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

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Abstract:
In this study, the effect of Treated Distillate Aromatic Extract (TDAE) was investigated in medium styrene/high vinyl solution styrene butadiene rubber (S-SBR) and high cis-polybutadiene rubber (BR). Three properties were evaluated: (i) molecular structure (polarity/aromaticity), (ii) molecular weight and (iii) chemical reactivity of the TDAE oil. The fore-mentioned properties of the oil allow the prediction of its behavior in a rubber compound. It was known from literature that the addition of oil causes a shift in the glass transition temperature ($T_g$) of the compound [2]. Therefore, the study was focused on the variation in the $\alpha$-relaxation process or $T_g$ of a rubber compound upon addition of TDAE. The conventional techniques for determination of $T_g$ such as Differential Scanning Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA) as well as more sophisticated relaxation studies using Broadband Dielectric Spectroscopy (BDS) were used to characterize the TDAE-extended S-SBR and BR compounds. Theoretical prediction of the $T_g$ of TDAE-extended compounds was obtained based on the Fox equation for miscible mixtures. Ultimately, the theoretical predictions were correlated with experimental findings.

Keywords: TDAE, $\alpha$-relaxation ($T_g$) process, TDAE-extended S-SBR/BR compounds, Fox Equation

Introduction:
The tire tread is the outer layer of the tire which makes the contact with the surface of the road. Especially for original equipped (OE) tires more than 20 property criteria have to be balanced to reach the overall requirements by car manufacturers. There are three major properties that determine the overall performance and efficiency of the tire tread: rolling resistance, wet skid resistance and abrasion resistance. There is a peculiar trade-off in these properties in a way that while improving one of the properties the other two are deteriorated. The achievement of a good trade-off in these properties is a challenge for each compounder. The main ingredients which a compounder can play with are type of polymer, amount and type of filler used, amount and type of process aids and the vulcanization system.

Process oil, which acts as a process aid, is an inevitable component in the mixing formulation of a rubber compound for a passenger car tire tread application. It confers numerous advantages to the compound; for example, manufacturing cost reduction, energy saving, reduction of compound viscosities, improving homogeneity of rubber mixes, higher filler loading and hence, better final properties. In a nutshell, the cost to performance ratio of the final compound is improved with the use of process oil. Until 2009, the most commonly used process oils in tire tread compounds have been highly aromatic oils or Distillate Aromatic Extract (DAE) as
they were able to provide good compatibility with both natural and synthetic rubbers. Additionally, they contributed to a better wet skid resistance of the compound. However, the highly aromatic oils are composed of a high level of carcinogenic elements which are present in the oil in the form of polycyclic aromatic hydrocarbons (PAHs). The PAHs are organic compounds possessing two or more aromatic rings. Eight PAH types present in highly aromatic oils have been identified as carcinogens. Due to the tire tread wear, all PAHs can be released into the environment. The release of these carcinogens into the environment can have deleterious effects on human health. Considering the potential risks from the use of PAH-based process oils, an European Commission Regulation (EC) No. 552/2009 limited the use of eight carcinogenic elements in the aromatic (process) oils [1]. This served as the driving force to produce ‘safe’ process oils, which contain lower amounts (<10 mg/kg of the eight listed PAHs) of PAHs. Since 2010, all tire manufacturing companies had to replace the most commonly used DAE oils with the new generation ‘safe’ process oils such as Treated Distillate Aromatic Extract (TDAE), Mildly Extracted Solvate (MES), Residual Aromatic Extract (RAE) and Naphthenic oil (NAP) for the European market based on the legislative regulation. Nonetheless, this shift to the ‘safe’ process oils calls upon the need to study structure-property relationships of these oils and the interactions between them and the polymer matrix. The focus of this study lies on the new generation of aromatic oils, TDAE, and its effect on the polymer chain dynamics.

Due to the fact that the focus of the work is concentrated on studying the compounds for passenger car tire tread, the polymers and the oil are chosen accordingly. The compound of choice is not limited to a single polymer-based compound for a tire tread. Mostly blend systems of two or more polymers are used to balance the tread properties according to the major properties. In fact, the blends of SBR/BR, NR/BR or SBR/NR in different ratios are the most commonly used blends for the tread compound of a tire. The choice of polymers for the present study is thus, functionalized solution styrene-butadiene copolymer (S-SBR) and high-cis polybutadiene (BR). The process oil used for this study is TDAE, which is a low PAH content aromatic oil.

