The Vibro-Acoustic Properties of Epoxidised Natural Rubber

Mahmud Iskandar Seth A Rahim
PhD Student

Supervisors:
Kirill V Horoshenkov
Jem A Rongong
Presentation Outline

• Introduction
• Problem Statement
• Aim & Objectives
• Research Activity
• Summary
• Future Work

First and oldest rubber tree in Malaysia, at 139 years old
Introduction

Natural Rubber (NR)
- Made from a milky liquid called latex
- Latex is tapped from a rubber tree
- A polymer & viscoelastic material

Epoxidised Natural Rubber (ENR)
- Chemically modified natural rubber
- Produced by *epoxidation process* at the latex stage
- It is classified as a green material

Epoxidation Process:

![Epoxidation Process](image)
Introduction

Advantages of ENR over NR

- Good resistance to oils
- High damping
- Low air permeability
- Good wet grip performance

Oil immersion test of Rubber O-Ring after 4 days

Rebound test of rubber ball

Butyl Rubber

Nitrile Rubber

(Malaysian Rubber Board, 1984)
**Problem Statement**

- Isolating vibrations at **moderate frequency**
- The implication in a **broader frequency range** is often less certain.

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**Vibration isolation components**

**Synthetic Polymer Foams**

**Synthetic Rubber Foams**

**Latex (Liquid of natural rubber)**

Homogeneity is doubted:
- Foreign substances
- Critical storage

**Dry natural rubber**

- Stable & homogenous
- Eliminates complexities in the latex process
Problem Statement

Natural Rubber in Vibration & Noise Control Applications

**Structure-Borne Vibration**
- Vibration Isolation
  - Rubber Isolator
    - Synthetic Rubbers
      - NR
        (H. R. Ahmadi & J. Picken)
      - ENR
        (Blending with other polymers)
    - Extensional Damping / Constrained Layer Damping
      - Synthetic Polymers
        - NR Layer Damping
          (K.N.G. Fuller, C. Metherell, H.R. Ahmadi & A.H. Muhr)
        - ENR Layer Damping
          (H.R. Ahmadi & A.H. Muhr)
- Panel Damping
  - Synthetic Polymers
    - ENR Foam
      (H.R. Ahmadi & A.H. Muhr)

**Air-Borne Noise**
- Acoustic Barrier
- Anechoic Coating
  - Sound Insulation
  - Sound Absorption
    - Synthetic Polymers
      - NR Foam
        (C. Metherell / Z. M. Ariff)
      - ENR Foam
        ?
Aim & Objectives

**Aim**

To develop NR & ENR foam that can be used in vibration and noise control applications.

**Objectives**

**Preparation**
- Solid NR/ENR
  - Damping
  - Stiffness
  - Temperature
  - Frequency
- NR/ENR Foams Manufacturing
  - Mixing
  - Moulding
  - Blowing Agent

**Testing**
- NR/ENR Foams Characterisation
  - Mechanical
  - Acoustical
  - Non-Acoustical
- NR/ENR Foams Performance
  - Formulation
  - Production process

**Improvement**
- NR/ENR Foams vs Synthetic Rubber Foams
  - Process
  - Microstructure
  - Vibro-acoustic performance

**Preparation**

**Testing**

**Improvement**
Solid NR / ENR
Research Activity

<table>
<thead>
<tr>
<th>#</th>
<th>Rubber</th>
<th>Name</th>
<th>Epoxidation Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NR</td>
<td>SMR-CV60</td>
<td>0 mol%</td>
</tr>
<tr>
<td>2</td>
<td>ENR</td>
<td>ENR-25</td>
<td>25 mol%</td>
</tr>
<tr>
<td>3</td>
<td>ENR</td>
<td>ENR-50</td>
<td>50 mol%</td>
</tr>
</tbody>
</table>

