

PAHs • DAE • TDAE • MES • natural rubber • styrene butadiene rubber

The influences of DAE-, TDAE- and MES-oils on the properties of carbon black filled NR and NR/SBR blend compounds are discussed. The properties are strongly affected by oil contents, but less by the oil types. Compounds with DAE have the lowest Mooney viscosity but highest complex viscosity and Payne effect. SEM micrographs show that carbon black is finely dispersed in the compounds, except for MES which shows slightly poorer filler dispersion than TDAE and DAE. The use of TDAE and MES in NR clearly influences the properties related to changes in  $T_g$  and viscoelastic behavior. Use of MES gives the best elastic response in NR, while TDAE gives the best response for NR/SBR blend vulcanizates.

### Erdöl-basierte sichere Prozess-Öle in NR und NR/SBR-Blends

PCA • DAE • TDAE • MES • Naturkautschuk • Styrol-Butadien-Kautschuk

Der Einfluss von DAE-, TDAE- und MES-Ölen auf die Eigenschaften von rußgefülltem NR und NR/SBR wurde untersucht. Die Eigenschaften werden stark beeinflusst durch die Öl-Konzentration, weniger durch den Öl-Typ. Mischungen mit DAE zeigen die niedrigsten Mooney-Viskositäten, die komplexe Viskosität und der Payne Effekt erreichen die höchsten Werte. SEM Aufnahmen zeigen, dass der Ruß gleichmäßig verteilt ist mit Ausnahme der NR/SBR Mischung mit MES. Die Verwendung von TDAE und MES in NR beeinflusst die auf eine Änderung des  $T_g$  und der Viskoelastizität beruhenden Eigenschaften. Die höchste Elastizität in NR wird bei Verwendung von MES erreicht, in NR/SBR bei Verwendung von TDAE.

Figures and tables:  
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## Petroleum-based Safe Process Oils in NR and NR/SBR Blends: Part III. Effects of Oil Types and Contents on the Properties of Carbon Black Filled Compounds

Rubber compounds are commonly reinforced with fillers to achieve the desired properties, and carbon black is the most commonly used reinforcing filler for rubber products including tires, while silica is increasingly used for tread compounds to produce low rolling resistance tires. To achieve the desired performance, carbon black must be sufficiently dispersed in the rubber, as poor dispersion leads to detrimental effects, e.g. reduced product life, poor processing characteristics and poor performance [1]. The filled rubber compounds are highly complex systems in which various solid and liquid ingredients are dispersed in the rubber matrix [2]. Filler-rubber interactions give rise to additional crosslinks in the network structure, and the immobilized elastomeric layers on the filler surface have an influence on the dynamic response of the material [3].

Natural rubber (NR) is a unique material with special characteristics derived from its strain-induced crystallization [4,5]. NR is needed for production of truck and aviation tires. It is also employed as a blend component for different parts of passenger tires, e.g. tread and sidewall. NR provides very good tensile and tear strength, flexing and fatigue resistance, and elastic properties [6]. Passenger tire treads are generally made of blends from either Natural Rubber (NR) or Butadiene Rubber (BR) and Styrene Butadiene Rubber (SBR). NR and BR are used to provide elastic properties while SBR is needed for damping, e.g. wet skid resistance or wet grip. For highly filler-loaded compounds such as tire tread formulations, process oils are used to control compound viscosity and filler dispersion. The incorporation of oil also improves processing characteristics and helps to reduce the price of the compounds and resulting products. The use of process oil allows the addition of filler at higher loadings while maintaining the same hardness. Fillers in combination with process oils are essential ingre-

dients for rubber compounds based on both natural rubber and synthetic rubbers. Different oil-types may be used including Distillate Aromatic Extract (DAE) oil, Treated Distillate Aromatic Extract (TDAE) oil, Mildly Extracted Solvate (MES) oil, Naphthenic (NAP) oil and natural oils.

Because of the toxicity of the high amounts of Polycyclic Aromatic Hydrocarbons (PAHs) in DAE-oil [7], replacement of DAE with safe process oils, such as TDAE, MES, NAP and natural oils, is taking place. It has been reported that the use of PAH-low process oils, such as TDAE, MES and NAP resulted in changes in rheological, physical and mechanical properties of un-aged vulcanizates of NR, SBR, NR/SBR and NR/brominated-isobutylene-isoprene rubber (BIIR) [8]. Therein, MES- and TDAE-oils provided si-

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imilar ageing behavior to DAE for NR compounds, but improved the aging resistance of NR/SBR and NR/BIIR-based vulcanizates. The NR, SBR and NR/SBR compounds plasticized with epoxidized palm oil (EPO) showed comparable cure characteristics and processing properties as well as mechanical and dynamic properties of the vulcanizates when compared to compounds with DAE oil [9]. The replacement of DAE by TDAE, MES and NAP in carbon black- and silica-filled tire compounds slightly shifted the wet grip performance and improved the rolling resistance relative to carbon black-filled compounds [10]. Furthermore, some natural oils were reported to give better abrasion resistance in NR, NR/BR and S-SBR/NR/BR compounds, compared to DAE oil [11].

Our previous work "Petroleum-based safe process oils in NR, SBR and their blends: Study on unfilled compounds, Part I showed the solubility of DAE-, TDAE- and MES-oils in which the solubility parameters ( $\delta$ ) were calculated based on the group contribution method, and the  $\Delta\delta$  values between oils and rubbers were correlated with the mass swelling of lightly crosslinked pure NR and SBR at different temperatures. It was found that at high temperatures in the range of mixing temperatures, MES oil showed less compatibility with NR and SBR compared to TDAE and DAE, respectively [12]. Then, Part II of the series [13] reported the influences of oil types and content on the properties of unfilled/non-reinforced NR, SBR and their blend compounds. To complete the series of this study, the present work discusses the influence of the oil types at varying contents on processing properties, cure characteristics, filler dispersion, filler-filler interaction, mechanical and dynamic properties of High Abrasion Furnace (HAF) or N330 carbon black reinforced NR and NR/SBR compounds, typically used for passenger car tire treads.

## Experimental

### Materials

Natural rubber (Ribbed smoked sheet 3, RSS3) was locally produced in Vietnam. Styrene butadiene rubber (Buna® SB 1502-Schkopau) was obtained from Styron HoldCo GmbH, Germany. Three types of oils, i.e. DAE (Tudalen 65), TDAE (Vivatec 500) and MES (Vivatec 200), were supplied by Hansen & Rosenthal KG (Hamburg, Germany). Carbon black

1 Formulations for the compound studies		
Ingredients	Amount (phr)	
NR (RSS 3)	100.0	50.0
SBR (1502)	–	50.0
Carbon black (N330)	60.0	60.0
Oil	Varying types and loadings	
Zinc oxide	3.0	3.0
Stearic acid	1.0	1.0
6PPD	1.5	1.5
TMQ	2.0	2.0
Microcrystalline wax	0.5	0.5
CBS	1.2	1.2
DPG	0.3	0.3
Sulfur	1.5	1.5

N330 or HAF (VULCAN®) was obtained from Cabot Corporation, United States. N-cyclohexyl-2-benzothiazolesulfenamide (CBS) and diphenyl guanidine (DPG) were obtained from Flexsys B.V., Belgium. Sulfur was obtained from Sigma Aldrich, the Netherlands. The other compounding ingredients including stearic acid, zinc oxide, polymerized 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD) and microcrystalline wax, were commercial grades for industry. All elastomers and compounding ingredients were used as received.