The main reason behind this choice of polymers is to study the blend characteristics and the distribution of process oils in individual phases of the blend. Through the present study, a better understanding of the effect of TDAE on S-SBR and BR compounds is developed.

The investigations done in the present study are performed considering three oil properties: (i) molecular structure (polarity/aromaticity), (ii) molecular weight and (iii) chemical reactivity. This allows the prediction of the behavior of process oil in the oil-extended compound. The degree of shift in the glass transition temperature ($T_g$) of the oil-extended compound is used as the criteria to compare the compatibility of the oil with the polymer [2]. A shift in $T_g$ is a well-accepted parameter to evaluate the plasticising efficiency of the process oil. Therefore, techniques for determination of $T_g$ like Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Broadband Dielectric Spectroscopy (BDS) are used for the current work. The differences in the governing principles behind the measurement of $T_g$ through the above mentioned techniques are discussed below.

The $T_g$ can be observed as a transition in the physical state of an amorphous polymer from a soft, rubber-like state to a hard, glassy-like state. It is often termed as
the state of frozen segmental motions in a polymer [3]. It is commonly accompanied by detectable changes in the thermal properties of the material, such as a change in heat capacity ($c_p$) [4]. The phenomenon of glass transition is often referred to as a pseudo-second order thermodynamic transition. The accompanying thermodynamic changes are exploited using DSC-method for determination of the ‘calorimetric' $T_g$. However, these measurements are performed at fixed rates of heating and cooling, which may not be very reliable in terms of thermodynamic information [3-5]. This is due to the observed variation of the $T_g$ value with the heating or cooling rate. $T_g$ can also be related to the α-relaxation or segmental relaxation of the polymer. In terms of relaxation time, $T_g$ is conventionally defined as the temperature at which the segmental relaxation time ($\tau_\alpha$) of a polymeric material equals 100 seconds [3]. The relaxation times may be measured by a variety of experimental methods such as DMA or BDS. In the case of DMA, a well-established way of determination of $T_g$ is available. The DMA is able to measure a phase shift between the applied stress (sinusoidal) and the measured strain (sinusoidal), which is produced in response to the applied stress at a particular frequency [6]. A complex modulus ($E^*$) is measured by DMA. $E^*$ consists of a real part (storage modulus, $E'$) and an imaginary part (loss modulus, $E''$). Both moduli deliver material-specific dynamic elastic characteristics. The ratio of loss modulus to storage modulus, which is defined as tanδ gives a peak in the temperature sweep, which is an indicator of the $T_g$ of the polymer. DMA enables the measurement mostly at a single frequency during a temperature sweep for a polymer. Although a frequency sweep is possible with DMA, but the range of frequency is limited to $10^2$ Hz. In that respect, BDS is known to be a more efficient and sensitive technique compared to both, DSC and DMA. BDS has the ability to cover a broad dynamic range between $10^{-2}$ to $10^9$ Hz in one single run [7-9]. It allows the investigation of the various motional processes in a polymeric system, which take place on extremely different time scales in a broad frequency and temperature range. These motional processes in polymeric systems are dependent on the morphology and microstructure of the investigated system. The main principle behind the working of BDS is that it is sensitive to molecular fluctuations of dipoles within the system. These fluctuations can be related to the molecular mobility of groups, segments or whole polymer chains, which can be observed as different relaxation processes [7]. Therefore, BDS is adapted as one of the techniques to study the changes in the segmental dynamics of S-SBR and BR. Conclusive remarks are made on the effect of TDAE on the segmental dynamics of the individual polymers. The extent of effect of TDAE on both, S-SBR or BR compounds is also considered to be related to the level of compatibility between the polymers (S-SBR/BR) and oil (TDAE). The compatibility between S-SBR/BR and TDAE is compared in terms of similarity/dissimilarity between the solubility parameters ($\delta$) of S-SBR/BR and TDAE. Ultimately, an attempt to correlate the theoretical prediction (based on the Fox equation [10]) with experimentally obtained BDS, DMA and DSC data is made.

**Experimental:**

**Materials**

The polymers used in this study are the ones which are commercially available and widely used by tire manufacturers nowadays. The trade name of the S-SBR used is SPRINTAN™ SLR 4602 - Schkopau, manufactured and supplied by Trinseo Deutschland GmbH and the high-cis BR is BUNA CB24, supplied by
Lanxess Deutschland GmbH. TDAE, the process oil used for this study is also a very commonly used commercial oil with the trade name, VIVATEC 500, manufactured and supplied by H&R Ölwerke Schindler GmbH, Hamburg.