Raw Rubber: ENR-50 : ENR-25 : SMR-CV60

Sample Preparation

Mixing: Two roll mill
- Raw Rubber + Sulfur
- 20 mins

Rubber Sheet

Rubber Mould

Compression Moulding:
- 150°C / 20 mins

Double Shear Test Piece
Research Activity

Preparation of Double Shear Test Piece

1. Metal Substrates
2. Sandblasting Process
3. Metal Substrates
4. Immersing in solvent (Acetone)
5. Applying adhesive (Chemosil)
6. Curing preparation
**Research Activity**

**Large Sample**
- Rubber ø: 25.3 mm; Thickness: 2mm
- Temperature: -30°C to 50°C
- Frequency: 1Hz to 30 Hz
- Strain: 1%

**Small Sample**
- Rubber ø: 10 mm; Thickness: 2mm
- Temperature: -40°C to 50°C
- Frequency: 0.1 Hz to 175 Hz
- Strain: 0.1%

**Double Shear Test Sample**

**Schenck**

**Metravib**

**Thermocouple**
Dynamic Mechanical Properties: Effect of Temperature

"ENR exhibits a higher $T_g$ than NR, by 1°C for every mol% epoxidation."

(Sjoberg, 2002)

(Cook et al., 2008)

- Storage Modulus = Stiffness behaviour / Elastic nature
- Curves plotted at 10 Hz
Research Activity

Dynamic Mechanical Properties: Effect of Temperature

- Tan $\delta$ / Loss Factor = Damping behaviour / Viscous nature
- Curves plotted at 10 Hz
Research Activity

Dynamic Mechanical Properties: Effect of Frequency

- Example of ENR-50
- Small double shear tested at Metravib machine

(Mahapatra & Tripathy, 2006)
Research Activity
Effect of Frequency

Time-temperature superposition principle:

- The curves can be shifted.
- Define dynamic behaviour in a broader frequency range.

0 mol% 25 mol% 50 mol%
Research Activity

Time-Temperature Superposition

- Reference Temperature, $T_0$

Limited frequency range

→ Broader frequency range

Horizontal Shift (Frequency Axis) $a_T$

Vertical Shift (Modulus Axis) $b_T$

(Rouleau et al., 2013)
Research Activity

Time-Temperature Superposition

- **Limited frequency range**
- **Broader frequency range**

- Reference Temperature, $T_0 = 20^\circ C$

- Known as **MASTER CURVE**
- Simple & Inexpensive measurement
- Allow to correlate data under any conditions
## Research Activity

### Time-Temperature Superposition

#### Horizontal Shift (Frequency Axis), $\alpha_T$

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Empirical Horizontal Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>-10</td>
<td>18000</td>
</tr>
<tr>
<td>-05</td>
<td>1400</td>
</tr>
<tr>
<td>00</td>
<td>185</td>
</tr>
<tr>
<td>05</td>
<td>36</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td><strong>20</strong></td>
<td><strong>1</strong></td>
</tr>
<tr>
<td>25</td>
<td>0.4</td>
</tr>
<tr>
<td>30</td>
<td>0.17</td>
</tr>
<tr>
<td>35</td>
<td>0.06</td>
</tr>
<tr>
<td>40</td>
<td>0.02</td>
</tr>
<tr>
<td>45</td>
<td>0.007</td>
</tr>
<tr>
<td>50</td>
<td>0.003</td>
</tr>
</tbody>
</table>

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#### Vertical Shift (Modulus Axis), $b_T$

$$b_T = \frac{\rho_0 T_0}{\rho T}$$

- Assumption: $\rho$ did not change significantly with temperature.

(Etchessahar et al., 2005)
Research Activity

Time-Temperature

Superposition

Storage Modulus, G' (Stiffness Behaviour)

Loss Modulus, G'' (Damping Behaviour)
Research Activity

Time-Temperature Superposition

**MASTER CURVE of Schenck vs Metravib**

**Storage Modulus, G’**

- High Freq. = Low Temp.
- 50 mol% epoxidation level

**Loss Modulus, G”**

- 50 mol% epoxidation level

- At low temperatures = harden sample = tested near to $T_g$ = machine compliance issue.
- At high temperatures = soften sample = tested at low strain = machine compliance issue.
Research Activity

