Volume change in stretched crystallizable rubbers

J.-B. Le Cam and E. Toussaint
Motivations

- Physical mechanisms involved in the deformation of rubber

Stress-induced crystallization: $V \downarrow$

Cavitation / Decohesion: $V \uparrow$

Literature $\rightarrow$ not sufficient to establish the competition between these phenomena and to determine characteristic stretch ratios

Context

Experimental set-up

Results

Conclusion

\[ \frac{\Delta V}{V_0} \]

$400\%$

- Shippel (1920);........
- Mullins and Tobin (1957)
- Lord Kelvin (1890)
- Joule (1884)
- Mallock (1889)
- Holt and McPherson (1936)
- Feutcher (1925)

Stretch ratio $\lambda = l/l_0$
Objectives

Volume variation measurement?

- competition between cavitation/decohesion and stress-induced crystallization
- characteristic $\lambda$
- hysteresis loop
- mechanical cycles

*A review on volume change in rubber: effect of stretching*, J.-B. Le Cam, to appear
Experimental set-up

Table: Material formulation (phr)

<table>
<thead>
<tr>
<th>Material</th>
<th>Amount (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural rubber</td>
<td>100</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>9.85</td>
</tr>
<tr>
<td>Oil</td>
<td>3</td>
</tr>
<tr>
<td>Sulfur</td>
<td>3</td>
</tr>
<tr>
<td>Carbon black</td>
<td>34</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>3</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>2</td>
</tr>
<tr>
<td>Accelerators</td>
<td>4</td>
</tr>
</tbody>
</table>

Cyclic loading conditions

- 50N Instron testing machine
- Unfilled NR: $1 < \lambda < 4.7$
- Filled NR: $1 < \lambda < 2.55$
- Strain rate = 1.3 min$^{-1}$
Volume variation measurement

DIC technique
Correlation of the grey levels between two images
- a white paint sprayed on the surface: each ZOI $\rightarrow$ displacement field $\rightarrow$ the deformation tensor.

- Tranversely isotropic behavior

- Resolution (the smallest distance between two independent points): 0.1 pixel corresponding to 5.9 $\mu$m
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RESULTS
Unfilled NR: first cycle

**Context**

**Experimental set-up**

**Results**

**Conclusion**

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**loading**

- **[OA]:** $V \uparrow \rightarrow$ cavitation and growth of cavities (ZnO, metallic oxides)
- **[AB]:** $V \downarrow \rightarrow$ crystallization begins (first order phenomenon)

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**unloading**

- **[BC]:** $V_{\text{unloading}} < V_{\text{loading}} \quad |_{\lambda}$
  - $\rightarrow$ 1) difference between the kinetics of crystallization and of crystallyte melting
  - $\rightarrow$ 2) cavities close more rapidly than they open
- **[CD]:** cavities finish to close
**Test 1**  \( \lambda < \lambda_{\text{crystallization}} (4.2) \)

No crystallization \( \rightarrow \) behavior purely elastical in terms of stress and relative volume change.

*At the macroscopic scale the cavities seems to deform elastically*

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**Test 2**  Stopped test

Melting is instantaneous

*Difference between the kinetics of crystallization and crystallite melting that is responsible of the hysteresis loops.*
Filled NR: first cycle

**Loading**

- **[OA]**: $V \uparrow \Rightarrow$ cavitation and growth of cavities (Zn0, metallic oxides, carbon black, rubber lability)
- **[AB]**: $V \uparrow$ but change in the curve slope (crystallization begins at a lower stretch ratio) and is a second order phenomenon compared to cavitation/decohesion

**Unloading**

- **[BG]**: $V_{\text{unloading}} < V_{\text{loading}} \mid \lambda$ $\Rightarrow$ cavities begin to close and melting starts
- **[GC]**: the slight change in the slope curve indicates that melting continues with a higher rate (also observed by Marchal 2006)
- **[CD]**: melting is complete, cavities finish to close
Kinetics of crystallization

Volume Variation in Stretched Natural Rubber: Competition between Cavitation and Stress-Induced Crystallization, J.-B. Le Cam and E. Toussaint, Macromolecules (41) 2008
Cyclic loading

- Same characteristic stretch ratios
- No significant residual volume variation under uniaxial loading

*Cyclic volume change in rubbers*, J.-B. Le Cam and E. Toussaint, Mechanics of Materials (41) 2009
## Conclusion

- A new measurement method $\rightarrow$ *competition*

- **Fillers** $\rightarrow$ *cavitation/decohesion amplified* $\rightarrow$ *crystallization at a lower $\lambda$*

- **First mechanical cycles** : *no influence on the characteristic stretch ratios + volume variation stabilized after the first cycle.*
Perspectives

- Multiaxial loadings (currently carried out)
- Fatigue loadings
- Various strain rate and temperature!
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