MIMICKING THE NATURE: HOOK-AND-LOOP ADHESION SYSTEMS FOR ELASTOMERS

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ORIGIN OF CONCEPTS
WHERE DO IDEAS COME FROM? – BIOMIMICRY: CASE STUDY

Gecko Feet Adhesives
Shark skin
Velcro

Annoying feature of weeds
Useful technical solutions

**INTRODUCTION**

**CHARACTERISTICS OF MICROSCOPIC VS. MOLECULAR VELCRO SYSTEMS**

<table>
<thead>
<tr>
<th>Microscopic Velcro system</th>
<th>VS.</th>
<th>Molecular Velcro system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superior fatigue resistance</td>
<td></td>
<td>Superior fatigue resistance</td>
</tr>
<tr>
<td>Superior reconnectability performance</td>
<td></td>
<td>Superior reconnectability performance</td>
</tr>
<tr>
<td>Good mechanical properties</td>
<td></td>
<td>Good mechanical properties</td>
</tr>
<tr>
<td>Good ageing resistance</td>
<td></td>
<td>Good ageing resistance</td>
</tr>
<tr>
<td>Stiff hooks, elastic loops</td>
<td></td>
<td>Stiff/elastic hooks, stiff/elastic loops</td>
</tr>
<tr>
<td>Hooks and loops materials chemical compatibility – not relevant</td>
<td></td>
<td>Hooks and loops materials chemical compatibility – very relevant (mutual solubility/miscibility)</td>
</tr>
<tr>
<td>Molecular mobility – not relevant</td>
<td></td>
<td>Molecular mobility – very relevant</td>
</tr>
</tbody>
</table>
**INTRODUCTION**

**FOCUS ON PHYSICAL INTERACTIONS**

**Chemical interactions:**
- Covalent bonds
- Ionic bonds
- Coordinate bonds

**Strong physical interactions:**
- Hydrogen bonds
- Ion/dipole and ion-induced/dipole interactions
- Dipole/dipole interactions

**Physical interactions:**
- Dispersion interactions
- Steric hindrance
- Macromolecular entanglements
- Chemical affinity (miscibility/solubility)

**Velcro-like approach** – grafting of relatively large molecules onto the silica surface of good chemical affinity to the rubber, enhancing interactions via physical entanglements and steric hindrance.

*Telechelic mono-hydroxy polybutadiene oligomer (o-BR) was used as a backbone for the modifier.*

Molecular weight of the o-BR: **4691 g/mol**  
Length of straightened molecule: **~30 nm**  
Number of vinyl mers: **~60 per molecule**
INTRODUCTION
SCHEME OF SILICA-SURFACE MODIFICATION

1 – Attaching the isocyanate silane molecule to the telechelic o-BR chain

2 – Grafting on the silica surface

3 - Additional treatment with trimethylethoxysilane in order to cover residual, reactive silanol groups
INTRODUCTION
SCHEME OF SILICA-SURFACE MODIFICATION

4 – Attaching thioles moieties to the vinyl groups of o-BR

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SYNTHESIS OF OLIGOMER-BACKBONE REACTION PROGRESS TRACKING BY FTIR

Isocyanate silane – 0.527 g + o-BR – 10 g: mixed together and heated at 50 °C for 24, 48 and 72 hours.
SYNTHESIS OF OLIGOMER-BACKBONE
REACTION PROGRESS TRACKING BY FTIR

Isocyanate silane – 0.527 g + o-BR – 10 g: mixed together and heated at 80 °C for 24, 48 and 72 hours.
SYNTHESIS OF OLIGOMER-BACKBONE
REACTION PROGRESS TRACKING BY FTIR

The reaction rate increases significantly with the increase of temperature from 50 °C to 80 °C.
PROCEDURE CHARACTERISTICS

Procedure:
- Duration - 24 hours
- Air atmosphere
- Temperature - 100 °C
- Mechanical stirring – 150 rpm
- Extraction in toluene after the reaction – 20 hours

Composition of the samples

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Weight ratio</th>
<th>Precipitated silica (MP)</th>
<th>IsocySilane/o-BR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica + 20 silane_o-BR_extr20h</td>
<td>1/5</td>
<td>100 g</td>
<td>20 g</td>
</tr>
<tr>
<td>Silica + 50 silane_o-BR_extr20h</td>
<td>1/2</td>
<td>100 g</td>
<td>50 g</td>
</tr>
<tr>
<td>Silica + 100 silane_o-BR_extr20h</td>
<td>1/1</td>
<td>50 g</td>
<td>50 g</td>
</tr>
</tbody>
</table>

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OLIGOMER-BACKBONE GRAFTING ON SILICA SURFACE

GRAFTING RESULTS ANALYSED BY FTIR

FTIR spectra of silica modified with various amounts of the oligomer-backbone (indicated bands from unsaturated groups)
OLIGOMER-BACKBONE GRAFTING ON SILICA SURFACE