Time-Temperature Superposition

Schenck vs Metravib

- 0 mol%
- 25 mol%
- 50 mol%
Research Activity

Williams-Landel-Ferry (WLF)

\[ \log a_T = - \frac{C_1(T - T_s)}{C_2 + T - T_s} \]

- \( C_1 \) and \( C_2 \): viscoelastic coefficients
- \( T \): Temperature
- \( T_s \): Reference temperature

\[ T_s = T_g + 50^\circ C \]

- \( C_1 = 8.86; C_2 = 101.6 \)
- \( T_s = 243K (-30^\circ C) \) for polyisobutylene

(Williams et al., 1955)

Empirical vs Analytical

- If \( T_s \neq -30^\circ C \)
- New reference temperature is introduced, \( T_0 = 20^\circ C \)
- New viscoelastic coefficients, \( C_1^0 \) & \( C_2^0 \) are calculated.

\[
\begin{align*}
C_1^0 &= \frac{C_1 C_2}{C_2 + T_0 - T_s} \\
C_2^0 &= C_2 + T_0 - T_s
\end{align*}
\]

<table>
<thead>
<tr>
<th>Viscoelastic Coefficient</th>
<th>0 mol%</th>
<th>25 mol%</th>
<th>50 mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1^0 )</td>
<td>6.36</td>
<td>7.72</td>
<td>9.83</td>
</tr>
<tr>
<td>( C_2^0 )</td>
<td>141.6</td>
<td>116.6</td>
<td>91.6</td>
</tr>
</tbody>
</table>

New analytical equation used:

\[ \log a_T = - \frac{C_1^0(T - T_0)}{C_2^0 + T - T_0} \]
Research Activity

The empirical horizontal shifts were subjective.

Differences due to uncertainty in testing temperature: 1°C = huge changes in modulus.

Inaccuracy in the Tg value used in the analytical horizontal shifts.

(Hambric et al., 2007)
Research Activity

Empirical vs Analytical
(Storage Modulus, G’)

0 mol% Metravib: Empirical Shifting — 0 mol% epoxidation level
Metravib: WLF Shifting □

0 mol% Schenck: Empirical Shifting — 0 mol% epoxidation level
Schenck: WLF Shifting △

25 mol% Metravib: Empirical Shifting — 25 mol% epoxidation level
Metravib: WLF Shifting □

25 mol% Schenck: Empirical Shifting — 25 mol% epoxidation level
Schenck: WLF Shifting △

50 mol% Metravib: Empirical Shifting — 50 mol% epoxidation level
Metravib: WLF Shifting □

50 mol% Schenck: Empirical Shifting — 50 mol% epoxidation level
Schenck: WLF Shifting △
Research Activity

Empirical vs Analytical
(Loss Modulus, $G''$)

Metravib

Schenck

0 mol%

25 mol%

50 mol%
NR / ENR Foams Manufacturing
Research Activity

NR/ENR Foams Manufacturing

**TARGET:**
- Open cell structure foam
- $\rho \leq 300 \text{ kg/m}^3$

<table>
<thead>
<tr>
<th>Open Cell</th>
<th>Closed-cell</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="open_cell.jpg" alt="Image" /></td>
<td><img src="closed_cell.jpg" alt="Image" /></td>
</tr>
<tr>
<td>Interconnecting to other cells</td>
<td>Not interconnecting to other cells completely</td>
</tr>
<tr>
<td>Inorganic blowing agent</td>
<td>Organic blowing agent</td>
</tr>
<tr>
<td>Provides viscous nature / damping</td>
<td>Provides elastic nature / stiffness</td>
</tr>
</tbody>
</table>