### Preparation of rubber compounds

The compound preparation was carried out by using a two step-mixing procedure. In the first step, a rubber masterbatch was prepared by using an internal mixer with a chamber volume of 5 liters and intermeshing rotor system (Werner & Pfleiderer GK5E, Germany), a mixer temperature setting of 50 °C, a fill factor of 0.70 and a rotor speed of 40 rpm. The formulations are given in Table 1. The oil contents of the three different types of process oils, i.e. DAE, TDAE and MES were varied between 0, 5, 10 and 15 phr.

To minimize variation due to the mastication effect of NR and to homogenize the rubber after storage prior to being used, NR was pre-masticated for 3 mins on a two-roll mill with setting of the nip gap at 3 mm, and kept at room temperature overnight. The oils were heated at 60 °C before being added into the mixer. For NR compounds, the mixing procedures in the internal mixer started with a re-mastication of the rubber for 1 min, followed by the addition of stearic acid,

zinc oxide, 6PPD, TMQ, microcrystalline wax and 2/3 carbon black, and mixed for 3 mins. Subsequently, 1/3 carbon black and process oil were added and mixed for another 4 mins. After that, the masterbatch was dumped and made into a sheet on the two-roll mill. The first step mixing of NR/SBR blends was started by adding pre-masticated NR and SBR into the internal mixer and mixed for 2 mins, followed by the same mixing procedure as that of the NR compound.

The second mixing step for both of NR and NR/SBR compounds was to add the curatives, i.e. CBS, DPG and sulfur into the masterbatch by using a two-roll mill. The final compounds were sheeted to a thickness of approximately 3 mm.

### Testing of unvulcanized compounds and vulcanization

Mooney viscosity was determined using a Mooney viscometer (MV2000vs, Alpha Technologies, USA) at 100 °C and large rotor according to ISO 289-1. Complex viscosity of the uncured compounds was tested in the frequency sweep mode from 0.1 to 30 Hz by using a Rubber Process Analyzer (RPA2000, Alpha Technologies) at 100 °C and a strain of 7%. Cure or vulcanization characteristics of NR compounds were tested at 150 °C using the RPA2000 according to ISO 6502, and the cure rate index equal to  $[100/(90\% \text{ optimum cure time} - \text{scorch time})]$ , was calculated. The rubber compounds were cured to their 90% optimum cure times by compression molding at 150 °C. The resulting vulcanizates were left to condition at room temperature at least 16 h prior to being tested.

### Characterization of filler-filler interactions and filler dispersion

Filler-filler interactions were characterized by strain sweep measurements that determine the change of storage modulus ( $G'$ ) as a function of strain of uncured compounds by using the RPA2000 at 100 °C and a frequency of 0.5 Hz. The strains were varied in the range of 0.56% - 100%. The so-called Payne effect was determined from the difference of  $G'$  at 0.56% and 100%, i.e.  $G'(0.56\%) - G'(100\%)$ .

Filler dispersion was analyzed by Scanning Electron Microscopy (SEM) FEI Quanta 400. The rubber vulcanizates were cryogenically cracked after immersing in liquid nitrogen, and the newly cracked surface was coated with gold prior to analysis.

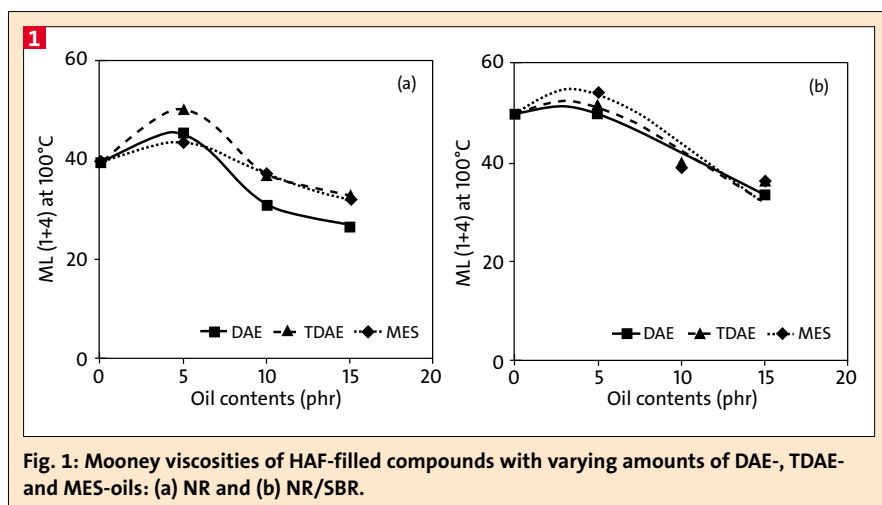


Fig. 1: Mooney viscosities of HAF-filled compounds with varying amounts of DAE-, TDAE- and MES-oils: (a) NR and (b) NR/SBR.

### Testing of vulcanizate properties

**Hardness** – Indentation hardness was measured using a Zwick hardness tester, Shore A type, according to ISO 7619-1.

**Tensile properties** – The tensile properties were tested according to ISO 37 by using a Zwick Z1.0 tensile testing machine operated at a constant crosshead speed of 500 mm/min and the dumbbell test pieces (type 2).

**Abrasion resistance** – A DIN abrasion tester was employed to determine the volume loss of abraded rubber vulcanizates according to ISO 4649.

**Fatigue to failure** – Fatigue life of the specimens was tested using a Monsanto fatigue-to-failure tester as described in ASTM D4482. Dumbbell shape specimens were stretched at an extension ratio of 2.0 and subjected to a tensile strain cycle at 1.7 Hz. The number of cycles required to cause failure was recorded.

**Rebound resilience** – A Dunlop tripsometer (Wallace Test Equipment, England) was used for measuring rebound resilience of NR vulcanizates according to ISO

4662. The test was carried out at 60°C, and resilience was calculated in percent according to equation (1):

$$\% \text{ Resilience} = \frac{1 - \cos B}{1 - \cos A} \times 100 \quad (1)$$

When A is the angle at which the plunger was released (45 degrees), and B is the angle which the plunger bounced back to after hitting the specimen.

**Heat build-up (HBU)** – The test was performed by using a Goodrich Flexometer (Ferry Industry, USA) according to ISO 4666/3. A cylindrical shaped sample having a height of 25 mm and a diameter of 17.5 mm was tested at 100°C for 25 min by applying a weight of 11 kg, stroke 4.45 mm and frequency of 30 Hz. The increase in temperature ( $\Delta T$ ) from the beginning of the test ( $T_0$ ) to 25 mins test time ( $T_{25}$ ) was recorded.

**Dynamic mechanical properties** – Thin sheets of rubber vulcanizates with dimensions of 10 x 24 x 1 mm<sup>3</sup> were tested by using a dynamic mechanical thermal analyzer (Rheometric Scientific DMTA V,

USA) in the tension mode. The measurement was performed with a frequency of 10 Hz, a heating rate of 5°C/min over a temperature range of -130°C to +100°C. In the range of -130°C to -20°C, the strain was set at 0.002%, and in the temperature range of -20°C to +100°C, a strain of 0.02% was applied.

### Results and discussion

It should be noted that due to unexplained erratic behavior of the NR/SBR blend compound with 10 phr of DAE oil, this compound is omitted from this Results and Discussion part.

#### Viscosity and cure characteristics of the compounds

Change of oil contents has a larger effect on the Mooney viscosities of the NR and NR/SBR compounds than change of oil types, as shown in Fig. 1. In the filled compounds, the cause of different viscosities may be related to the level of filler dispersion, interactions between filler and rubber, and the mutual solubility between oils and rubber. For the rubber-oil types studied, DAE oil has a higher compatibility with both NR and SBR rubbers than the TDAE- and MES-oils, respectively, as determined from the smallest difference in solubility parameter ( $\Delta\delta$ ) between rubbers and oils at high temperature ( $\geq 100^\circ\text{C}$ ) [12]. A better rubber-oil compatibility and filler dispersion results in lower compound viscosities [9]. Therefore, the good compatibility between DAE oil and rubber is expected to lead to a more homogeneous mixture and a better filler dispersion.

