

Epoxidized natural rubber · TDAE · MES · PAR · plasticizer oil · compatibility · ageing

The present paper reports about the effect of the plasticizers on the performance of natural rubber (NR) and epoxidized natural rubber (ENR) used in tyre applications. The influence of the chemical structure of the oil (paraffinic, naphthenic and aromatic) and oil loading on carbon black and silica filled compounds was studied considering the following aspects: i) the compatibility of plasticizers with polymers, ii) processability, iii) cure characteristics, iv) dynamic mechanical properties and v) physical properties before and after ageing. It was demonstrated that the choice of the right plasticizers is crucial for obtaining end products with desired properties. These products must meet not only the technical requirements but also the ecological demands.

Einfluss von Weichmachern auf die Eigenschaften von Gummimischungen auf Naturkautschuk Basis

Epoxidierte Naturkautschuk · TDAE · MES · PAR · Weichmacher Öl · Verträglichkeit · Alterung

Die vorliegende Arbeit beschäftigt sich mit dem Einfluss von Weichmacherölen auf die Leistung von Naturkautschuk (NR)- und Epoxidierten Naturkautschuk (ENR)-Mischungen, die in der Reifenherstellung Anwendung finden. Der Einfluss der chemischen Struktur (paraffinisch, naphthenisch und aromatisch) und der Konzentration des Öls in mit Ruß und Silika verstärkten Kautschuk Mischungen wurde auf die folgenden Aspekte hin untersucht: i) die Verträglichkeit des Weichmachers mit den Polymeren, ii) Verarbeitbarkeit, iii) Vulkanisationscharakteristika, iv) dynamisch mechanische Eigenschaften und v) physikalische Eigenschaften vor und nach Alterung. Es wurde gezeigt, dass die Wahl des richtigen Weichmachers wichtig ist, um Produkte mit den gewünschten Eigenschaften zu erhalten. Diese müssen nicht nur technischen sondern auch ökologischen Anforderungen genügen.

Figures and Tables:
By a kind approval of the author.

Influence of Plasticizers on the Properties of Natural Rubber based Compounds

By the chemical modification of 1, 4-polyisoprene, namely epoxidation, materials with increased glass transition and polarity can be obtained [1 - 3]. These changes are translated on higher damping properties [4], greater tensile and fatigue due to the fact that the epoxidized natural rubber undergoes strain crystallization [5], reduced air permeability [6], lower rolling resistance and increased wet grip [7] than natural rubber. Thus, ENR represents a potential source for the tyre market [8 - 10], general rubber goods [11], adhesive [12] and thermoplastic sector [7]. Therefore, extensive research works studied the influence of different types of filler on ENR properties, the quantitative distribution of the filler between immiscible rubber blends based on ENR [4, 13, 14], the chemical interaction between modified carbon black surface and ENR [15] and the use of ENR as compatibility stabilizer for organoclay/rubber nanocomposites [16 - 18]. Additionally, the vulcanisation, the oxidative ageing behaviour, compression set and compatibility of ENR with other polymers were also investigated thoroughly [19 - 23].

As reviewed, many works have been performed with epoxidized natural rubber, but the influence of process oils on the properties of ENR based compounds is precarious. In the literature the diffusion and* equilibrium uptake measurements of ester plasticizers [24], benzene and substituted benzenes [25] in ENR have been described. The oil resistance measurements of this polymer in ASTM oils were carried out by Baker et al. [4]. The improvement of flex crack growth resistance by using the emulsion of vegetable oil was demonstrated in [26].

Accordingly, the present paper reports about the influence of chemical structure of the oil (paraffinic, naphthenic and aromatic) and oil loading on carbon black and silica filled compounds considering the following aspects: i) the compatibility of plasticizers with polymers, ii) processability, iii) cure characteristics, iv) dynamic mechanical properties and v) physical properties before and after

ageing. A major task of the study was the replacement of the conventional carcinogenic aromatic oils DAE (Distillate Aromatic Extracts) by non-toxic mineral oils like TDAE (Treated Distillate Aromatic Extracts) and MES (Mild Extracted Solvate) in NR and ENR used in tyre applications as a consequence of the health, safety and environmental issues that have intensified in recent years [27 - 30]. For the manufacturer of tires, the use of unlabelled oils is imposed by legislation. Under REACH (Registration, Evaluation, Authorisation of Chemicals) the use of extender oils in tires is allowed if the oils contain less than 1 mg/kg (0,0001% by weight) benzo[a]pyrene (B[a]P) and less than 10 mg/kg (0,001% by weight) of the sum of 8 priority PAHs. Furthermore, these limit values are thought to be fulfilled if the extract of polycyclic aromatics (PCA) prepared with dimethyl sulfoxide (DMSO-extract) is less than 3% by weight as measured by the Institute of Petroleum standard method IP346. For rubber tyres these limits are regarded as kept, if the organic extract of the vulcanized rubber material does not exceed the limit of 0,35% bay protons (H_{bay}) as measured and calculated by ISO 21461 [31, 32].

