The Wear and Tear of Polyurethane rubber

Investigation into properties, degradation and treatments

Suzan de Groot
Anna Laganà
Henk van Keulen
Thea van Oosten
Marta Palmeira

Loris Cecchini, Stage Evidence Finestre II
2000, Private collection

27 October 2011, Future Talks 011, Munich
PUR ester and ether elastomer objects

Loris Cecchini, Finestre II, 2000, Private collection
Hella Jongerius, Urn, 1994
Centraal Museum Utrecht
Hella Jongerius, Soft vase, 1994, Centraal Museum Utrecht
Saar Oosterhof, Table cloth with bowl, 1998, Centraal Museum Utrecht
Gaetano Pesce, ring, 2011
Gaetano Pesce, bracelet, 2003
Gaetano Pesce, Pratt chair no. 2
Heringa van Kalsbeek, Untitled, 2011
How is PUR made?

epoxide

\[ \text{diol} \]

\[ \text{polyether} \]

\[ \text{PUR ether prepolymer} \]

\[ \text{ epitoxide} \rightarrow \text{diethylene glycol} \rightarrow \text{PUR ether prepolymer} \]

\[ \text{dil} \]

\[ \text{ethyleneglycol-adipic acid polyester} \]

\[ \text{PUR ester prepolymer} \]

\[ \text{adipic acid} \]
How is PUR made?

**PUR ester elastomers: internally plasticized**
(chain extenders) 1,4, butanediol

**PUR ester elastomers: externally plasticized:**
Phthalate esters
How is PUR ether made?

Part A
Toluene Diisocyanate < 1%
Diisononylphthalate 5-15%

Part B
Polyol/Plasticizer Blend 90-95%
Diethyltoluenediamine 1-5%

<table>
<thead>
<tr>
<th>Vitaflex</th>
<th>Component A</th>
<th>Component B</th>
<th>Shore hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>100</td>
<td>100</td>
<td>10 A</td>
</tr>
<tr>
<td>20</td>
<td>100</td>
<td>100</td>
<td>20 A</td>
</tr>
<tr>
<td>30</td>
<td>100</td>
<td>100</td>
<td>30 A</td>
</tr>
<tr>
<td>40</td>
<td>100</td>
<td>100</td>
<td>40 A</td>
</tr>
</tbody>
</table>
How is PUR ester made?

| Parts by weight |
|-----------------|---------------|---------------|---------------|
| Shore hardness  | Component A   | Component B   | Component C   |
| 40 A            | 10            | 100           | 0             |
| 25 A            | 10            | 100           | 20            |
| 15 A            | 10            | 100           | 40            |
| 10 A            | 10            | 100           | 60            |
| 6 A             | 10            | 100           | 80            |

Part A: TDI prepolymer

Part B: diisocyanate + kaolin

Part C: Butylbenzyl phthalate

![Diagram of PUR ester structure](image)

- Urethane group
- Diphenyl methane group
- Urethane group

Ester groups

Polyethylene glycol segment

Chemical structure of PUR ester: $\text{H}_m\text{C}_n\text{O}_p$
Problems with PUR elastomers

### Physical/chemical change
- Loris Cecchini, *Stage evidence, Finestre II*, 2000, Private collection
- PUR Ester

### Efflorescence
- Saar Oosterhof, *Soft Tiles*
- Centraal Museum Utrecht
- PUR ether

### Mechanical damage
- Loris Cecchini, *Finestre II*, 2000
- Galleria Continua
- PUR Ester

- PUR ethers oxidize
- PUR ester hydrolyze

- Olaf Metzel, *'Wurfeisen und Zwille'*, 1990
- Hamburger kunsthalle
- PUR Ester

- Loris Cecchini, *Stage evidence, Fotocopiatrice*, 2002
- Museo de Novecento, Milano
- PUR Ester

- Hella Jongerius, *Soft vase*
- Private Collection
- PUR Ester
Stress

Skate wheel Bayer 2010

Damaged skate wheel

Broken part Soft Vase
Set up Research

Identification PUR objects:
• FTIR, Py-GCMS

Mimic physical/chemical change:
• find suitable PUR (artist interviews)
• making test samples
• artificial ageing

Measuring physical/chemical change of test samples:
• FTIR
• elasticity test
• shore hardness

Testing adhesives:
• FTIR
• refractive index
• artificial ageing
Identification FTIR

Soft Vase Hella Jongerius (PUR ester)

Skate wheel (PUR ether)

Finestre II, Loris Cecchini (PUR ester)

Urn, Hella Jongerius (PUR ether)

Hella Jongerius, Soft vase, Private Collection

Skate wheel

Loris Cecchini, Finestre II, 2000, Private collection

Hella Jongerius, Urn, 1994 Centraal Museum Utrecht
Identification PY-GCMS

Hella Jongerius, Soft vase, Private Collection

Saar Oosterhof, Table cloth with bowl, 1998, Centraal Museum Utrecht
Degradation PUR ether
‘Soft Tiles’, Saar Oosterhof

Soft Tile
Efflorescence
PTMEG
Poly tetramethylene glycol
Degradation PUR ester
‘Finestre II’, Loris Cecchini

Finestre II not weeping
Phthalic ester
Kaolin

Finestre II not weeping
Finestre II weeping
Making PUR ester test samples

Smooth-on PMC 724

Finestre, Cecchini
**Important:** This rubber will last and perform in production, often for hundreds of castings (depending on what you are casting into the mold). It also exhibits good physical properties and chemical resistance. But **PMC-724®** does not have a long “library life”. Molds will soften and revert to a liquid within 2 – 5 years, depending on exposure to moisture. Smooth-On makes many different mold rubbers that offer a very long library life (25 years and more depending on application). Contact Smooth-On for information about its complete line of silicone and polyurethane mold rubbers.

