Reversibility of the Mullins Effect for Extending the Life of Rubber Components

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The Mullins effect

Stress-softening phenomenon first observed in the 1940s

Connected with rubber ‘damage’ to

Cross-links

Rubber-filler interface

Filler

Rubber chains


** Effect of Stretching on the Properties of Rubber**

L. Mullins

Research Association of British Rubber Manufacturers, Croydon, England

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Deformation history affects many aspects of rubber behaviour, such as

- Constitutive response
- Stress-relaxation behaviour
- Swelling behaviour
- Dynamic response

Unintended deformation can change the properties of a rubber component, rendering it unsuitable for its function!

From most practical points of view, this softening is of a permanent nature, for at normal temperatures the recovery towards the initial stress-strain properties is very slow.

Several attempts at speeding up ‘healing’ of the Mullins effect through temperature, starting with

Mullins (1948): “…excessive material degradation when attempting to ‘heal’ rubber at 100°C…”

Annealing cycle may not be a true healing of the Mullins effect, but rather an additional curing cycle from unreacted cross-linker.

In practical terms it has some of the same effects and may be useful in extending the life of overloaded rubber components.
Reversing the Mullins effect

Contents

• Experimental protocols and materials
• Measuring reversal of the Mullins effect
• Time-temperature superposition
• Annealing in vacuum bags and vacuum ovens
• Conclusions
Materials and methods

Sheet-rolled EPDM rubber from JFlex, 0.5mm thick

Dumb-bell specimens cut using a Wallace specimen cutter

Mechanical testing using Instron 5969 and travelling extensometer

Heating cycles using a Memmert programmable oven, a laboratory vacuum oven, and vacuum bags
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Measures of reversal of Mullins effect

<table>
<thead>
<tr>
<th>Material Property</th>
<th>Virgin Specimen</th>
<th>Deformed Specimen</th>
<th>Heat Treated Specimen</th>
<th>Deformed + Heat Treated Specimen</th>
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<tbody>
<tr>
<td>Secant modulus (MPa, 100% strain)</td>
<td>2.25 ± 0.04</td>
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<td>Energy to deform to 300% (MJ/m³)</td>
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<td>Failure strain (%)</td>
<td>671.61 ± 12.45</td>
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Diagram:

- **σ_max**: Maximum stress
- **ε_max**: Maximum strain
- **S**: Maximum stress point
- **E**: Maximum strain point

Graph showing stress-strain relationship with key points labeled.
Measures of reversal of Mullins effect

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Deformed specimens experienced 4 cycles of 300% strain
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Heat treatment:

Temp = 60, 70, 80°C
Time = 3, 8, 14, 24 hours
### Measures of reversal of Mullins effect

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Failure strain (%) | 671.61 ± 12.45 | 709.89 ± 3.40 | 486.93 ± 16.02 | 548.39 ± 12.26
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Deformed specimens experienced 4 cycles of 300% strain

Heat treatment:
- Temp = 60,70,80°C
- Time = 3,8,14,24 hours

\[
R_s = \frac{E_{DH}^{100\%} - E_D^{100\%}}{E_{V}^{100\%} - E_D^{100\%}}
\]
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Healing...

...and damage
Time-temperature superposition

Measures of recovery increase with time and temperature

Are they related?

\[ R(T, t) = R(T_0, a_T t) \]

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<th>Temperature (°C)</th>
<th>Shift factor (a_T)</th>
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<tr>
<td>60</td>
<td>0.59 ± 0.03</td>
</tr>
<tr>
<td>70</td>
<td>1</td>
</tr>
<tr>
<td>80</td>
<td>1.53 ± 0.03</td>
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Shift factors obey an Arrhenius relationship

$$\log_{10}(a_T) = \frac{\Delta H}{2.303R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

$$\Delta H = 46.8 \pm 3.5 \text{ kJ/mol}$$

In line with typical $\Delta H$ values for EPDM curing
e.g. 46.4kJ/mol (Fathurrohman e al (2015), Bull Chem React Eng & Catalysis 10(2) pp104-110)
Applying TTS to other measures