The most important properties of these raw materials (BR [11], S-SBR [12], TDAE [13]) are reported in Table 1-2.

### Table 1. Properties of BR [11], S-SBR [12]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Styrene (wt%)</th>
<th>1,2 (vinyl) (%)</th>
<th>cis-1,4 (%)</th>
<th>trans-1,4 (%)</th>
<th>Tg(DSC) (°C)</th>
<th>Mooney Viscosity (MU)</th>
<th>Density (g/cm³)</th>
<th>Weight average molecular weight (Mw) (kg.mol⁻¹)</th>
<th>Number average molecular weight (Mn) (kg.mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BUNA CB24</td>
<td>-</td>
<td>&lt;1</td>
<td>&gt;96</td>
<td>~2</td>
<td>-109</td>
<td>44</td>
<td>0.91</td>
<td>460 [14]</td>
<td>135 [14]</td>
</tr>
<tr>
<td>SPRINTAN™ SLR 4602 – Schkopau</td>
<td>21 (wt%)</td>
<td>63 (wt%)</td>
<td>-</td>
<td>-</td>
<td>-25</td>
<td>65</td>
<td>0.93</td>
<td>475 [15]</td>
<td>315 [15]</td>
</tr>
</tbody>
</table>

### Table 2. Properties of TDAE [13]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Standard test method</th>
<th>VIVATEC 500 (TDAE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color ASTM</td>
<td>ASTM D156</td>
<td>8.0D</td>
</tr>
<tr>
<td>Density at 15°C, kg/m³</td>
<td>ASTM D1298</td>
<td>950</td>
</tr>
<tr>
<td>Density at 20°C, kg/m³</td>
<td>ASTM D1298</td>
<td>947</td>
</tr>
<tr>
<td>Kin. Viscosity at 40°C, mm²/s</td>
<td>ASTM D445</td>
<td>410</td>
</tr>
<tr>
<td>Kin. Viscosity at 100°C, mm²/s</td>
<td>ASTM D445</td>
<td>18.8</td>
</tr>
<tr>
<td>Sulfur, wt%</td>
<td>DIN ISO 14596</td>
<td>0.8</td>
</tr>
<tr>
<td>Carbon distribution, wt%:</td>
<td>ASTM D2140</td>
<td></td>
</tr>
<tr>
<td>C_A</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>C_N</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>C_P</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>DMSO extract, wt%</td>
<td>IP346</td>
<td>&lt;2.9</td>
</tr>
<tr>
<td>Glass transition temperature, °C</td>
<td></td>
<td>-49</td>
</tr>
</tbody>
</table>

**Mixing**

The compound formulation given on the basis of a total of 100 parts of raw polymer (S-SBR or BR) by weight (phr) is as follows: S (1.6 phr), ZnO (4 phr), stearic acid (3 phr), and CBS (N-cyclohexyl-2-benzothiazole sulphenamide) (2.5 phr) and TDAE (0/10/20 phr). The compounds were prepared in an internal batch mixer (Brabender Plasticorder 350S (390cc) with Haake mixing elements). The mixing was done at 50 °C and 50 rpm. The compounds were mixed in the internal mixer in the
first stage. After mixing of the polymers with ZnO, stearic acid, and oil in the internal mixer. The vulcanization system was added to the compound in a second stage mixing, which was done on a two roll mill and here the compounds were also formed into sheets. The prepared samples are referred to as BR_x or S-SBR_x, where ‘x’ is the amount of TDAE (in phr).

**Viscosity**

Mooney Viscosity measurements were performed with an Alpha Technologies Mooney 2000VS, using large type rotor (L), at 100 °C, according to ISO 289.

**Curing**

Finally, the samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 160 °C to sheets with a thickness of 2 mm, according to their t90 + 2 minutes optimum vulcanization time, as determined by a Rubber Process Analyzer RPA 2000 of Alpha Technologies, following the procedure described in ISO 3417. Also, a separate batch of vulcanization was carried out with the same apparatus for each sample to form very thin (~0.1-0.2 mm) sheets, which were vulcanized at the t90 at 160 °C, by placing 2 g of milled compound in between two steel plates. These very thin vulcanized sheets are suitable for the enhancement of the signal obtained from BDS measurements.