The NR filled-compounds with DAE oil show the lowest Mooney viscosities, but it is interesting to note, that the first 5 phr of all oil types give a rise in Mooney viscosity relative to the compound without oil added, as observed in Fig. 1(a). This can be attributed to the mastication effect of NR. Without oil, higher shear forces were generated during mixing when the molecular chains were more broken down, as NR is well-known for its sensitivity to mastication due to its reactive double bonds in the polymer backbone. As the molecular weight is strongly related to viscosity [2] and shorter chains have better mobility, so the viscosity of this compound is lower when compared to the compound with small amounts of oil, at 5 phr. The use of 5 phr of oil helps to lubricate the rubber chains and carbon black particles/aggregates, so the shear forces generated during mixing

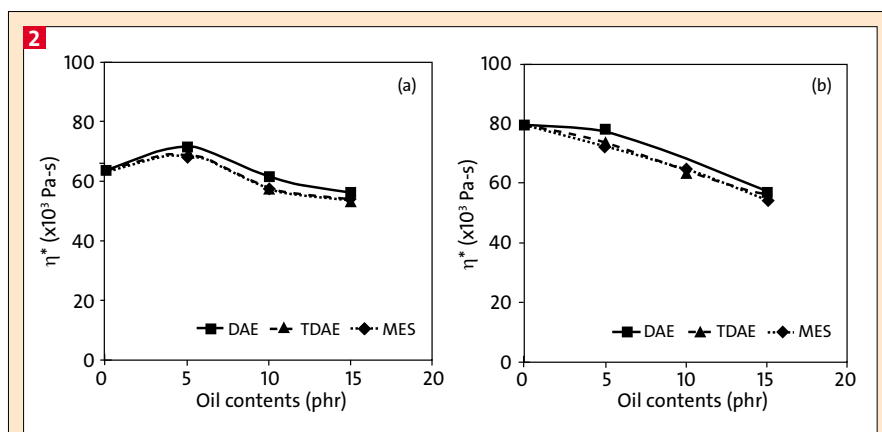


Fig. 2: Complex viscosities of the HAF-filled compounds with different oil types and contents at 0.5 Hz at 7% strain and 100°C: (a) NR and (b) NR/SBR.

were lower than for the un-plasticized compound. The NR/SBR masterbatches with 5 phr of DAE- and TDAE-oils show similar Mooney viscosities and the one with MES oil shows a higher value when compared with the compound without oil, as shown in Fig. 1(b). The phenomenon of increased Mooney viscosity at 5 phr of oil loading is quite similar to what had been observed for HAF-filled NR compounds, but the difference of Mooney viscosities of the compounds without oil and with 5 phr of oil is smaller in the blend that has SBR as a component because SBR is not sensitive to mastication unlike NR. Further increase of the oil contents to 10 and 15 phr decreases the Mooney viscosity of the compounds, mainly owing to the plasticization and the lubrication effect.

The complex viscosities ( $\eta^*$ ) at frequency of 0.5 Hz of the compounds with different oil loadings are typically shown in Fig. 2. Herein, both the NR and NR/SBR blend compounds with DAE oil show the highest complex viscosities, while the TDAE and MES plasticized compounds show almost the same values. The filled-NR compound without oil shows a lower complex viscosity when compared to the one with oil 5 phr; Fig. 2 (a), but further increase of oil loading thereafter reduces the complex viscosities. Increasing oil contents gradually reduce the complex viscosities of the blend compounds. However, it is quite conspicuous that in the complex viscosity case DAE gives the highest viscosities, vs. the lowest in the Mooney case. The different trend of Mooney viscosity and complex viscosity can be attributed to their totally different range of shear rates applied during the tests and their different deformation levels.

The NR/SBR compound without oil initially has higher complex viscosity than the NR compound, and the difference underlines the mastication effect in the NR compounds that plays a role on processing properties. However, with increasing oil loadings, the complex viscosities of the filled-NR/SBR are reduced to a greater extent, compared with the filled-NR compounds. DAE oil has better compatibility with NR and SBR than TDAE- and MES-oils, and so it can better dissolve in both types of rubber. Carbon black dispersion is also expected to be best in the presence of DAE oil. Under dynamic deformation, the compounds with DAE therefore exhibit a higher elastic response from interactions between

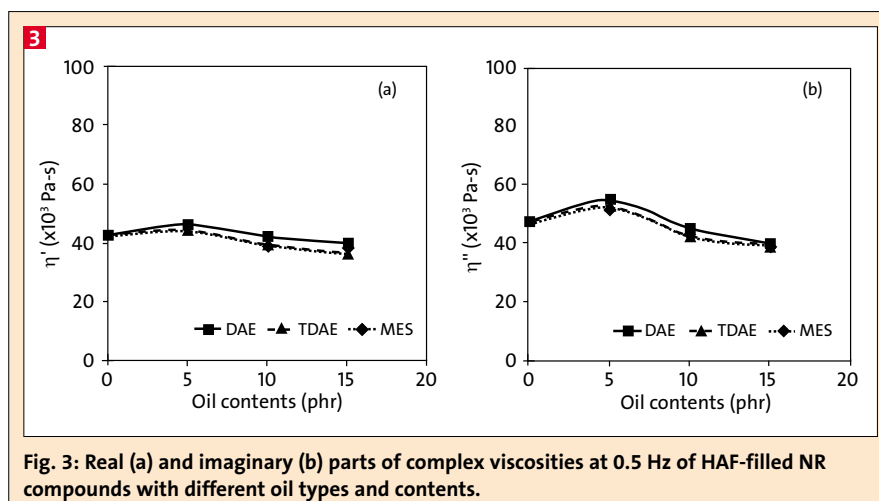


Fig. 3: Real (a) and imaginary (b) parts of complex viscosities at 0.5 Hz of HAF-filled NR compounds with different oil types and contents.

various components, while the TDAE- and MES-oils that have lower rubber-oil compatibility exhibit more a viscous nature.

As the complex viscosity of the materials consists of a real ( $\eta'$ ) and imaginary ( $\eta''$ ) part, Figs. 3 and 4 displays the contribution from each part to the complex viscosity of the HAF-filled NR and NR/SBR compounds. The real or dynamic viscosity is related to the steady state viscosity that measures the rate of energy dissipation, while the imaginary part measures the elasticity or stored energy [14, 15], i.e.  $\eta'$  represents the viscous behavior and  $\eta''$  corresponds to the elastic behavior. The results clearly show that the addition of oils into the rubber compounds contributes more to the elastic component due to the better chain mobility and flexibility. The relationship of  $\eta''$  at different oil contents: Fig. 3 (b) resembles the plot of  $\eta^*$  in Fig. 2 (a). For all cases, the filled NR compounds with DAE-oil show slightly higher viscosities over the compounds with TDAE and MES,

indicating that apparently the higher elasticity of DAE-plasticized compounds prevails over the viscous dissipation. For the blend compounds in Fig. 4, the addition of oils again contributes more to the elastic component like in the case of the filled NR-compounds. A significantly higher  $\eta''$  of the blend with DAE-oil compared to the ones with TDAE and MES indicates a stronger elastic response of this blend in the uncured state.