Additionally, the performance of benchmark compounds NR silica-silane was compared with ENR 25 and ENR 50 silica compounds without the use of the silane coupling agent.

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1 Properties of NR and ENR				
Properties	Unit	NR	ENR 25	ENR 50
Epoxide level	%	---	25	50
Glass Transition (DSC)	°C	-61	-37	-14
ML (1+4) 100 °C	MU	60	75	88
Density	g/cm ³	0.93	0.97	1.02

Experimental

Materials and sample preparation

The test species evaluated in this work were prepared employing natural rubber and epoxidized natural rubber with different epoxidation level of 25% and 50% respectively (Table 1). Mineral extender oils with different chemical structure (paraffinic, naphthenic and aromatic) produced in the H&R refinery were tested in various concentrations: 0 phr, 5 phr, 10 phr and 15 phr. Table 2 depicts the physical and chemical properties of the processing oils used: DAE (Tudalen 65), TDAE (Vivatec 500), MES (Vivatec 200), PAR (Tudalen 12).

The tyre tread formulations investigated in this work are presented in table 3. Carbon black and silica based compounds were mixed in an internal mixer (1.6 litre Banbury type) in accordance with the mixing procedures described in table 4. Addition of curing agents to the compounds was done on a two-roll mill at 50 °C. The silica based tyre treads were prepared according to ISO 5794/3.

Cure characteristics of the compounds were determined at 150 °C with a MD-R2000E Rheometer according to ISO 6502. Test sheets were vulcanized in an electrically heated press at optimum cure time.

Instruments used for the characterisation of masterbatches and vulcanisates

The Mooney viscosity of the compounds was determined on Rubber Process Analyzer MV 2000 according to DIN 53523/3 and the Payne effect was investigated on a RPA2000 instrument at 100 °C and 20 cpm.

The thermal analyses were conducted with a Differential Scanning Calorimeter (DSC), DSC1 STAR[®] System from Mettler Toledo at a heating rate of 10 °C/min in conformity with DIN 53765.

The mechanical properties were tested according to DIN 53504 using a Zwick tensile test machine, and the hardness was measured according to

2 Physical and chemical properties of extender oils						
Properties	Test method	Unit	DAE	TDAE	MES	PAR
Viscosity @ 100°C	DIN 51562	mm ² /s (cSt)	26	19	16	10
Density @ 20°C	DIN 51 757	kg/m ³	987	947	912	878
Refractive index	DIN 51 378	-	1,561	1,528	1,505	1,482
Refractivity intercept	DIN 51 378	-	1,067	1,055	1,049	1,044
Aniline point	DIN ISO 2977	°C	41	68	97	113
VGC	DIN 51378	-	0.94	0.89	0.84	0.80
C-Distribution	DIN 51378					
CA		% by weight	40	25	15	2
CN		% by weight	25	30	27	33
CP		% by weight	35	45	58	65
Sulfur	DIN ISO 51400	% by weight	1.2	0.8	0.5	0.2
DMSO-extract	IP 346	% by weight	22	<2.9	<2.9	0.5
Benzo[a]pyrene	GC-MS	ppm	17	<1	<1	<0.1
Total 8 EU PAH	GC-MS	ppm	320	<10	<10	<0.7
Glass Transition	BP/GRE 208TA2	°C	-38	-49	-59	-70

3 Tyre tread formulations using filling material, carbon black and silica (in phr)						
1) carbon black						
Material	M1	M2	M15	M15	M27	M28
	-	-	-	-	-	-
		M14		M27		M40
TSR-10	100	100				
ENR-25			100	100		
ENR-50					100	100
HAF- N330		60		60		60
Zinc oxide	5	5	5	5	5	5
Calcium stearate			2	2	2	2
Stearic acid	2	2	2	2	2	2
6PPD	1	1	1	1	1	1
TMQ	1	1	1	1	1	1
TBBS	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
Oil ^{a)}	A	B	A	B	A	B
a) Type of oil: DAE, TDAE, MES, PAR. A = 0 phr, B = 0 phr, 5 phr, 10 phr, 15 phr						
2) silica						
Material	M41	M42	M55	M56	M68	M69
	-	-	-	-	-	-
		M54		M68		M81
TSR-10	100	100				
ENR-25			100	100		
ENR-50					100	100
Ultrasil 7000 GR		60		60		60
Si69		6				
Zinc oxide	5	5	5	5	5	5
Calcium stearate			2	2	2	2
Stearic acid	2	2	2	2	2	2
6PPD	1	1	1	1	1	1
TMQ	1	1	1	1	1	1
TBBS	1.5	1.5	1.5	1.5	1.5	1.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
DPG	1	1	1	1	1	1
Oil a)	A	B	A	B	A	B
a) Type of oil: DAE, TDAE, MES, PAR. A = 0 phr, B = 0 phr, 5 phr, 10 phr, 15 phr						