**Determination of T_g by DMA, DSC and BDS**

Dynamic mechanical analysis of the vulcanized samples was done in tension mode in a Metravib DMA2000 dynamic spectrometer. The DMA measurements were performed from -150 °C to +80 °C in steps of five degrees at a dynamic strain of 0.5% and frequency of 1 Hz. The glass transition temperatures were obtained from temperature sweep measurements in tension mode. Differential scanning calorimeter (DSC) from Netzsch was used to obtain the ‘static’ glass transition temperature of the vulcanized samples. The DSC measurements were carried out using a cooling flow rate of 10 °C/min. A cooling curve was generated by freezing the samples up to -150 °C from room temperature (20 °C). Dielectric measurements were performed using a high precision dielectric analyzer (ALPHA analyzer, Novocontrol Technologies). The complex dielectric permittivity, ε*, was measured by performing consecutive isothermal frequency sweeps (10^{-1}-10^{7} Hz) in the temperature range from -150 °C to +80 °C in steps of 5 °C. The vulcanized, thin sheets of rubber were cut in a disk shape and were mounted in the dielectric cell between two parallel gold plated electrodes. For the TDAE, a special cell designed for studying dielectric properties of liquids was used.

**Results and Discussions:**

I. **Segmental dynamics of Oil Extended S-SBR and BR by BDS:**

In the case of BDS, it can be considered that the permanent dipoles along the chain bonds behave like ‘markers’ that help in assessing the movement of the chains as a function of the frequency of the electric field and temperature. For polymers, it is common to expect a distribution of relaxation times on application of an electric field. The experimentally measured quantity in the case of BDS is the complex dielectric permittivity (ε*), which can be expressed in terms of the real and imaginary part as follows [7,9]:
\[ \varepsilon^* = \varepsilon' - i\varepsilon'' \]  

(1)

where, \( \varepsilon' \) and \( \varepsilon'' \) are real and imaginary part of the complex dielectric permittivity. They are experimentally obtained quantities, which characterize the dielectric dispersion over a range of frequencies. In order to correlate these observable quantities with the molecular properties of the polymer, a model is required that describes the response of polymers to an applied electric field.

A unique model for the description of the relaxation times in polymers is the Havriliak-Negami (HN) equation [7,9,16,19],

\[ \varepsilon_{HN}(\omega) = \varepsilon_\infty + \frac{\Delta \varepsilon}{1 + (i\omega\tau_{HN})^b} \]  

(2)

where, \( \tau_{HN} \) is the characteristic Havriliak-Negami relaxation time, which represents the most probable relaxation time from the relaxation time distribution function, \( \Delta \varepsilon \) (relaxation strength) = \( \varepsilon_s - \varepsilon_\infty \), \( \varepsilon_\infty \) and \( \varepsilon_s \) are the unrelaxed and relaxed values of the dielectric constant, \( \omega \) is the frequency, \( \varepsilon_{HN}(\omega) \) is the frequency dependent Havriliak-Negami complex dielectric permittivity, and \( b \) and \( c \) are the shape parameters, which describe the symmetric and asymmetric broadening of the relaxation time distribution function, respectively.

\( \tau_{HN} \) is related to the frequency of maximum loss [7,17,19], \( F_{\text{max}} = 1/2\pi \tau_{\text{max}} \) by the following equation:

\[ \tau_{\text{max}} = \frac{1}{2\pi F_{\text{max}}} = \tau_{HN} \left[ \sin \frac{b\pi}{2+2c} \right]^{-1/b} \left[ \sin \frac{b\pi}{2+2c} \right]^{1/b} \]  

(3)

Where, \( F_{\text{max}} \) is the frequency of maximum loss, which is related by the above equation to \( \tau_{\text{max}} \), the relaxation time of maximum loss.

All the experimentally obtained dielectric spectra (permittivity loss (\( \varepsilon'' \)) vs. frequency) are fitted using the Havriliak-Negami (HN) equation (2). This preliminary fitting is done with the WINFIT software from Novocontrol technologies. The fitting parameters obtained from such a fitting protocol are, \( \Delta \varepsilon \), \( b \), \( c \) and \( \tau_{HN} \). These parameters are tabulated in Table 3 for S-SBR compounds and TDAE, and Table 4 for BR compounds.