For rubber processing, the Mooney viscosity test is still the most commonly employed method in the rubber industry to determine the flow behavior of compounds. However, rubber compounds with the same viscosity can often be found to process differently [16]. Mooney viscosity is tested under large deformation as the rotor imbedded in the rubber is rotated at a constant speed of 2 rpm, imparting a shear rate of only  $1 \text{ s}^{-1}$  [17]. So, the Mooney viscosity is measured at a very low shear rate. Under large deformation, contact points and temporary network structures in the system

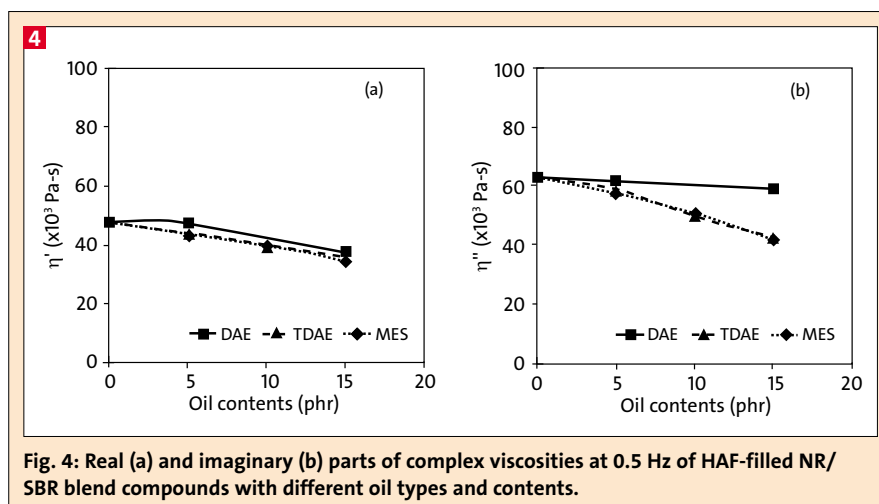


Fig. 4: Real (a) and imaginary (b) parts of complex viscosities at 0.5 Hz of HAF-filled NR/SBR blend compounds with different oil types and contents.

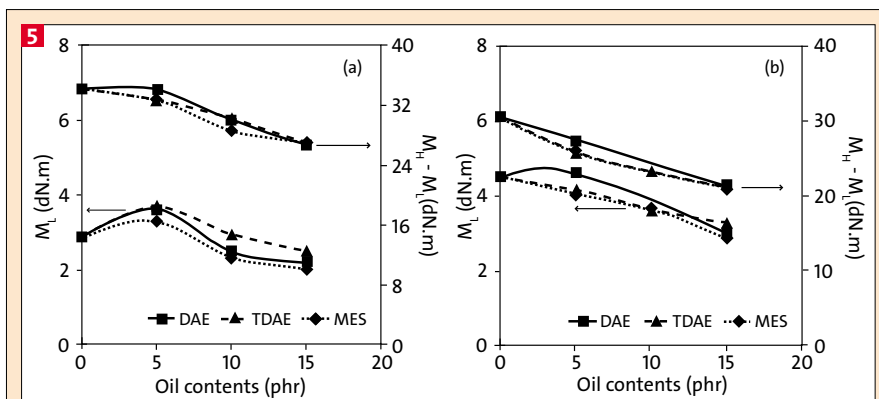


Fig. 5: Minimum torque and torque difference of HAF-filled (a) NR and (b) NR/SBR compounds with varying amounts of DAE-, TDAE- and MES-oils.

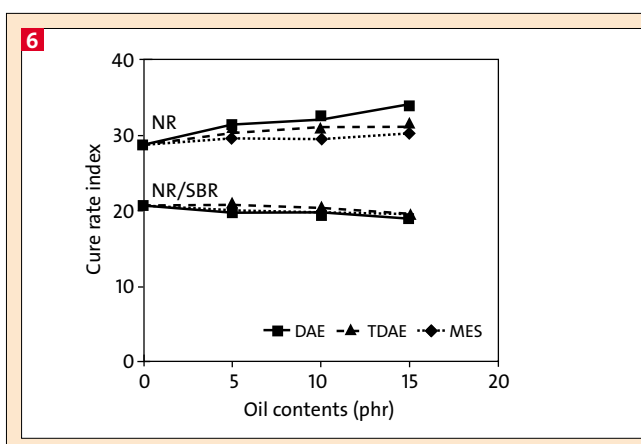


Fig. 6: Cure rate indices of NR and NR/SBR compounds with varying amounts of DAE, TDAE and MES oils at 150 °C.

decrease causing softening of the compound. The DAE which can better dissolve in NR and SBR than the other types of oils, therefore results in lower Mooney viscosity. On the other hand, on testing at low strain at varying frequencies for the complex viscosity, the materials are more prominently influenced by the elastic response from the filler network and interactions between the various components. This explains why DAE plasticized NR and NR/SBR compounds with

good oil-rubber compatibility therefore exhibit the highest complex viscosity.

The minimum torque ( $M_L$ ) from the cure curve also indicates the compound viscosity. As shown in Fig. 5, the change of minimum torque with oil content is in agreement with the Mooney viscosity and complex viscosity, but the difference between the oil types again shows a different trend. Herein, the NR compounds with TDAE oil tend to show a slightly higher minimum torque than the com-

pounds with DAE- and MES-oils. Whereas, the NR/SBR compounds with DAE show the highest minimum torque difference over the ones with TDAE and MES that give more or less the same values. When considering the torque difference which is generally related to the level of cure or crosslink density, both filled NR and NR/SBR compounds with DAE oil show higher torque differences ( $M_H - M_L$ ). The better compatibility of DAE and rubber leads to better carbon black dispersion and interactions between phases. Furthermore, DAE oil contains nitrogen- and sulfur-heterocyclic compounds that can additionally accelerate the cure [13]. Therefore, the DAE containing filled compounds show the highest torque increase. Increasing oil contents result in a decrease of the torque difference due to the dilution and plastization effects on the rubber and its components, which affects the reduced crosslink density of the NR and NR/SBR vulcanizates [9]. The plastization effect also has an influence on stiffness of the vulcanizates which results in a lower maximum torque ( $M_H$ ).

The change of oil types in NR/SBR compounds has only a very minor effect on cure rate indices as shown in Fig. 6. DAE oil gives a slightly higher cure rate index in NR compounds when compared to TDAE and MES at the same oil content, and increases with increasing oil contents. This means that DAE oil accelerates the curing reaction slightly because of the presence of nitrogen- and sulfur-heterocyclic species in this oil [13]. The cure rate indices of the NR compounds with TDAE oil are further marginally higher than those for the compound with MES oil, as the MES is the most inert type due to its highest paraffinic content.

#### Filler-filler interactions and filler dispersion

The addition of fillers to rubber compounds has an influence on both static and dynamic properties. Besides the strain-independent contributions of the hydrodynamic effect, the filler-to-rubber interaction and the crosslink network of the rubber matrix, the dynamic modulus ( $G^*$ ) shows also a strain dependency which is attributed to filler-filler interactions. This stress softening known as the Payne effect plays an important role in the understanding of the reinforcement mechanism of filled-rubber compounds and can be attributed to the breakdown of the filler-filler network [18, 19]. The degree of the filler-filler interaction can be

