EFFECT OF AROMATIC OIL ON PHASE DYNAMICS OF S-SBR/BR BLENDS

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PASSENGER CAR TIRE TREAD

Main performance indicators:

- Rolling Resistance (RR)
- Abrasion Resistance (AR)
- Wet Skid Resistance (WSR)

ROAD SAFETY!
MOTIVATION:

EC No 552/2009 - Shift to ‘safe’ process oils with lower PAHs content

Effects on compound properties:

- Improvement in the RR.
- Negative effect on the WSR and AR.

*Roughly drawn for UHP tread compound; Source: ETRMA
SBR/BR blends in different ratios (commonly, 50:50 and 70:30)

**Mol.wt. Styrene/Vinyl**

- High-cis BR
- S-SBR/BR (50:50/70:30)
- WSR
- Tg
- RR

**Process Oils**:

- **Improve processability**: increase the scope of using high mol.wt. polymers
- **Improve physical properties**: elasticity, flex life, aids filler dispersion.
- **Extend the rubber compound**: increases the free volume of the compound, thereby increasing filler loading capacity
- **Reduce the cost of final compound**
POLYMERS:

*Functionalized solution styrene-butadiene copolymer (FsS-SBR)*

\[
\begin{align*}
\text{T}_g &= -25 \degree C \\
\end{align*}
\]

High-cis polybutadiene (BR)**

\[
\begin{align*}
\text{T}_g &= -109 \degree C \\
\end{align*}
\]

PROCESS OIL:

*TDAE***, a low PAH content aromatic oil

\[
\begin{align*}
\text{T}_g &= -49 \degree C \\
\end{align*}
\]

*Supplied by Trinseo GmbH **Supplied by Lanxess GmbH ***Supplied by H&R Ölwerke Schindler GmbH
TDAE (Treated Distillate Aromatic Extract)

Two main properties of a process oil

MOLECULAR STRUCTURE
(Polarity or aromaticity)

Determines the degree of compatibility with the rubber

↑Mol.wt. = ↑Viscosity = ↑Shear in banbury mixer and improved mixing/dispersion

MOLECULAR WEIGHT

MATERIALS
Steps in preparation of S-SBR/BR (50/50) blends with 0/10/20 phr TDAE:

1\textsuperscript{st} Stage: Internal Mixer
50 rpm, 50 °C; Oil addition stage

2\textsuperscript{nd} Stage: Two roll mill
R.T.; Curative addition stage

$T_{90}$ measurement (RPA) & vulcanization at 160 °C
STRUCTURE OF S-SBR/BR (50/50) BLENDS

MECHANICAL BLENDING

SOLUTION CASTING

Callan et al., Rubber Chemistry and Technology, 1969.
Scale bar: 2 μ

Inoue et al., Rubber Chemistry and Technology, 1985.
Scale bar: 10 μ
COMPARISON OF $T_g^{\text{eff}}$ FROM DSC, DMA, BDS & theoretical model

Differential Scanning Calorimetry (DSC)
www.netzsch-thermal-analysis.com

Dynamic Mechanical Analysis (DMA)
www.paralab.pt

Broadband Dielectric Spectroscopy (BDS)

Lodge and McLeish model

\[
\frac{1}{T_g^{\text{eff(BR)}}} \left( \frac{\phi_{\text{eff(BR)}}}{T_g^{\text{S-SBR}}} \right) + \frac{1 - \phi_{\text{eff(BR)}}}{T_g^{\text{BR}}} = \frac{\phi_{\text{eff(BR)}}}{T_g^{\text{S-SBR}}} + \frac{1 - \phi_{\text{eff(BR)}}}{T_g^{\text{BR}}}
\]
DSC

0 TDAE
10 TDAE
20 TDAE

CHARACTERIZATION

DMA

BDS

Single, broad peak associated with the T_g
SEGMENTAL DYNAMICS OF OIL-EXTENDED FsS-SBR* AND BR

Local motions
<< 1 nm

Segmental mobility
1-2 nm

Chain dynamics
10 nm

SECONDARY RELAXATIONS
(For e.g. β)