**Table 3. HN fitting parameters for SBR and TDAE at T= -15 °C**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta \varepsilon )</th>
<th>( b )</th>
<th>( c )</th>
<th>( \tau_{HN} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-SBR_0</td>
<td>0.026</td>
<td>0.766</td>
<td>0.397</td>
<td>4.804e-1</td>
</tr>
<tr>
<td>S-SBR_10</td>
<td>0.185</td>
<td>0.615</td>
<td>0.546</td>
<td>1.169e-1</td>
</tr>
<tr>
<td>S-SBR_20</td>
<td>0.016</td>
<td>0.543</td>
<td>0.686</td>
<td>7.266e-2</td>
</tr>
<tr>
<td>TDAE</td>
<td>0.407</td>
<td>0.596</td>
<td>0.818</td>
<td>2.566e-4</td>
</tr>
</tbody>
</table>
Table 4. HN fitting parameters for BR at $T = -70 \, ^\circ\text{C}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta \varepsilon$</th>
<th>b</th>
<th>c</th>
<th>$\tau_{HN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR_0</td>
<td>0.229</td>
<td>0.308</td>
<td>1</td>
<td>3.353e-7</td>
</tr>
<tr>
<td>BR_10</td>
<td>0.884</td>
<td>0.196</td>
<td>1</td>
<td>3.941e-5</td>
</tr>
<tr>
<td>BR_20</td>
<td>0.550</td>
<td>0.525</td>
<td>0.286</td>
<td>4.44e-3</td>
</tr>
</tbody>
</table>

It is worth mentioning that the average relaxation times ($\tau_{HN}$) for the S-SBR compounds there is a tendency to decrease with the oil content, while in the case of the BR compounds, the relaxation time increases as oil content increases. This behavior could be indicating that the oil is restricting the BR dynamics.

In the next step, the $\tau_{max}$ is calculated for each $\tau_{HN}$ using (3). The determination of $\tau_{max}$ allows to estimate the temperature dependence of the relaxation process which normally follows a Vogel-Fülcher-Tamman (VFT) dependency [7,18].

The VFT equation is the most suitable way to model the relaxation times in terms of temperature dependency. It can be mathematically expressed as follows:

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

(4)

Where, $\tau_0$ and B are empirical parameters, and $T_0$ is the ideal glass transition or Vogel temperature, which is generally 30-70 K below $T_g$. For avoiding the effect of misleading parameters, a value of log $\tau_0 = 14$ is adapted for the data fitting using the VFT equation, based on the study of Angell [24]. The VFT equation considers that the relaxation rate increases rapidly at lower temperatures due to the reduction of free volume [7].
The activation plot (Fig 1) depicts the inherent differences in the segmental dynamics of S-SBR, BR and TDAE very clearly. The polymer chains of S-SBR are evidently more restricted in terms of segmental dynamics as compared to the highly linear and mobile chains of BR. The reason for this observation can be the difference in the amount of steric hindrances present in the S-SBR and the BR. The S-SBR is known to contain approx. 21 wt% of styrene [12] moieties in addition to the different isomeric forms of polybutadiene such as, 1,2- (vinyl), cis-1,4- and trans-1,4- content, which plays a detrimental role regarding the ease of the motion of polymer segments/chains. The presence of styrene (a bulky aromatic group) in the main chain of the S-SBR seems to slow down the segmental dynamics of the S-SBR chains. It is crucial at this point to remember that the S-SBR used in this study is a functionalized polymer. There are several options described in the literature, how to introduce a functionality or combinations of it into a polymer chain [20-22]. These functionalizations are introduced into the S-SBR in order to enhance the extent of compatibility as well as interaction between the relatively non-polar polymer (S-SBR) matrix and rather polar fillers, such as silica. The introduction of polar functional groups to the polymer chain leads to an increase in the hydrophilicity of the S-SBR,
thereby promoting better interaction between the S-SBR and polar fillers, but losing its compatibility with TDAE. The activation plot reflects this compatibility loss, since no significant effect on the dynamics of S-SBR is observed when adding 10 or 20 phr of TDAE. However, another reason for a lower effect on the \( T_g \) in the case of S-SBR compounds can be the lower difference between the \( T_g \) of pure S-SBR and \( T_g \) of pure TDAE.

The solubility parameter (\( \delta \)) is a good indicator for the degree of interaction between materials. The smaller the difference in the solubility parameters (\( \Delta \delta \)), the higher is the expected thermodynamic compatibility between blended components. The solubility parameters for the materials used in this study are presented on Table 5.