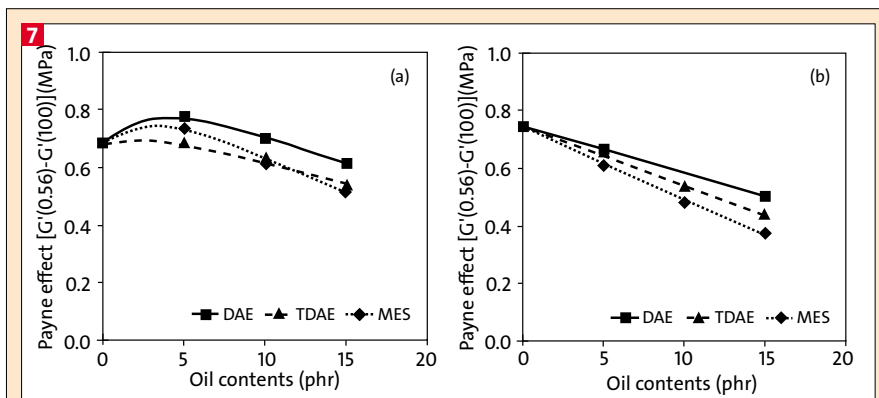
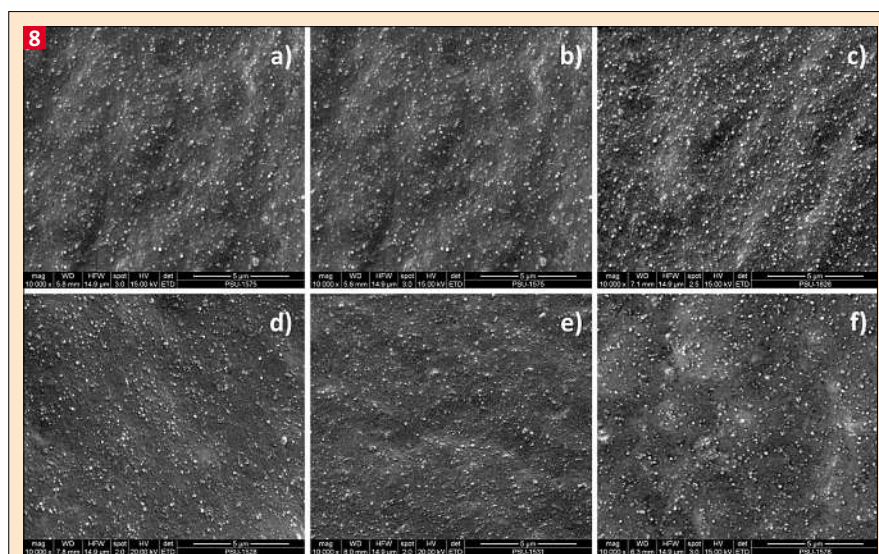


Fig. 7: Payne effects of HAF-filled NR (a) and NR/SBR (b) masterbatches with various oil types and amounts.

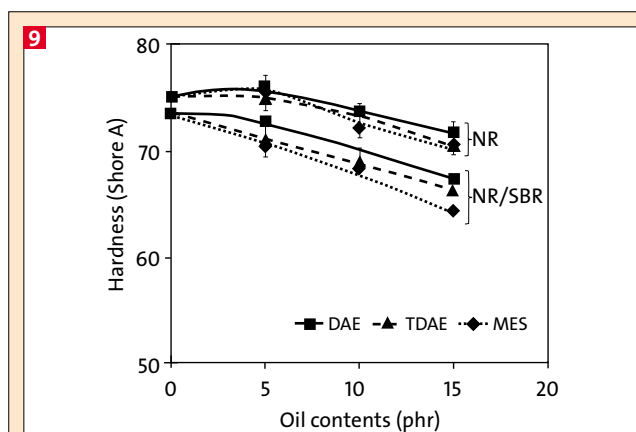
derived from the difference in storage moduli ( $\Delta G'$ ) at low and high strains, i.e.  $G'(0.56\%) - G'(100\%)$ . Regarding the Payne effect of NR and NR/SBR masterbatches as respectively shown in Fig. 7(a) and 7(b), DAE oil gives a higher Payne effect than the other two oils at every oil content, indicating that the masterbatch has a higher filler-filler interaction. The Payne effects of these masterbatches are decreased with increasing oil content, which correlates with decreasing filler-filler interactions due to the presence of oils in between the rubber molecules and carbon black particles/aggregates. Increasing oil contents decrease the contact between filler aggregates/agglomerates and so provide less interactions between them. The reduction of Payne effect with increasing oil content in NR/SBR-filled compounds is sharper when compared to that of the NR-filled compounds. This difference may be related to their rubber-oil compatibility levels. At the temperatures of 100°C and 140°C, SBR has a larger  $\Delta\delta$ , i.e. is less soluble in oils [12].

The filled-NR masterbatches with 5 phr oil again show a peculiar higher Payne effect when compared to the masterbatch without oil. As discussed above for the viscosities, the addition of 5 phr of oil lubricates the filled system and lowers the shear forces generated during mixing, when compared to the masterbatch without oil. So, the break-up of filler agglomerates into aggregates may happen to a lesser extent, resulting in a slightly poorer dispersion and higher filler-filler interactions. However, when higher amount of oils penetrate into the interstices between rubber and filler, the interactions between mutual filler particles become weaker.

As determined by the difference in solubility parameters of rubber and oil [12], DAE oil has better compatibility with both NR and SBR rubbers in the mixing temperature range than the TDAE- and MES-oils. Therefore, DAE oil can diffuse in between the rubber molecules and swell the rubber to a greater extent, leaving less oil located in between the rubber-filler interface and between the filler aggregates. The filler-filler interaction is therefore higher in the case of DAE-plasticized masterbatches. Moreover, the DAE oil that can dissolve and swell the rubber to the greater extent than the other oils results in lower Mooney viscosity and lower shearing forces during mixing, causing less disruption of the filler-filler interactions. TDAE- and MES-oils which have less com-



**Fig. 8:** SEM images of HAF-filled NR with 10 phr of (a) DAE; (b) TDAE and (c) MES oils (top row); and NR/SBR blend with 15 phr of (d) DAE; (e) TDAE and (f) MES oils (bottom row) compounds.



**Fig. 9:** Hardness of HAF-filled NR and NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

patibility with rubbers compared to DAE move to interstices between filler particles/aggregates, facilitates the filler dispersion, reduces the interactions between the filler aggregates/agglomerates, and so lowers the storage modulus especially at low strain.

The influence of oil types and amounts on the carbon black dispersion in NR and NR/SBR compounds was also analyzed by means of scanning electron microscopy (SEM) by using the cryogenically fractured surface of both filled vulcanizates. The SEM micrographs of NR and NR/SBR vulcanizates are displayed in Fig. 8. One of the roles of process oils for the filled-rubber compounds is to improve processing. The softening effect of oils leads to an easier filler incorporation and dispersion. Even though all the three oil types show a good solubility in NR and SBR as the differences in solubility parameters ( $\Delta\delta$ ) are small [12], their compatibility with the

rubber is not the same. At the temperatures during mixing, rubbers (NR and SBR) and MES oil are less compatible while the rubbers and DAE are best compatible, as interpreted by the  $\Delta\delta$  values.

The SEM micrographs in Fig. 8 show that all of the NR compounds display overall similar micrographs, and carbon black is uniformly dispersed within the rubber matrix. It is well-known that carbon black can easily be dispersed in NR, provided that the mixing conditions are suitable. The high viscosity of NR in the early stage of the mixing cycle generates high shear forces to break up the filler agglomerates, and to disperse the aggregates into the rubber. For heterogeneous blend compounds, the addition of carbon black to the blends encounters a difference in filler affinity in each rubber phase. It had been reported that NR/SBR is a heterogeneous blend and the addition of carbon black to pre-blended rub-