### Natural Rubber Foam

<table>
<thead>
<tr>
<th>Metherell, 1992</th>
<th>Kim et al., 2007</th>
<th>Ariff et al. 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho = 280 \text{ kg/m}^3$</td>
<td>$\rho = 460 - 470 \text{ kg/m}^3$</td>
<td>$\rho = 260 - 360 \text{ kg/m}^3$</td>
</tr>
<tr>
<td>2 steps manufacturing; Compression Moulding &amp; Air-Oven</td>
<td>1 step manufacturing; Compression Moulding</td>
<td>2 steps manufacturing; Compression Moulding &amp; Air-Oven</td>
</tr>
<tr>
<td>Organic blowing agent: BSH (Benzene sulphonylhydrazide)</td>
<td>Organic blowing agent: DPT ($N,N'$-dinitrosopentamethylenetetramine)</td>
<td>Inorganic blowing agent: Sodium bicarbonate</td>
</tr>
<tr>
<td>No figure available</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Closed-cell foam | Closed-cell foam | Not 100% open cell foam
Research Activity
NR/ENR Foams Manufacturing

Mixing: Two roll mill
- Raw Rubber + Sulfur + Blowing Agent
- 20 mins
- \( \leq 30^\circ C \)

Compression moulding
- 20 mins
- 150°C

NR/ENR foams

Rubber sheet in the mould
Rubber foam in the mould
Research Activity

Chronology through Microscopy Image:

First attempt
SMR-CV60 Foam (0 mol%)

↑ blowing agent
↑ viscosity of raw rubber

Mastication process

Thinning effect of the cell wall thickness

ENR-25 Foam (25 mol%)

Surfactant (lubricant)
Blowing agent (releases polar gas)
Process oil (plasticiser)

ENR has low air permeability

ENR-50 Foam (50 mol%)

Physical properties:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measurement</th>
<th>F0</th>
<th>F50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Foam Density (kg/m³)</td>
<td>( \rho_f = \frac{m_f}{V_f} )</td>
<td>286.2</td>
<td>266.4</td>
</tr>
<tr>
<td>Expansion Ratio</td>
<td>( ER = \frac{1}{\rho_f/\rho_s} )</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>Average Cell Size &amp; Cell Size Distribution</td>
<td>Morphological Study</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>No. of cell per unit volume</td>
<td>( N = \frac{6}{d^3 \pi} \left( \frac{\rho_r}{\rho_f} - 1 \right) )</td>
<td>TBD</td>
<td>TBD</td>
</tr>
</tbody>
</table>

SMR-CV60 Foam (F0)

ENR-50 Foam (F50)
Summary

Three rubbers;  
• SMR-CV60: 0 mol%  
• ENR-25: 25 mol%  
• ENR-50: 50 mol%  

Dynamic mechanical properties;  
• Viscous = Damping  
• Elastic = Stiffness  
• The $T_g$ increases with increasing epoxidation level.  
• Temperature & frequency dependent

Master curve;  
• Limited to a broader frequency range.  
• Experimental: Time-temperature superposition  
• Analytical: Williams-Landel-Ferry model

NR/ENR Foams Manufacturing;  
• Mixing  
• Moulding: Compression Moulding  
• Blowing Agent: Sodium Bicarbonate

Process and formulation;  
• Mastication process of raw rubber  
• Introduction of surfactant, ammonium bicarbonate & plasticiser.
## Future Work

<table>
<thead>
<tr>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. <strong>NR/ENR foams characterisation</strong></td>
</tr>
<tr>
<td>• Physical, morphological, mechanical, acoustical &amp; non-acoustical properties.</td>
</tr>
<tr>
<td>2. <strong>NR/ENR foams performance</strong></td>
</tr>
<tr>
<td>• Formulation: blowing agent (amount &amp; organic/inorganic)</td>
</tr>
<tr>
<td>• Production process: temperature &amp; pressure</td>
</tr>
<tr>
<td>3. <strong>NR/ENR foams modelling</strong></td>
</tr>
<tr>
<td>• Model the in-situ mechanical/acoustical behaviour</td>
</tr>
<tr>
<td>4. <strong>NR/ENR foams vs synthetic rubber foams</strong></td>
</tr>
<tr>
<td>• Process, microstructure, vibro-acoustic performance</td>
</tr>
<tr>
<td>5. <strong>NR/ENR foams in action</strong></td>
</tr>
<tr>
<td>• Automotive / Industrial / Aerospace / Pipeline</td>
</tr>
</tbody>
</table>
THANK YOU