<table>
<thead>
<tr>
<th>Polymer/Oil</th>
<th>( \delta ) (MPa(^{0.5}))</th>
<th>( \Delta \delta ) (( \delta_{\text{polymer}} - \delta_{\text{oil}} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPRINTAN™ SLR 4602 - Schkopau</td>
<td>17.33</td>
<td>0.13</td>
</tr>
<tr>
<td>BUNA CB-24</td>
<td>17.20</td>
<td>0.00</td>
</tr>
<tr>
<td>VIVATEC 500</td>
<td>17.20</td>
<td>-</td>
</tr>
</tbody>
</table>

For the BR, it is clear that the segmental motions of this highly linear polymer are getting more restricted with the addition of oil containing bulky aromatic groups, contrary to normal trends where the addition of a process oil lowers \( T_g \) and increases mobility. It is noticeable from Fig 1. that the TDAE oil has a stronger effect on the segmental dynamics of BR as compared to S-SBR. A plausible explanation of this can be the lower \( \Delta \delta \) for BR and TDAE as compared to S-SBR and TDAE, which leads to a substantial effect on the segmental relaxation dynamics of BR chains. The restricted motion of BR chains with the addition of TDAE can also be explained based on the fact that the BR chains are highly linear thus, their movement gets restricted by addition of TDAE, which contains 25 wt% of aromatics (C\(_A\)).

II. **Comparison of the effect on \( T_g \) for functionalized S-SBR and BR by Fox Eqn, BDS, DMA and DSC:**

For the theoretical prediction of the effect of oil on the polymer matrix, an advanced version of the Fox equation [10] for miscible mixtures is used to calculate the \( T_g \) of oil-extended rubber,

\[
\frac{1}{T_g^{OE-R}} = \frac{W_{oil}}{T_g^{oil}} + \frac{W_R}{T_g^{R}}
\]
Where, $T_g^{OE-R}$ is $T_g$ of the oil extended-rubber; $T_g^{oil}$ is $T_g$ of the oil; $T_g^{R}$ is $T_g$ of the rubber; $W_{oil}$ is the weight fraction of the oil; $W_R$ is the weight fraction of the rubber.

The calculated $T_g(s)$ of the oil-extended compounds by using the Fox equation are listed in Table 6. Fig 2 and 3 show the trend line which depicts the effect of addition of TDAE in the BR and S-SBR compounds, respectively.

**Fig 2. Comparison of $T_g$ from Fox Eqn, BDS, DMA and DSC for BR with 0/10/20 phr of TDAE**

**Fig 3. Comparison of $T_g$ from Fox Eqn, BDS, DMA and DSC for S-SBR with 0/10/20 phr of TDAE**
Table 6. T<sub>g</sub> values for BR and S-SBR compounds from Fox Eqn, BDS, DMA, DSC and Mooney Viscosity

<table>
<thead>
<tr>
<th>Compound</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; – Fox Eqn (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; – BDS (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; – DMA (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; – DSC (°C)</th>
<th>Mooney Viscosity ML (1+4), 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>BR_0</td>
<td>-</td>
<td>-98.6</td>
<td>-94.9</td>
<td>-113.4</td>
<td>36.1</td>
</tr>
<tr>
<td>BR_10</td>
<td>-101.5</td>
<td>-90.3</td>
<td>-93.4</td>
<td>-111.0</td>
<td>27.4</td>
</tr>
<tr>
<td>BR_20</td>
<td>-93.2</td>
<td>-75.6</td>
<td>-92.4</td>
<td>-105.9</td>
<td>21.0</td>
</tr>
<tr>
<td>S-SBR_0</td>
<td>-</td>
<td>-27.6</td>
<td>-12.4</td>
<td>-30.4</td>
<td>40.3</td>
</tr>
<tr>
<td>S-SBR_10</td>
<td>-31.5</td>
<td>-29.7</td>
<td>-14.9</td>
<td>-31.0</td>
<td>31.6</td>
</tr>
<tr>
<td>S-SBR_20</td>
<td>-32.6</td>
<td>-30.5</td>
<td>-15.9</td>
<td>-32.2</td>
<td>22.1</td>
</tr>
</tbody>
</table>

An increase in the T<sub>g</sub> of BR by addition of an increasing amount of TDAE is observed by various experimental techniques (BDS, DMA, DSC). Whereas, an opposite but much smaller trend can be observed for the S-SBR upon addition of increasing amount of TDAE.