The table at right indicates the effect of different percentages of Part C on the Shore A hardness of the cured rubber. (Important: Use of ‘Part C’ to soften the rubber may shorten mold life.) *Shore A Hardness after 72 hours at 73°F/25°C.*
Artificial ageing

Ageing: 70°C, 30-80% 3 hrs interval for 2 weeks

Physical/mechanical test: Weight 2,5 kg

Smooth-on PMC 724, 25 shore test sample shows sticking soft material (weeping)

Smooth-on PMC 724 25 shore test sample: 20% increase in length

Smooth-on PMC 724 25 shore test sample **AGED**: 70% increase in length

After test:
Both test samples back to original size
Change in elasticity due to artificial ageing
What went wrong?

**Loris Cecchini**
Stage evidence series, PUR ester urethane
- Finestre II
  - 2000, Private Collector
- Weeping

**Hella Jongerius**
Soft vases, PUR ester urethane
- Soft vase,
  - 1999, Private Collector
- Soft vases, 1994

**Fotocopiatrice**
2002, Museo del Novecento, Milano
What can we do?

Hella Jongerius, Soft vase, 1999, 25 x Ø 19 cm 1,5 / 2 cm thickness

Crack

Broken parts

Research on adhering

Shore hardness 20A

Bubbles
Making test samples and dummies

- PUR ether elastomer (VytaFlex® 20 – Smooth on)
- Colour (Amber)
- Translucency
- Shore hardness

Test samples

Thick test samples 1,5 cm

Mimic mechanical damages
Selecting adhesives

- the ability to adhere polyurethane elastomers
- comparable optical properties
- comparable refractive index,
- the ability to make a flexible bond
- enough strength suitable working time to adhere large surfaces,
- preferably not yellowing,
- appropriately viscosity,
- chemical and physical stable
- preferably reversible.

<table>
<thead>
<tr>
<th>ADHESIVES</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bison Rubber repair</td>
<td>Polyester/polyether-urethane dispersion of aliphatic isocyanate</td>
</tr>
<tr>
<td>Bison Soft plastic adhesive</td>
<td>Polyester urethane</td>
</tr>
<tr>
<td>Bison kit transparent</td>
<td>Polyester urethane</td>
</tr>
<tr>
<td>Bison Kombi power</td>
<td>Polyester urethane (filled)</td>
</tr>
<tr>
<td>Bison stick Universal</td>
<td>Polyester urethane</td>
</tr>
<tr>
<td>Smooth-on Vitaflex 20</td>
<td>Polyether urethane</td>
</tr>
<tr>
<td>Bison Universal kit</td>
<td>Siliconated acrylate dispersion</td>
</tr>
<tr>
<td>Bison Alleslijm</td>
<td>Polyvinylacetate</td>
</tr>
<tr>
<td>Paraloid F10</td>
<td>Butylacrylate in mineral spirit</td>
</tr>
<tr>
<td>Plextol D 360</td>
<td>Acrylic Aqueous dispersion</td>
</tr>
<tr>
<td>Plextol B 500</td>
<td>Acrylic Aqueous dispersion</td>
</tr>
<tr>
<td>Plextol D 498</td>
<td>Acrylic Aqueous dispersion</td>
</tr>
</tbody>
</table>
Testing adhesives

Research include:

- Identifying all the adhesives using Fourier Transform Infrared spectroscopy
- Light aging of the adhesives using a Xenon 160 hours of artificial light equals 40 years at museum condition at 200 lux.
- Measuring the refractive index of the adhesives and the polyurethane objects
- Testing bond strength.

6 adhesives selected:
Plextol B500,
Plextol D480,
Plextol D360,
Bison soft plastic adhesive,
Bison Rubber repair
VytaFlex®20
Testing applicability

Plextol D 360
Polyurethane rubber repair
VytaFlex® 20

Testing appearance

BEFORE ADHERING

AFTER ADHERING

Plextol D 360
Polyurethane rubber repair
VytaFlex® 20
Conclusions

- It was possible to mimic the weeping of soft sticky material and loss in elasticity as in Finestre II

- PUR ester elastomer casting materials with external plasticizers turn to soft sticky material within 5 years (as nowadays mentioned in the datasheet) due to materials composition

- Preliminary good results were obtained with adhering PUR ethers elastomers

Ongoing research

- Adhering tests on translucent PUR ester elastomers based on the experience with PUR ether elastomers

- Strength tests for the selected adhesives

- Test consolidents on test samples and perform E-modulus tests after artificial ageing using heat and humidity
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