GRAFTING RESULTS ANALYSED BY XPS

XPS analysis of the silica sample modified with 50 parts of the o-BR per 100 parts of the silica

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>O</th>
<th>Na</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amount on the Surface [%]</td>
<td>46.19</td>
<td>16.65</td>
<td>36.57</td>
<td>0.40</td>
<td>0.19</td>
</tr>
</tbody>
</table>
OLIGOMER-BACKBONE GRAFTING ON SILICA SURFACE

GRAFTING RESULTS ANALYSED BY TGA

<table>
<thead>
<tr>
<th>Sample description</th>
<th>Summary mass loss [%]</th>
<th>Mass loss of organic component [%]</th>
<th>Density of grafted molecules [1/nm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Silica + 20 silane_o-BR_extr20h</td>
<td>20.2</td>
<td>15.8</td>
<td>6.37</td>
</tr>
<tr>
<td>Silica + 50 silane_o-BR_extr20h</td>
<td>26.4</td>
<td>22.9</td>
<td>4.07</td>
</tr>
<tr>
<td>Silica + 100 silane_o-BR_extr20h</td>
<td>24.8</td>
<td>21.3</td>
<td>4.46</td>
</tr>
</tbody>
</table>

Average silanol group concentration on silica surface according to literature is ~5 -OH/nm²

Single o-BR molecule terminated with the silane can react with up to 3 silanol groups (ca. 10-15 % of all -OH groups)

Additional treatment is required to cover the residual, reactive -OH groups

ADDITIONAL SILANIZATION
SILANIZATION RESULTS ANALYSED BY FTIR

Additional treatment with trimethylethoxysilane in order to cover residual, reactive silanol groups.

- Suspension in toluene
- Temperature: 70 °C
- Duration: 24 hours
PROGRESS OF THE MODIFICATION
SCHEME OF SILICA-SURFACE MODIFICATION

1 – Attaching the silane molecule to the telechelic o-BR chain

2 – Grafting on the silica surface

3 – Additional treatment with trimethylethoxysilane in order to cover residual, reactive silanol groups

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4 – Attaching thioles moieties to the vinyl groups of o-BR
BRANCHING OF OLIGOMER-BACKBONE
TELECHELIC BUTADIENE OLIGOMER REACTIONS WITH THE THIOLES

Procedure parameters:
Duration – **1 hour**
Temperature – 65-70 °C (constant growth)
Mechanical stirring – **150 rpm**
Atmosphere – **nitrogen**
Evaporation – 24 hours, 70 °C
Degassing - 24 hours, 70 °C (vacuum)

After evaporation
After degassing in vacuum oven

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BRANCHING OF OLIGOMER-BACKBONE
OLIGOMER BRANCHING RESULTS ANALYSED BY LS-NMR


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BRANCHING OF OLIGOMER-BACKBONE
OLIGOMER BRANCHING RESULTS ANALYSED BY LS-NMR

Presence of aromatic groups seems to influence negatively the effectiveness of the reaction.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Integration ratio (d/(a+b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-BR</td>
<td>1.351</td>
</tr>
<tr>
<td>o-BR + tert-Dodecanethiol</td>
<td>0.287</td>
</tr>
<tr>
<td>o-BR + Cyclohexanethiol</td>
<td>0.427</td>
</tr>
<tr>
<td>o-BR + 1-Hexadecanethiol</td>
<td>0.319</td>
</tr>
<tr>
<td>o-BR + 2-Thionaphthol</td>
<td>1.099</td>
</tr>
<tr>
<td>o-BR + Triphenylmethanethiol</td>
<td>1.316</td>
</tr>
</tbody>
</table>

Possibly presence of electron-donor alkyl group is necessary for effective grafting to vinyl groups.

Side reaction – recombination of thiole radicals?
BRANCHING OF OLIGOMER-BACKBONE
OLIGOMER BRANCHING RESULTS ANALYSED BY GPC

Molecular weight distribution before and after reaction with the thiole

---
- o-BR
- o-BR + tert-Dodecanethiol
- o-BR + 1-Hexadecanethiol
- o-BR + Cyclohexanethiol
- o-BR + 2-Thionaphthol
- o-BR + Triphenylmethanethiol

Molecular mass [g/mol]
BRANCHING OF OLIGOMER-BACKBONE
PROCEDURE CHARACTERISTICS

Procedure parameters:
- Duration – 1 hour
- Temperature – 65-70 °C (constant growth)
- Mechanical stirring – 150 rpm
- Atmosphere – nitrogen
- Evaporation – 24 hours, 70 °C
- Degassing - 24 hours, 70 °C (vacuum)

Thioles used for oligomer-backbone branching:
- tert-Dodecanethiol
- 1-Hexadecanethiol
BRANCHING OF Oligomer-Backbone Grafted-Oligomer Branching Analysed by FTIR