Energy needed to deform to 300% strain

Energy Recovery, $R_E$ (%) vs. $\log(t \cdot a_T)$

- $60^\circ C$
- $70^\circ C$
- $80^\circ C$

$T_{\text{ref}} = 70^\circ C$
Applying TTS to other measures

![Graph showing failure strain vs. log(t ⋅ a_T). The graph includes data points for different temperatures: 60°C (diamonds), 70°C (squares), and 80°C (triangles). The line at the top represents the virgin state, with T_ref = 70°C.](image)

- **Failure strain**
- **Virgin line**
- **T_ref = 70°C**

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Applying TTS to other measures

Tensile strength

Tensile Strength (MPa)

- 60°C
- 70°C
- 80°C

Virgin

$T_{ref} = 70°C$

$T_{ref} = 70°C$

Tensile strength

$log(t.a_T)$

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‘Healing’ or more cure?

Is it ‘healing’ or new cross-linking?

Evidence for cross-linking:

- Activation enthalpy is in line with typical enthalpy of cure

- Changes to tensile strength and failure strain (beyond the preconditioning strains)

ΔH = 46.8 ± 3.5 kJ/mol

ΔH EPDM curing: 46.4kJ/mol
(Fathurrohman e al (2015))
‘Healing’ or more cure?

Is it ‘healing’ or new cross-linking?

**Evidence for Mullins healing:**

Monitored ‘permanent’ set by tracking lines on specimens before and after deformation, and after annealing.

As specimen is not under load when annealed, new cross-links should not significantly affect its length!

Permanent deformation recovers after the heating cycle.

*Both ‘healing’ and cross-linking are taking place!*
Several studies employed vacuum ovens to reduce material degradation. For example, Bueche (1961), Harwood et al. (1966), Laraba-Abbes et al. (2003).

Vacuum ovens are not readily available in industry and require longer procedures to evacuate air.

Vacuum bagging may be more practical.

- Standard oven, specimen exposed
- Specimen vacuum-bagged and heat-treated in standard oven
- Laboratory vacuum oven, specimen exposed
Heat treatment at 70°C for 24 hours

<table>
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<tr>
<th>Treatment</th>
<th>Secant Modulus Recovery (%)</th>
<th>Energy Recovery (%)</th>
<th>Tensile Strength (Mpa)</th>
<th>Failure Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin</td>
<td>-</td>
<td>-</td>
<td>11.10 ± 0.18</td>
<td>671.6 ± 12.4</td>
</tr>
<tr>
<td>Standard Oven</td>
<td>57.67 ± 3.09</td>
<td>69.48 ± 9.23</td>
<td>12.14 ± 0.20</td>
<td>608.0 ± 15.1</td>
</tr>
<tr>
<td>Vacuum Bag</td>
<td>53.93 ± 4.07</td>
<td>63.71 ± 8.76</td>
<td>12.05 ± 0.23</td>
<td>600.5 ± 18.9</td>
</tr>
<tr>
<td>Vacuum Oven</td>
<td>62.11 ± 2.69</td>
<td>80.02 ± 10.79</td>
<td>11.82 ± 0.28</td>
<td>592.5 ± 12.1</td>
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Results suggest marginally greater recovery in vacuum oven but not in vacuum bag

On the whole, results are within measurement accuracy – no significant difference
Conclusions

• Experimentally measured the effects of heat treatments on mechanical properties of deformed EPDM rubber to reverse the Mullins effect

• Recovery is time and temperature dependent, and follows TTS with an Arrhenius temperature dependence ($\Delta H=46.8\text{kJ/mol}$) – same as cure $\Delta H$

• Secant modulus and energy to deform can be recovered with very small changes to stress and strain to failure

• Evidence suggests that reversal of Mullins effect is simultaneous ‘healing’ and new cross-linking

• Could not observe significant differences when annealing in either a vacuum bag or a vacuum oven
TTS of permanent set

![Graph showing the relationship between log(\(a_Tt\)) and permanent set recovered (%). The graph includes data points for 60°C, 70°C, and 80°C.](image-url)