TEMPERATURE SCANNING STRESS RELAXATION: CHALLENGES AND OPPORTUNITIES FOR RUBBER ANALYSIS

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1. CLASSICAL DETERMINATION OF RUBBER CROSSLINKS
Crosslink structure

Sulphur-crosslinked rubber network

'Soft' probe
selectively cleaves/dissolves only polysulphidic crosslinks.

'Shard' probe
selectively cleaves/dissolves poly- and disulphidic crosslinks.

Crosslink structure

‘Soft’ probe

- Polysulphidic, disulphidic and monosulphidic crosslinks
  - Soft probe selectively cleaves polysulphidics.

‘Hard’ probe

- Hard probe selectively cleaves poly- and disulphidics.

- Monosulphidic crosslinks

\[ T = \text{Total crosslink density} \]
\[ T - S = \text{Polysulphidic crosslink density} \]
\[ S - H = \text{Disulphidic crosslink density} \]
\[ H = \text{Monosulphidic crosslink density} \]


Alternative safer method is required!
2. PRINCIPLE OF TEMPERATURE SCANNING STRESS RELAXATION (TSSR)
Temperature Scanning Stress Relaxation

Measurement procedure

- Electrically heated chamber
- Linear drive unit with force cell
- Clamps

TSSR thermogram

Gough-Joule effect:
The slope is proportional to crosslink density.

\[ \kappa \sim \nu_e \]

Thermal relaxation:
- Decomposition of crosslinks
- Debonding of bound rubber chains
- Crystalline phase melting

Thermo-oxidative degradation of rubber matrix

Can the relaxation spectrum be used to describe the crosslink structure?

3. POSSIBILITY OF TSSR TO CHARACTERISE CROSSLINK STRUCTURES
Detection of polysulphidic crosslinks

Unfilled NR vulcanised with a conventional vulcanising system

Relaxation of polysulphidic crosslinks

Detection of polysulphidic crosslinks

Unfilled NR/CR blend vulcanised with an accelerated sulphur system

Detection of polysulphidic and monosulphidic crosslinks

Unfilled ENR vulcanisates with an accelerated sulphur system

Decomposition of polysulphidic bonds \((-\text{C-S}_x\text{-C-})\)

Decomposition of mono- \((-\text{C-S-C-})\) and disulphidic bonds \((-\text{C-S}_2\text{-C-})\)

Temperature \(\text{°C}\)

Relaxation spectrum H (T)/MPa

activator with stearic acid
activator without stearic acid
Relationship between crosslink structure and TSSR spectrum

More shorter crosslinks → Shifting of the relaxation peak to higher temperatures and intensities.

Silica-silane filled SBR/BR compounds vulcanised with an increasing quantity of accelerated sulphur system

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Sek M., PDEng thesis, University of Twente, The Netherlands, (2020)
CONCLUSIONS
Conclusions

• Thiol-amine method is the only quantitative characterisation method for different crosslink structures of vulcanisates.

• There is a demand for an alternative method to replace the thiol-amine probes.

• TSSR relaxation spectrum reflects unique crosslinking characteristics of vulcanisates.

• Different crosslink structures can be detected from the relaxation spectrum.

• The relaxation spectrum seems to give a rough qualitative indication of rubber crosslink structures.
Acknowledgements
Thank you for your kind attention.
3. CRITICAL PARAMETERS FOR TSSR ANALYSIS
Critical parameters for TSSR analysis

Crosslink density measurement

\[ \frac{F}{A_0} \approx T \]

\[ \sigma = \nu_e R T (\lambda - \lambda^{-2}) \]

\[ \left( \frac{\partial \sigma}{\partial T} \right)_\lambda = \nu_e R (\lambda - \lambda^{-2}) = \kappa_{\text{entropy}} \]

\[ \nu = \frac{\kappa}{R(\lambda - \lambda^{-2})} \]

\[ \kappa = \kappa_{\text{relaxation}} + \kappa_{\text{entropy}} \]

Critical parameters for TSSR analysis

Crosslink density measurement

\[ \sigma(t) = a + b \cdot t^{-c} \]

\[ \kappa_{\text{short relaxation}} = b t_{\text{max}}^{-c-1} \]

\[ \kappa_{\text{long relaxation}} \approx 0 \]

2 hours

Critical parameters for TSSR analysis

**Influence of variable initial strains**

Sulphur-cured SSBR vulcanize

Gough-Joule effect is observed above ~20% strain

The slope of force-temperature curve is positive enabling the calculation of crosslink density

Fremuth, K. et al., TPE Mag. 114–116 (2012)
Possibility of TSSR in characterising crosslink structure

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<thead>
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<th>Amount by weight</th>
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<td>n₁</td>
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</tbody>
</table>

Preparation:
- Masterbatch: internal mixer
- Final mixing: two-roll mill

Vulcanization:
- t₉₅ at 160 °C

Crosslink structure analysis:
- 'Soft' and 'hard' thiol-amine cleaving

TSSR procedure:
- 1.5h isothermal relaxation
- 20-280 °C nonisothermal relaxation

Sek M., PDEng thesis, University of Twente, The Netherlands, (2020)
Thermal behaviour of rubber
Possibility of TSSR in characterising crosslink structure