The observations discussed above are in agreement with the Fox equation, which states that the final T<sub>g</sub> of an oil-extended compound depends on the respective T<sub>g</sub>(s) of the oil (TDAE) and the polymer (S-SBR/BR). It is important to mention at this point that even though the trend on the effect of T<sub>g</sub> indicates a restricting effect (as seen from Fig 1.) in the case of BR, the Mooney Viscosity values give a first indication to improved processability (Table 6), but it is only a one point measurement in case of temperature and shear rate. Hence, an evident effect of the process oil (TDAE) for improving the processability of BR compounds can be observed through the Mooney Viscosity. But from the trend in the effect on T<sub>g</sub> for BR compounds upon addition of TDAE, there is not an improvement in the low temperature properties of these compounds, based on the fact that the T<sub>g</sub> of the process oil is related to a higher temperature. An improvement in the low temperature properties of an oil extended compound is often regarded as one of the key effects of a process oil for a compound, especially for an application in low temperature conditions like winter tires. However, with the present study, it has been clearly demonstrated that this is not the case for BR based TDAE-extended compounds due to the fact that the T<sub>g</sub> of BR is much lower than the T<sub>g</sub> of TDAE. An improvement in low temperature properties in the final compound can only be observed for polymers with a higher T<sub>g</sub> value compared to the process oil used. An appropriate example of such a case has been shown through the study of TDAE-extended S-SBR compounds. In this case as the T<sub>g</sub> of S-SBR is higher than the T<sub>g</sub> of TDAE a decrease in the T<sub>g</sub> of oil-extended S-SBR compounds is seen. The Mooney
Viscosity values (Table 6) also indicate an improvement in the processability of the S-SBR compounds.

Another important observation from this study is that the difference in the sensitivity of BDS, DMA and DSC for determination of T\textsubscript{g} were compared. Due to the difference in the principles of measurement, there is a different range of T\textsubscript{g} values obtained from each technique. It can be seen from Table 6 that the lowest values of T\textsubscript{g} are observed through DSC, followed by BDS and the highest values from the DMA data. The T\textsubscript{g} values measured from each technique are highly influenced by the heating rate (BDS, DMA, DSC) on one hand side and applied frequencies (BDS, DMA) on the other hand side. Even though the ranges of T\textsubscript{g} measured are different from each technique, the amount of change in T\textsubscript{g} with every 10 phr increase in the amount of TDAE, is seen to follow a similar trend (Table 6). Except for the compound ‘BR_20’, which gives a significantly higher T\textsubscript{g} (w.r.t. BR_0 and BR_10) from BDS as compared to both DSC and DMA. This peculiar result can be explained by carrying out ‘free volume’ studies in the near future, through Positron Annihilation Lifetime Spectroscopy (PALS) where the density of free volume can be measured. The changes occurring in the free volume density of the BR on addition of TDAE would lead to a better understanding of the high T\textsubscript{g} observed for ‘BR_20’. As this higher T\textsubscript{g} value for ‘BR_20’ can only be seen through BDS data, it is clear that BDS is a much more sensitive technique for studying T\textsubscript{g} or polymer chain dynamics compared to DSC and DMA.

CONCLUSIONS:

From the current study, the following conclusions can be drawn:

i. The solubility parameter is used for identifying the extent of compatibility between the materials to be mixed. Highly linear BR chains are seen to have a higher level of compatibility with TDAE oil, which can be explained in terms of the similarity in the solubility parameters of BR and TDAE. For S-SBR, an indication for lower compatibility with TDAE is observed, which can be explained either in terms of the difference in solubility parameter or by acknowledging the fact that the polymer chains of S-SBR are functionalized. The presence of additional functional groups in the polymer chain leads to hindrance in the chain relaxation.

ii. Relaxation studies from BDS shows a restricting effect for the BR chains and a plasticizing effect for the S-SBR chains, upon addition of TDAE. However, a clear indication to improved processability on addition of TDAE for both S-SBR and BR is given by the decrease in the Mooney viscosity of the oil-extended compounds.

iii. Fox equation holds true for the TDAE-extended S-SBR and BR compounds studied. This has been verified by experimental data from BDS, DMA and DSC.

Hence, a clear correlation between theoretical predictions and experimentally obtained data is drawn.

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[20] Personal communication from Somayeh Maghami, Former Ph.D. student at University of Twente.