<table>
<thead>
<tr>
<th>Sample</th>
<th>Unsaturated&lt;sub&gt;909/1067&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-BR</td>
<td>0.296</td>
</tr>
<tr>
<td>o-BR + tert-Dodecanethiol</td>
<td>0.197</td>
</tr>
</tbody>
</table>

Sample 909/1067

3150 2650

1642 cm<sup>-1</sup> 993 cm<sup>-1</sup> 909 cm<sup>-1</sup>

Silica + silane-o-BR_TMES
Silica + silane-o-BR_TMES_ tert-DodecaneThiol
tert-DodecaneThiol

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BRANCHING OF OLIGOMER-BACKBONE
GRAFTED-OLIGOMER BRANCHING ANALYSED BY FTIR

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<tr>
<th>Sample</th>
<th>Unsaturated_{909}/Si-O-Si_{1067}</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-BR</td>
<td>0.296</td>
</tr>
<tr>
<td>o-BR + 1-Hexadecanethiol</td>
<td>0.182</td>
</tr>
</tbody>
</table>

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BRANCHING OF OLIGOMER-BACKBONE GRAFTED VS NON-GRAFTED OLIGOMER BRANCHING ANALYSED BY HR-MAS NMR

<table>
<thead>
<tr>
<th>Sample</th>
<th>Integration ratio (d/(a+b))</th>
<th>% reacted vinyl groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-BR</td>
<td>1.351</td>
<td>78.8 %</td>
</tr>
<tr>
<td>o-BR + tert-Dodecanethiol</td>
<td>0.287</td>
<td></td>
</tr>
<tr>
<td>% reacted vinyl groups</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Sample | Integration ratio (d/(a+b)) | % reacted vinyl groups |
Silica + o-BR                     | 1.235                       |                        |
Silica + o-BR + tert-Dodecanethiol | 0.901                       | 27.0 %                 |

Negative influence of water? Immobilization of thioles on silica surface?
BRANCHING OF OLIGOMER-BACKBONE
BRANCHED VS NON-BRANCHED OLIGOMER ON SILICA ANALYSED BY EFTEM

Non-branched o-BR on silica surface

O-BR branched with tert-dodecanethiol on silica surface
GREEN MIXES PERFORMANCE
PREPARATION OF SILICA FILLED SSBR GREEN MIXES

SSBR 100 phr + 70 phr of:
- Silica + Trimethylethoxysilane (TMES)
- Silica + Dodecyltriethoxysilane (D-DTES)
- Silica + Isocy_silane_o-BR + tert-Dodecanethiol
- Silica + Isocy_silane_o-BR + 1-Hexadecanethiol

Introducing rubber
Introducing filler
Dispersion & homogenization

Mixing procedure
2 min
2 min
4 min

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GREEN MIXES PERFORMANCE
PROPERTIES OF THE MIXES

Relaxation 60 °C

- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol

[dNm] vs Time [s]

0 10 20 30 40 50 60 70 80 90

0 50 100 150 200 250 300 350
GREEN MIXES PERFORMANCE
PROPERTIES OF THE MIXES

Relaxation 200 °C

- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol

[Graph showing relaxation at 200 °C for different materials over time]

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GREEN MIXES PERFORMANCE
PROPERTIES OF THE MIXES

Share modulus vs. Strain; 60 °C
- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol

Shear modulus vs. Strain; 200 °C
- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol

Storage modulus vs. Strain; 60 °C
- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol

Storage modulus vs. Strain; 200 °C
- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol
GREEN MIXES PERFORMANCE
PROPERTIES OF THE MIXES

**Loss modulus vs. Strain; 60 °C**

- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol

**Loss modulus vs. Strain; 200 °C**

- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol

**Tan Delta vs. Strain; 60 °C**

- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol

**Tan Delta vs. Strain; 200 °C**

- SSBR
- TMES
- D-DTES
- tert-Dodecanethiol
- 1-Hexadecanethiol
SUMMARY

NEXT STEPS

O-BR modified with small-molecular thioles:
- TGA analysis of silica modified with the various compounds
- Enhancing efficiency and analysis of thioles reaction with vinyl groups of the oligomer backbone grafted and not-grafted on silica surface

Green mixes filled with the modified silica:
- Preparation of rubber samples filled with silica covered with o-BR and Cyclohexanethiol modified o-BR
- DMA analysis of the samples
- SEM and DisperGrader analysis of the samples

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Conclusions:

- Reaction between telechelic monohydroxy-butadiene oligomer (o-BR) and isocyanate silane allows grafting of relatively large organic chains on silica surface with high efficiency.
- Utilization of polybutadiene backbone containing vinyl groups enables effective branching of the macromolecule with various thioles.
- Developed procedure provides a simple and effective method of long branched-molecules grafting on silica surface.
- Addition of modified silica to SSBR rubber results in interesting dynamic properties, especially at elevated temperature when macromolecular mobility is high.
Thank you for your kind attention!