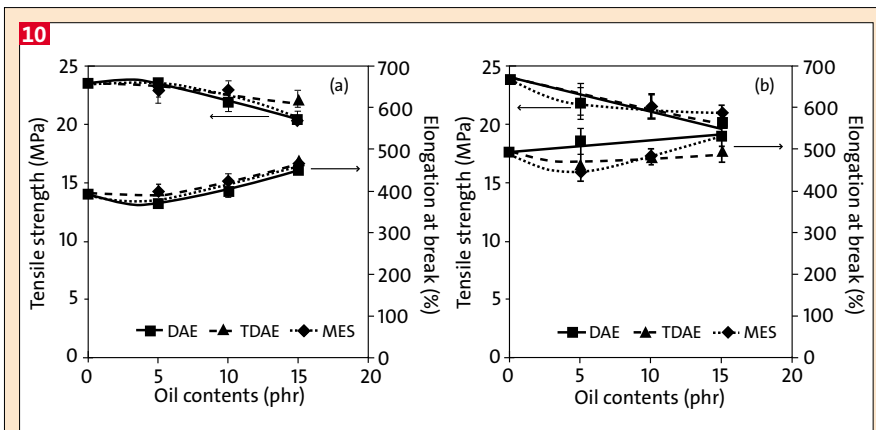


Fig. 10: Tensile strength and elongation at break of HAF-filled (a) NR vulcanizates and (b) NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

bers leads to a higher concentration of black in the SBR phase [20]. The higher filler affinity of carbon black in the SBR over the NR phase in the blends of NR/SBR has been reported also in a number of works [21-23]. In addition to the uneven carbon black distribution in NR and SBR phases, due to the difference in the compatibility between oils and rubbers, the diffusion of oil into each phase can also be different. Even though the two phases cannot be seen in the SEM micrographs, all of the compounds show similar morphology except the one with MES oil that shows clusters of aggregates and poorer carbon black dispersion. This is attributed to the lower compatibility of MES oil with NR and SBR compared to the other two oil types.

**Influence of oil types and amounts on mechanical properties**

The mechanical properties of carbon black filled-NR and NR/SBR vulcanizates with different oil types and amounts are shown in Figs. 9-13. Apparently, the

change of oil types by replacing DAE with TDAE- and MES-oils has only minor effects on the mechanical properties of the NR vulcanizates, but shows more influence on the NR/SBR blend. The increase of oil loading to 10 and 15 phr results in the same lower hardness and tensile strength, but higher elongation at break, as shown in Figs. 9-10. The hardness of the filled NR with various oils at the same oil contents is similar, but the filled-NR/SBR vulcanizates with DAE oil is slightly higher than that of the vulcanizates with TDAE- and MES-oils, respectively, as shown in Fig. 9. The elongation at break of the vulcanizates tends to increase with increasing oil loadings, as shown in Fig. 10.

Increased oil contents especially to 15 phr clearly lower the hardness, which is in accordance with the lower cure torque difference ( $M_H - M_L$ ), as shown in Fig. 3. The decrease of torque difference implies a lower crosslink density either by physical or chemical influences or both. The addition of higher oil content softens the

vulcanizates and dilutes the contact points between polymer chains and filler aggregates, resulting in less resistance to deformation (i.e. lower hardness) and strength, but higher ultimate strain. The mechanical properties of the filled rubber vulcanizates are further mainly affected by the filler loading and filler dispersion level. As shown by SEM micrographs in Fig. 8, all of the three types of oil give similar levels of filler dispersion in the NR compounds and some difference in the blend. Basically, a good dispersion of reinforcing fillers improves all fundamental properties of the rubber. Therefore, change of the oil types causes no significant changes in the mechanical properties of the carbon black-filled NR compounds, but results in some variation in the properties of the blend.

The abrasion resistance of the vulcanizates was tested by measuring the volume loss after abrasion in a DIN abrader, and the results are given in Fig. 11. The replacement of DAE with MES at every oil content results in an improvement of abrasion resistance of NR vulcanizates, while the use of TDAE oil shows more or less the same level of abrasion resistance compared to the use of DAE oil. Increasing oil content reduces the abrasion resistance of the NR vulcanizates, as reflected in an increase of volume loss in Fig. 11. The presence of oils in between rubber molecules and on the rubber-filler interface reduces the hardness and consequently increases the loss of rubber while being abraded. Contrary to the filled NR, the addition of oils in filled-NR/SBR compounds improves the abrasion resistance of these vulcanizates as observed by the lower volume loss. The lowest volume loss is observed when 5 phr of oil was added. Increasing oil contents to 10

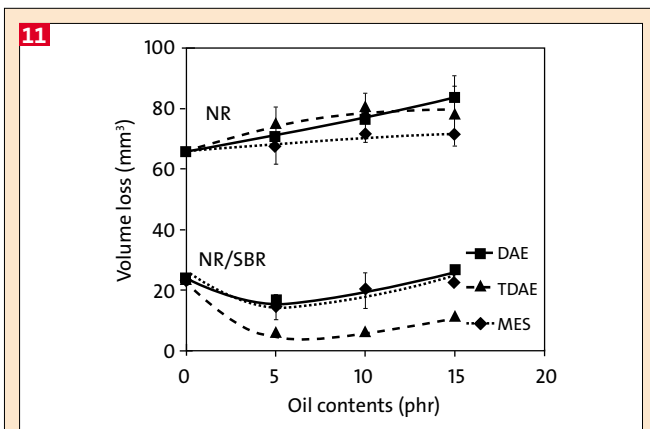


Fig. 11: DIN abrasion loss of HAF-filled NR and NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

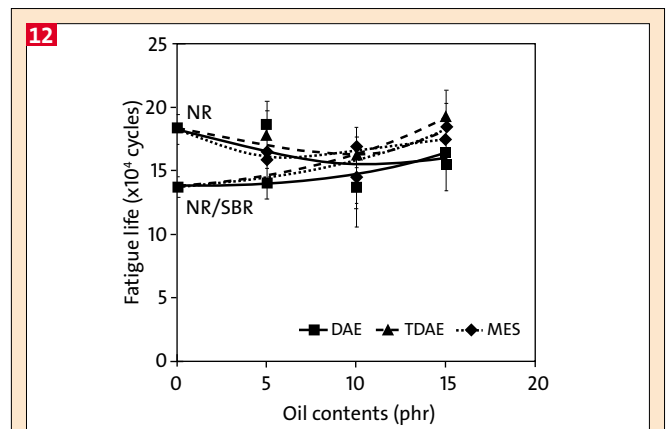


Fig. 12: Fatigue life of HAF-filled NR and NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

and 15 phr deteriorate the abrasion resistance of the vulcanizates, but the volume loss is still lower than that of the one without oil. When compared to the use of DAE oil, the blend vulcanizates with MES oil show only a slightly better abrasion resistance, but the use of TDAE oil drastically reduces the volume loss of the blend vulcanizates at every oil content. The improvement of abrasion resistance of the blend in the presence of oils when compared to the unplasticized one may be attributed to a better homogeneity in the material and a better flexibility of chains. However, the increasing oil loadings soften the material causing the increased volume loss of rubber. Abrasion loss is a complex behavior of the materials that is affected by various factors and is closely related to viscoelastic properties. In the NR/SBR case, the situation is even more complicated due to the presence of binary rubber phases in which each phase has different filler affinity and oil compatibility.

