Accelerated ageing tests of vulcanized rubber

Deventer, May 14th 2009

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Ageing is a collective term for changes in properties of materials that occur on longer term storage, without the action of chemicals, that lead to partial or complete degradation.

These changes can occur in form of degradation processes, embrittlement-, rotting-, softening and fatigue processes, and/or static crack formation.
Influence on ageing resistance

1) Type of polymer
   - Saturated or unsaturated polymer backbone

2) Type of vulcanization system
   - Crosslink density and distribution

3) Type of antidegradant
   - staining or non-staining
   - fatigue-, oxygen or ozone resistant
Ageing factors causing degradation

- Oxygen
- Heat
- Ozone
- Dynamic fatigue
- Light and weathering
- Moisture and/or steam
- Solvents and/or chemicals
Oxygen

Depending on the type of rubber oxygen can:

- cause molecular chain cleavage, whereby the molecular network is “loosened” (degradation, softening)
  - NR, IR, IIR

- cause crosslinking, whereby a higher crosslink density is effected (hardening, embrittlement)
  - SBR, NBR, CR, EPDM
Ageing factors causing degradation

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Oxygen in combination with heat

- Heat accelerates oxidation and the effects of oxidation are observed sooner and more severe as the temperature increases.

- At low temperatures oxygen uptake is roughly linear, while at higher temperatures it changes to an autocatalytic reaction.
Heat stability and crosslink length

- Sulphur links exhibit increasing bond energies with decreasing sulphur content.
- Vulcanizates with high bond strength crosslinks (C-C bonds) obtain a significantly better heat resistance than those with crosslinks of lower bond strength (C-S$_X$-C bonds).
- Vulcanizates with shorter crosslinks (semi-EV, EV, sulphur donor and peroxide systems) have generally better heat stability than those with polysulphudic crosslink (CONV vulcanization).
Heat ageing
ISO 188

• Geer en cell ovens

• Results are expressed in change (%) in:
  – Hardness
  – Stress-strain properties
  – Tear resistance
Temperature resistance of some elastomers

[Diagram showing temperature resistance of various elastomers with different markers for permanent and short periods temperature ranges.]
Life-time estimation
ISO 11346

- 100% certainty can only be obtained by actual long-term testing

- Rate of chemical reaction normally increases with increase in temperature

- Exposing test pieces to a series of elevated temperatures can obtain the reaction rate of degradative mechanisms

- Extrapolating to the temperature of use gives an estimation of the life-time
Arrhenius equation

– The Arrhenius equation can be used for properties where only chemical degradation occurs

\[ \ln K(T) = B - \frac{E}{RT} \]

– At least three temperatures and three time-periods should be taken

– Temperatures should be chosen in such a way, that the threshold value is reached within the time-periods
Life-time estimation
ISO 11346

(■): 70°C; (●): 80°C; (▲): 90°C; (▼): 100°C; (◄): 110°C; (►): 120°C and (♦): 130°C

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# Life-time expectancy

<table>
<thead>
<tr>
<th>Rubber</th>
<th>Life-time expectancy in years at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
</tr>
<tr>
<td>1</td>
<td>9.9</td>
</tr>
<tr>
<td>2</td>
<td>28</td>
</tr>
<tr>
<td>3</td>
<td>132</td>
</tr>
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<td>4</td>
<td>4641</td>
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</tbody>
</table>
Ageing factors causing degradation

- Oxygen
- Heat
- **Ozone**
- Dynamic fatigue
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Ozone

- Ozone attack occurs via reaction of ozone with the unsaturated bond → double bonds break and cracks are initiated
- Without extension of the vulcanizates cracks are not formed
- Cracks appear slowly and perpendicular to the direction of the applied stress
- Speed of crack formation depends on temperature, ozone concentration and relative humidity
Ozone resistance
ISO 1431-1
Effect of anti-ozonant

Control

TMQ

6PPD
## Oxygen vs. Ozone degradation

<table>
<thead>
<tr>
<th>Oxygen degradation</th>
<th>Ozone degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>- Mass effect</strong></td>
<td><strong>- Surface effect</strong></td>
</tr>
<tr>
<td>- degradation takes place in whole rubber article by diffusion of oxygen</td>
<td></td>
</tr>
<tr>
<td><strong>- Slow reaction</strong></td>
<td><strong>- Very quick reaction</strong></td>
</tr>
<tr>
<td><strong>- Autocatalytic reaction:</strong></td>
<td><strong>- Increased by stress</strong></td>
</tr>
<tr>
<td>- low levels already start the oxidation</td>
<td></td>
</tr>
</tbody>
</table>
Ageing factors causing degradation

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Fatigue

– When rubber is subjected to prolonged mechanical stress, cracks will slowly develop on the surface, ending in a complete rupture of the article

– The cracks develop perpendicular to the stress direction

– Higher temperatures and higher frequencies accelerate crack formation

– Fatigue is a combination of both physical and oxidative processes
Fatigue resistance and crosslink length

- Fatigue cut growth resistance is larger in vulcanizates with longer crosslinks
- Cut growth is slowed with increasing $X$ in $C-S_X-C$
- High sulphur systems clearly give better fatigue resistance than those which are sulphur free
Fatigue testing
De Mattia flex test
ISO 132

Frequency = 5 Hz
De Mattia flex tester in action

- Crack formation
- Crack growth (L/L+2, L+2/L+6, L+6/L+10)
Fatigue-to-failure test
ISO 6943

- After how many cycles do the samples break?
- What is the final deformation (tension set) after the test?

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Fatigue-to-failure

• Compound fatigue performance is measured at constant extension ratios (or constant strain energies)

• Dumbbell specimens are subjected to a repeated strain cycle and the number of cycles to failure is recorded

• Frequency = 1.6 Hz
Ageing factors causing degradation

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Light and weathering

- Sunlight promotes free radical oxidation at the rubber surface resulting in a film of oxidized rubber

- A system of small and unoriented connected cracks can develop on the surface: elephant skin formation

- Heat and humidity then accelerate a crazing effect giving a chalking appearance

- Black stocks are more resistant due to better high energy radiation absorption characteristics of carbon black
Light and weathering

• Light spectrum (UV, visible and IR) → discolouration
• UV light → polymer degradation
Light and weathering
ISO 4892-2

Influenced by:
- Temperature
- Relative humidity
- Spraying (demi-water)
- "Acid rain" (acid solution)
Ageing factors causing degradation

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Steam and/or moisture

- In the presence of heat, various reactions can take place in the absence of oxygen, i.e. in steam or immersed in oil

  - slower structural changes than in oxygen, for oxidation sensitive rubbers → allows application at higher temperatures

  - breaking of C-N-, C-O-, resp. Si-C bonds in for example the hydrolyzable rubbers, AU, EVM and Q

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Ageing factors causing degradation

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Chemical resistancy
ISO 1817

Results expressed as change in:
- hardness, stress-strain properties, mass, volume, density

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