Structure-property relationships of ‘safe’ aromatic oil based passenger car tire tread compounds

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MOTIVATION:

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

Effects on compound (Tire tread) properties:
- Improvement in the rolling resistance (RR) and abrasion resistance (AR)
- Negative effect on the wet skid resistance (WSR).

GOAL:
- To study oil distribution and component relaxation dynamics in a SBR/BR (50:50 & 70:30) blend.
- To develop a compound with improved WSR for a Passenger car tire tread.
PASSENGER CAR TIRE TREAD

Main performance indicators:

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

ROAD SAFETY!
SBR/BR blends in different ratios (50:50 and 70:30)

**INTRODUCTION**

**PROCESS OILS:**

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

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

![High-cis polybutadiene (BR)](image)

**PROCESS OIL:**

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

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

2 main properties of a process oil

MOLECULAR STRUCTURE
(Polarity or aromaticity)

Molecular weight

Determines the degree of compatibility with the rubber

↑ Mol.wt. = ↑ Viscosity = ↑ Shear in banbury mixer and improved mixing/dispersion
TDAE-extended FsS-SBR and BR compounds

- Compounds were produced in an internal batch mixer (Brabender Plasticorder 350S (390cc) with Haake mixing elements).

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount (phr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR/FsS-SBR</td>
<td>100</td>
</tr>
<tr>
<td>ZnO</td>
<td>4</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>3</td>
</tr>
<tr>
<td>CBS</td>
<td>2.5</td>
</tr>
<tr>
<td>Sulphur</td>
<td>1.6</td>
</tr>
<tr>
<td>Vivatec 500</td>
<td>0/10/20</td>
</tr>
</tbody>
</table>
PROCESSABILITY

MOONEY VISCOMETER

Die configuration of MV2000vs

Serrated rotor moves at 0.1 to 15 rpm
Mooney viscosity of the compounds is used as an indicator for studying the processability of compounds.

- TDAE-extended BR compounds
  - Amount of oil (phr)
  - ML (1+4) 100°C (MU)
  - -24.1%
  - -41.8%

- TDAE-extended FsS-SBR compounds
  - Amount of oil (phr)
  - ML (1+4) 100°C (MU)
  - -21.6%
  - -45.2%
COMPARISON OF $T_g$ FROM FOX EQN, BDS, DMA & DSC

\[ \frac{1}{T_g^{OE-R}} = \frac{W_{oil}}{T_g^{oil}} + \frac{W_R}{T_g^R} \]

where,
- $T_g^{OE-R}$ is $T_g$ of oil-extended rubber
- $T_g^{oil}$ is $T_g$ of oil
- $T_g^R$ is $T_g$ of rubber
- $W_{oil}$ is weight fraction of oil
- $W_R$ is weight fraction of rubber


www.paralab.pt

www.netzsch-thermal-analysis.com
BR with 0/10/20 phr of TDAE

Shows restricting effect on the BR chains!
Shows plasticising effect on the S-SBR chains!
SEGMENTAL DYNAMICS OF OIL-EXTENDED FsS-SBR* AND BR: BDS

- Local motions: << 1 nm
- Segmental mobility: 1-2 nm
- Chain dynamics: 10 nm

SECONDARY RELAXATIONS (For eg. β)
GLASS TRANSITION ($T_g$)
Can only be seen at v. low frequencies
Reorientation of dipoles on application of an electric field

Net dipole moment = 0

Net dipole moment ≠ 0

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

MEASURED QUANTITY

Gold electrodes

Polymer film

Voltage

Impedance

Current

Capacity of the empty sample holder
Measured quantity: Complex dielectric permittivity ($\varepsilon^* = \varepsilon' - i\varepsilon''$)

- Real part (Dielectric storage modulus)
- Imaginary part (Dielectric loss modulus)

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

$\tau = \frac{1}{2\pi F_{max}}$

Dielectric dispersion curves corresponding to a Havriliak-Negami Process

CRYSTALLIZATION OF BR

SEGMENTAL DYNAMICS ($T_g$)

Peak shift to higher frequency

TDAE-extended BR
TDAE-extended FsS-SBR

SEGMENTAL DYNAMICS ($T_g$)

**Peak shift to higher frequency**

Frequency (Hz)

Permittivity ($\varepsilon/\varepsilon_{max}$)
FITTING OF DIELECTRIC LOSS SPECTRA

EXAMPLE: FsS-SBR

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>FIT VALUES</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta \varepsilon$</td>
<td>3.52e-2</td>
</tr>
<tr>
<td>$\tau_{HN}$</td>
<td>1.23e-4</td>
</tr>
<tr>
<td>b</td>
<td>0.464</td>
</tr>
<tr>
<td>c</td>
<td>0.974</td>
</tr>
</tbody>
</table>

$$
\varepsilon_{HN}^*(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i\omega \tau_{HN})^b}^c
$$

where, $\tau_{HN}$ is the characteristic relaxation time, $\Delta \varepsilon$ is the relaxation strength, $\omega$ is the angular frequency, $\varepsilon_{HN}^*(\omega)$ is the frequency dependent complex dielectric permittivity, and $b$ and $c$ are the shape parameters.
$\tau_\beta(T) = \tau_\beta^\infty \exp\left(\frac{E_\beta}{kT_0}\right)$

$\beta$-relaxations follow Arrhenius equation

Arrhenius equation

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

$\alpha$-relaxations ($T_g$) follow VFT equation

Vogel-Fülcher-Tamman (VFT)

ACTIVATION PLOT

MOBILITY

RESTRICTION
Activation plot for BR compounds, TDAE and FsS-SBR compounds

Activation Plot: BR

RESTRICTED DYNAMICS

\[ T_g = -75.6°C \]
\[ T_g = -90.3°C \]
\[ T_g = -98.6°C \]

- log (\(\tau_{\text{max}}\))

1000/T, K-1

BR_0
BR_10
BR_20
VFT Fit line
Activation Plot: TDAE

\[ -\log(\tau_{\text{max}}) \]

\[ 1000/T, \text{K}^{-1} \]

\[ T_g = -50.3^\circ C \]
Activation Plot: FsS-SBR

RESTRICTED DYNAMICS

$T_g = -27.6^\circ C$

$T_g = -29.7^\circ C$

$T_g = -30.5^\circ C$
Solubility parameter ($\delta$)

- $\delta$ is the square root of cohesive energy density.
- Can be used as an indicator for determining degree of interaction between materials.

$\Delta\delta_{FSS\text{-}SBR\text{-}TDAE} > \Delta\delta_{BR\text{-}TDAE}$
CONCLUSIONS

- The Fox equation holds true for the TDAE-extended FsS-SBR and BR compounds.

- Verification of theoretical predictions by experimentally obtained data from BDS, DMA and DSC.

- Chain relaxation in FsS-SBR is more hindered compared to BR.

- Improvement in processability on incorporation of TDAE for in FsS-SBR and BR.
ACKNOWLEDGEMENT

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THANK YOU FOR YOUR KIND ATTENTION!

Ask More Questions

speak aloud your suggestions
listen to all directions
& appreciate the location!