GLASS TRANSITION ($T_g$)

Detectable only at very low frequencies

Reorientation of dipoles on application of an electric field

Net dipole moment $= 0$

$\varepsilon^*(\omega) = \varepsilon' - i\varepsilon'' = \frac{1}{i\omega Z^*(\omega)C_0}$

Measured quantity: Complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$)

$\tau = 1/2\pi F_{\text{max}}$

$\tau$ is the relaxation time at frequency of maximum loss

Dielectric dispersion curves corresponding to a Havriliak-Negami Process

HAVRILIAK-NEGAMI EQUATION(S) BASED FITTING

A) S-SBR/BR (50/50) _0 phr N2X at T = −30 °C

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta \varepsilon_{\alpha} )</th>
<th>( \tau_{\text{HN}} (\alpha) ) (s)</th>
<th>b</th>
<th>c</th>
<th>( \Delta \varepsilon_{\alpha'} )</th>
<th>( \tau_{\text{HN}} (\alpha') ) (s)</th>
<th>b'</th>
<th>c'</th>
</tr>
</thead>
<tbody>
<tr>
<td>No oil</td>
<td>0.226</td>
<td>( 1.384 \times 10^{-4} )</td>
<td>0.609</td>
<td>0.131</td>
<td>0.089</td>
<td>( 5.317 \times 10^{-4} )</td>
<td>0.429</td>
<td>1</td>
</tr>
</tbody>
</table>
**ACTIVATION PLOT: VOGEL-FÜLCHER-TAMMAN (VFT) EQUATION**

\[ \tau_{\text{max}} = \tau_0 \exp \left( \frac{B}{T-T_0} \right) \]

- **\( T_g \):** Temperature at which \( \tau_{\text{max}} = 100 \text{ s} \)

MOBILITY (segmental motion)

RESTRICION (segmental motion)
VOGEL-FÜLCHER-TAMMAN (VFT) EQUATION BASED FITTING

A) Pure polymers (S-SBR & BR)_0/10/20 phr TDAE

B) S-SBR/BR (50/50) _0/10/20 phr TDAE

\[ -\log(t_{\text{max}}) \]
Calculate the relevant ‘self-concentration’, \( \phi_s \) factor.

Calculate the effective local composition, \( \phi_{\text{eff}} \).

Calculate the \( T_g^{\text{eff}} \) for each phase using a modified Fox equation.

\[
\frac{1}{T_g^{\text{eff}(BR)}} = \frac{\phi_{\text{eff}(BR)}}{T_g^{\text{eff}(BR)}} + \frac{1 - \phi_{\text{eff}(BR)}}{T_g^{\text{eff}(S-SBR)}} + \frac{1 - \phi_{\text{eff}(BR)}}{T_g^{\text{eff}(BR)}}
\]

LODGE & McLEISH MODEL


**S-SBR/BR (50/50) Blend**

- **S-SBR/BLEND**
- **BR/BLEND**
- **VFT Fitting line**

**T_g^{\text{eff}}**

- BDS
- Model based

- **S-SBR**
  - -43 °C
  - -42 °C

- **BR**
  - -69 °C
  - -60 °C
CONCLUSIONS

- Decoupling of individual S-SBR and BR phases via BDS.
- Effect of TDAE on the individual phases by observing the change in $T_{g}^{\text{eff}}$.
- Greater effect of the TDAE is observable on the BR phase.
- $T_{g}^{\text{eff}}$ values corroborated with the Lodge and McLeish model for dynamics of miscible blends*.

1st step towards the final goal i.e., quantification of the partitioning of TDAE.

*applicable only to the non-oil-extended blends.
FUTURE OUTLOOK

- **2nd step:** To achieve a quantification of the partitioning of TDAE oil in each phase of the S-SBR/BR (50/50) blend.

- To extend the protocol devised for the 50/50 blend to other blend ratios, such as 70/30 and 30/70.
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THANK YOU FOR YOUR KIND ATTENTION!

Supposing is good, but finding out is better.

Mark Twain