The previous study showed that the addition of oils had an influence on the glass transition temperature ( $T_g$ ) of the unfilled-NR and SBR compounds [13]. Therein, the use of DAE oil increased the  $T_g$ 's of both rubber types, while the addition of TDAE increased the  $T_g$  of NR but slightly decreased the  $T_g$  of SBR, whereas the addition of MES had almost no effect on the  $T_g$  of NR but reduced the  $T_g$  of SBR. The use of DAE-, TDAE- and MES-oils which have different  $T_g$ 's is also expected to result in a shift of the  $T_g$  of the carbon black-filled compounds. The use of MES which itself has the lowest  $T_g$  among the three types of oils studied, should also result in the lowest  $T_g$  of the carbon black-filled compounds. The change of  $T_g$  does affect the viscoelastic behavior of the materials. Generally, rubbers with lower  $T_g$  have a better abrasion resistance due to their good elastic behavior. The MES-containing NR compounds with the lowest  $T_g$  therefore show somewhat better elastic properties, as reflected in the better abrasion resistance (Fig. 11) and also fatigue life (Fig. 12), when compared to the compound with DAE oil. The influence of  $T_g$  of the rubber on abrasion resistance has previously been reported [24], in the sense that a higher  $T_g$  resulted in higher DIN abrasion loss. The present results are in agreement with that. Furthermore, the MES oil contains a high paraffinic portion and waxes, so the incompatible oil-components and waxes may migrate to the sample surface and

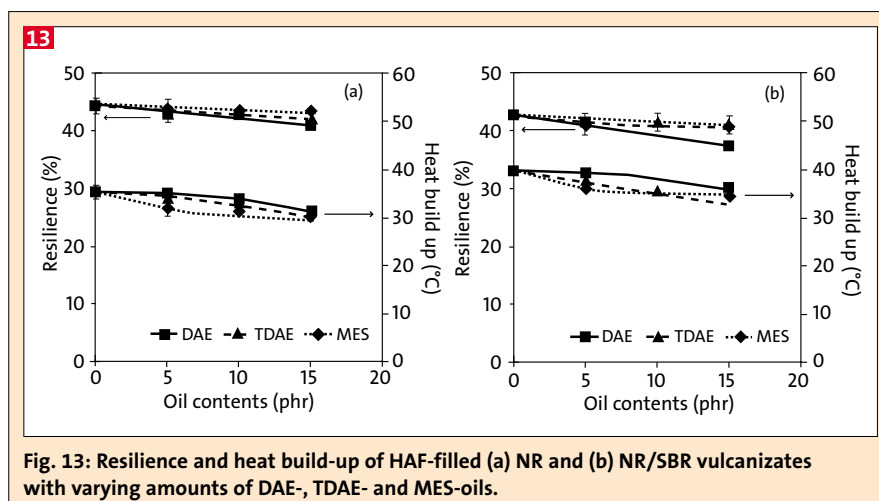


Fig. 13: Resilience and heat build-up of HAF-filled (a) NR and (b) NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

affect the abrasive wear [9]. By combined effects of the lower  $T_g$  and the incompatible oil-components that may migrate to the surface, the use of MES oil in the NR compounds results in the lowest abrasion volume loss. However, a different behavior is observed in the NR/SBR blends in which the TDAE gives a lower volume loss than MES. This can be attributed to the poorer dispersion of filler in the blend with MES oil, as observed in the SEM images in Fig. 8 and Payne effect in Fig. 7. The blend with TDAE oil thus has a better balance between good filler dispersion and a small change in  $T_g$  value of the SBR phase that provides the better abrasion resistance than NR.

Factors that influence the fatigue life of rubber vulcanizates include effects of mechanical loading history, environmental effects, rubber formulation and dissipation aspects of the constitutive response of rubber [25]. In the present study, the rubber formulation changed due to the variation of oil types and loadings. The addition of oil to the NR compounds tends to decrease the fatigue-to-failure properties of the vulcanizates especially in the case of DAE oil, as shown in Fig. 12. With 10 and 15 phr of oils, the NR compounds with DAE oil show significantly lower fatigue life when compared with TDAE- and MES-oils, which otherwise show similar results. The DAE-containing NR compounds show higher Payne effects when compared to the other compounds, and the vulcanizates show a little higher hardness which also means higher stiffness. This will have a negative effect on the fatigue life under the displacement controlled test. The highest  $T_g$  of the DAE oil among the oil types studied will also affect the  $T_g$  of the filled-rubber vulcanizates to some extent. The

shift of  $T_g$  to higher temperature affects the stiffness and hysteresis of the rubber, and thus results in a poorer fatigue life.

Contrary to NR, the fatigue life of filled-NR/SBR vulcanizates as also depicted in Fig. 12 shows an increase after the addition of oils and with increasing oil contents, which can be ascribed to the better homogeneity of the blend and better filler dispersion. The presence of two rubber phases in the NR/SBR blend introduces an additional complication. SBR rubber has bulky phenyl groups in the styrene part which hinder rotation of the polymer backbone [26], and therefore gives high viscoelastic energy dissipation during deformation that positively affects fatigue life. The lowest  $T_g$  of MES-oil which should impart better elasticity to the material is impeded by the poorest dispersion of carbon black in the blend. Therefore, the blends with TDAE oil show the best fatigue life. Like in the case of filled-NR vulcanizates, the use of DAE-oil with the highest  $T_g$  in the NR/SBR blend results in the lowest fatigue life. The difference between the oil types is larger at higher oil loadings. The poorest fatigue life of the DAE plasticized blends is the result of several contributions including its highest filler-filler interactions (Fig. 7), the highest hardness (Fig. 9) and the shift of  $T_g$ 's of both rubbers to higher temperatures. Furthermore, the smallest difference in solubility parameters ( $\Delta\delta$ ) between DAE and both NR and SBR makes them most compatible with each other and, consequently DAE can swell NR and NR/SBR to a greater extent [12]. The good oil-rubber compatibility will also affect the elastic modulus and dynamically stored energy, and finally have an influence on specimen fracture [27]. A study with ethylene propylene diene rubber (EPDM) by Jerrams et al. [27]



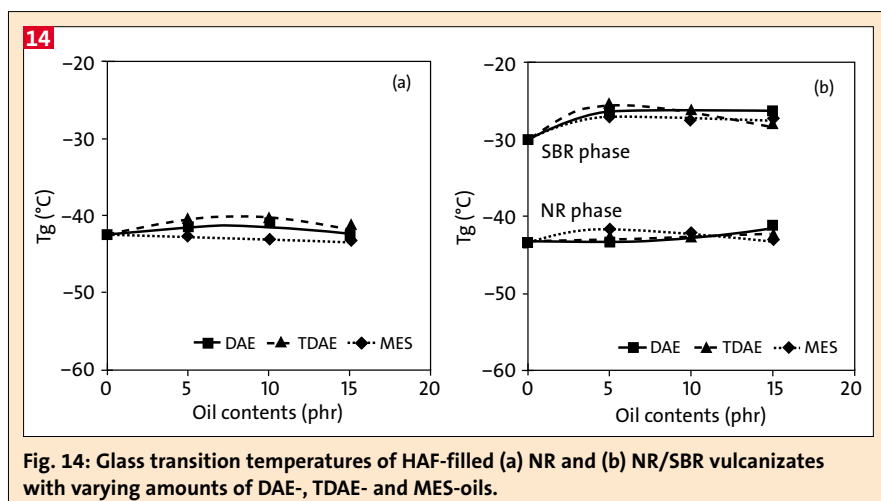


Fig. 14: Glass transition temperatures of HAF-filled (a) NR and (b) NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils.

showed that the fatigue life of rubber decreased in proportion to the degree of swelling. The greater swelling decreased the stiffness of the materials, and consequently increased the dynamically stored energy in the sample, which finally lead to failure.

The influences of DAE-, TDAE- and MES-oils on rebound resilience and heat build-up of NR and NR/SBR vulcanizates are illustrated in Fig. 13. As expected, increased oil contents, which is a viscous component, in the compounds decreases the rebound resilience of the vulcanizates: a higher energy loss during deformation. However, increasing oil content also gives reduction of the heat build-up of the vulcanizates. The addition of carbon black into a compound commonly increases the heat build-up as a result of breakage of the carbon black structure and consequent viscoelastic loss [28]. The oil molecules distributed in the free volume between the rubber molecules and at the filler-rubber interface may help to dissipate the heat and so cause

less temperature rise in the rubber vulcanizates. Higher oil loadings clearly reduce the heat build-up. The changes of rebound resilience and heat build-up as functions of oil contents and types of the filled NR vulcanizates are similar to the filled NR/SBR blends. That is, replacement of DAE with TDAE and MES in both NR and NR/SBR compounds gives some higher resilience and lower heat build-up, indicating some but little improvement in rubber elasticity. These two properties can again be related to the viscoelastic behaviors of the materials as affected by the glass transition temperatures of the oils. The results indicate that the replacement of DAE with these two types of safe process oils improves the rubber elasticity and consequently the resilience and lower heat build-up.

