system and put some aspiration hoods on the main hopper, on the degassing equipment and on the head of the extruder, the only points where some chemical hazardous substances can be produced.

The elastomeric material and the curing agents, employed for compounding it, can change the condensed liquid and vaporous emissions composition. Those emission must be treated in function of the environmental local laws.
1. About Maris company and CTSE
2. Continuous rubber recycling using a c-TSE

3. Conclusions
• Characterization and tests performed on the devulcanized material are very encouraging for different elastomeric materials. It is possible to reuse from 15 to 50% of recycled material (depending on final compound properties)
• The optimal process conditions are strongly depending on rubber composition and scraps homogeneity
• Although during the process several kind of chemical substances are produced, it is possible to manage those emissions with special equipment and be respectful of local environmental laws
• Rubber devulcanization is a project conceived with the aim of complying with the recent European environmental rules, paying also attention to the current economical crisis
Conclusions

Raw Material Purchasing
(rubber, oil, filler, additives, curing agent)

Production Cost
(personnel, energy and ancillaries, amortization...)

Vulcanizable Rubber Compound

LANDFIL

PROFIT

waste

product
A MEDIUM SIZE PLANT CAN BE AMORTIZED IN YEARS!

PRESERVE THE QUALITY

RESPECT THE ENVIRONMENT

SAVE MONEY
For a production rate of 400 kg/h

<table>
<thead>
<tr>
<th>Note</th>
<th>Individual cost</th>
<th>Production costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy consumption</td>
<td>0.70 kWh/kg</td>
<td>0.11€/kWh</td>
</tr>
<tr>
<td>People</td>
<td>1 people</td>
<td>7.00€/h</td>
</tr>
<tr>
<td>Maintenance</td>
<td>Standard</td>
<td>0.04 €/kg</td>
</tr>
<tr>
<td>Amortisation</td>
<td>Estimated for</td>
<td>0.125 €/kg</td>
</tr>
</tbody>
</table>

**THAT MEANS: LESS THAN 300 €/TONS**
## Conclusions

**MARIS c-TSE rubber recycling production rate**

<table>
<thead>
<tr>
<th>c-TSE size</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>58</th>
<th>70</th>
<th>80</th>
<th>92</th>
<th>112</th>
<th>133</th>
</tr>
</thead>
<tbody>
<tr>
<td>Output * (kg/h)</td>
<td>5</td>
<td>20</td>
<td>50</td>
<td>80</td>
<td>100</td>
<td>150</td>
<td>250</td>
<td>400</td>
<td>550</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>30</td>
<td>80</td>
<td>100</td>
<td>150</td>
<td>250</td>
<td>350</td>
<td>500</td>
<td>650</td>
<td>800</td>
</tr>
</tbody>
</table>

* Those data strongly depend on the quality of the vulcanized material
Thank you very much for your attention!

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