*Influence of oil types and amounts on dynamic mechanical properties of vulcanizates*

Dynamic properties are very important for tire applications, especially for wet

grip and tire rolling resistance. As reported previously [13], the  $T_g$ 's of unfilled NR- and SBR-vulcanizates were shifted according to the  $T_g$ 's of the oils. The variation of oil types and amounts also shows their influence on the  $T_g$  and loss tangent of HAF-filled NR and NR/SBR blend vulcanizates, as shown in Fig. 14 and Fig. 15, respectively.

For carbon black-filled NR, the  $T_g$ 's of all vulcanizates with varying oil types and contents are presented in Fig. 14(a). The  $T_g$  of the NR vulcanizate is practically not affected by the  $T_g$  of the oils; the shifts are smaller than 2 °C. Addition of TDAE and DAE in the NR compounds slightly increases the  $T_g$  of the vulcanizates when compared to the one without oil, while the use of MES oil results in a marginal decrease. Increasing oil contents show no clear influence on  $T_g$  of the vulcanizates. When considering the filled NR/SBR blend vulcanizates, they exhibit two  $T_g$ 's associated with each blend component. The  $T_g$ 's of NR and SBR in the blends with varying oil types and contents are plotted in Fig. 14(b). The addition of all oil types results in increased  $T_g$ 's of the NR and SBR phases when compared to the  $T_g$ 's of the rubbers without oil, but the extent of changes is different. Again, a minimal  $T_g$ -shift in NR is observed and no clear trend with oil contents and types. The shift of  $T_g$  for the SBR phase is larger. This  $T_g$ -shift may be a combined result of uneven carbon black distribution as it prefers the SBR phase [22-24], and the influence of the  $T_g$ 's of the oils. Based on the  $T_g$ -shift in the NR and SBR phases, it implies that the oils are preferentially located in the SBR- over the NR-phase. A study on oil distribution in blends of NR/SBR by Naito et al. [29] also showed that aromatic oil was favorably distributed to the SBR phase.

The loss tangent ( $\tan \delta$ ) values at 0 °C and 60 °C of the filled rubber-compounds are commonly used to indicate wet grip and rolling resistance for tires, respectively. The NR-vulcanizates with the three different oil types show almost identical values of  $\tan \delta$  at 0 °C, while the NR/SBR blends with DAE and TDAE also show almost identical  $\tan \delta$  values at 0 °C but higher than for the MES-plasticized vulcanizates (Fig. 15(a)). Consequently, among the three types of oils studied, MES oil indicates the poorest wet grip of the blend. The  $\tan \delta$  values at 0 °C generally increase with raising oil contents due to the large viscous contribution from the oils. Therefore, the incorporati-

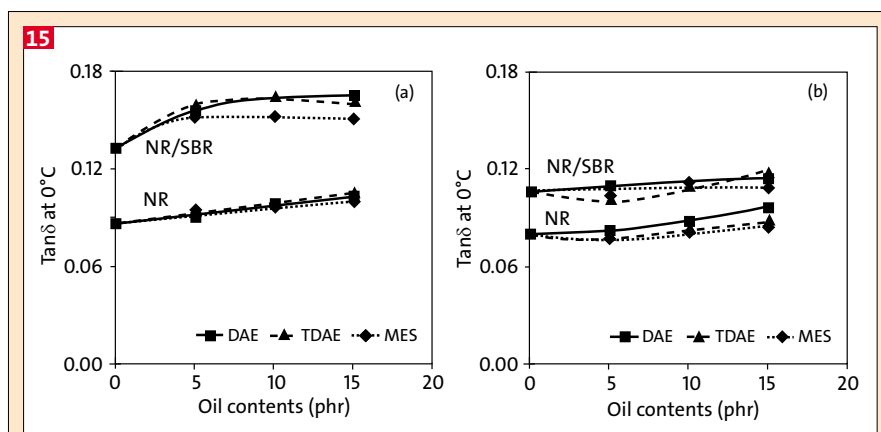


Fig. 15 Loss tangent at 0 and 60 °C of HAF-filled NR and NR/SBR vulcanizates with varying amounts of DAE-, TDAE- and MES-oils: (a) loss tangent at 0°C and (b) loss tangent at 60°C.

on of process oils generally improves the wet grip performance of tires. When compared to the  $\tan \delta$  values at 0 °C of NR, the NR/SBR blend shows a significantly higher  $\tan \delta$  due to the damping behavior of the styrene in the SBR blend component.

When considering the change of the loss tangent at 60 °C (Fig. 15 (b)), the NR and NR/SBR blend vulcanizates with DAE oil show a higher  $\tan \delta$  at 60 °C when compared with the rubbers with TDAE and MES, again due to its  $T_g$  influence. However, in this higher temperature regime there are apparently more factors involved in the energy storage and loss during deformation. These include filler dispersion, filler-rubber and filler-filler interactions. The addition of all oil types in the compounds except for 5 phr loading increases the loss tangent at 60 °C. The higher loss tangent at 60 °C for the DAE-containing vulcanizates correlates with its higher Payne effect, as displayed in Fig. 6. Furthermore, the better compatibility between DAE and both NR and SBR, which results in a larger degree of swelling of oils in the rubbers, is also expected to increase the energy loss in the rubbers during cyclic deformation. The conversely poorest elastic response of the DAE-plasticized HAF-filled rubber compounds correlates with the results of rebound resilience and heat build-up, as previously shown in Fig. 13, in which the rubber vulcanizates containing DAE-oil have lower rebound resilience and higher heat build-up, compared with the more elastic TDAE- and MES-plasticized blends. From these results it may be expected that the replacement of DAE with MES- and TDAE-oils leads to a slightly lower rolling resistance if applied in tire treads. Increased oil contents improve wet grip but deteriorate tire rolling resistance. Based on these dynamic mechanical properties, the use of TDAE-oil provides the best balance of wet grip and rolling resistance for tire treads.

### Conclusions

The influence of DAE-, TDAE- and MES-oils at different loadings on the properties of HAF-filled NR and NR/SBR compounds was investigated. The DAE-containing rubber compounds have lower Mooney viscosities but higher complex viscosities when compared with the mixes with TDAE- and MES-oils. The viscosities decrease with increasing oil contents, except for NR-compounds with 5 phr of oils where the values are higher

than for the unplasticized compound due to the mastication effect. The compounds with different oils show similar cure characteristics, but increasing oil contents prolong scorch and optimum cure times and lower the torque difference ( $M_H - M_L$ ). The use of DAE results in the highest Payne effect in both filled-NR and filled-NR/SBR compounds, but increasing oil contents reduce filler-filler interactions. SEM-micrographs reveal that carbon black is finely dispersed in all of the NR compounds. On the other hand, the NR/SBR blend with MES-oil shows a slightly poorer filler dispersion when compared to the blends without oil and with DAE- and TDAE-oils. The results show that the replacement of DAE- with TDAE- and MES-oils in the rubber compounds has no significant effect on the mechanical properties, but does influence the dynamic mechanical properties as a result of the different  $T_g$ 's of the oils that affect the  $T_g$  of the compounds. The replacement of DAE with TDAE and MES improves the elastic properties of the filled NR as well as the filled NR/SBR blend as indicated by an increased rebound resilience, decreased heat build-up and lowered loss tangent at 60 °C.

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