4 Mixing procedures	
1) NR carbon black based compounds	
First step: internal mixer (1.6 L), 50 °C, 76 rpm	
Mixing sequence	0.0 min rubber 1.0 min activator + ½ filler 2.5 min ½ filler + oil + rest 4.0 min sweep 5.0 min dump
Second step: open mill, 50 °C	
Mixing sequence	0.0 min mix from the second step 5.0 min cross blend and sheet off
2) ENR carbon black based compounds	
First step: internal mixer (1.6 L), 50 °C, 76 rpm	
Mixing sequence	0.0 min rubber + calcium stearate 0.5 min activator + ½ filler 2.0 min ½ filler + oil + rest 3.5 min sweep 4.5 min dump
Second step: open mill, 50 °C	
Mixing sequence	0.0 min mix from the second step 5.0 min cross blend and sheet off
3) NR and ENR silica based compounds	
First step: internal mixer (1.6 L), 50 °C, 76 rpm	
Mixing sequence	0.0 min rubber ^{b)} 1.0 min ½ silica + silane ^{c)} 2.0 min ½ silica + oil + rest 4.0 min sweep 5.0 min dump
Second step: internal mixer (1.6 L), 50 °C, 76 rpm	
Mixing sequence	0.0 min mix from the first step 5.0 min dump
Third step: open mill, 50 °C	
Mixing sequence	0.0 min mix from the second step 5.0 min cross blend and sheet off
b) NR was mixed 1.0 min, ENR was mixed 0.5 min c) ENR compounds were mixed without silane	

DIN 53505. The rubber plates were characterized before and after ageing in hot air for 72 hours at 100 °C by means of change in stress-strain properties and hardness.

The dynamic mechanical measurements were conducted by using a dynamic mechanical thermal analyzer (EPLXOR® 500 N/150N) at a frequency of 1Hz and amplitude of 0,5%.

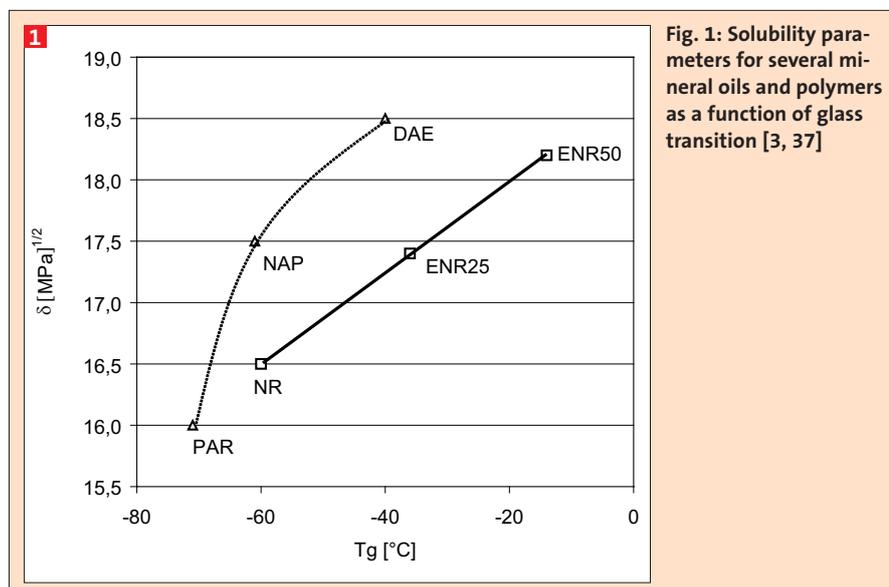


Fig. 1: Solubility parameters for several mineral oils and polymers as a function of glass transition [3, 37]

Swelling investigations

The plasticizer absorption measurements were carried out at 100 °C until equilibrium swelling was achieved. The tests were conducted with plasticizers described in Table 2.

Results and discussions

Compatibility of plasticizers with polymers

The plasticizers used for this study contain different portions of paraffins, naphthenes and aromates, heterocyclic or polar components. Their chemical structures can influence significantly the properties of the rubber material during processing and finishing. Valuable information about the composition of the oil is given by the viscosity, density and refractive index. Aromatic oils display higher viscosity, density and refractive index than paraffinic oils. Higher molecular weights are translated in higher viscosities, which may play an important role in the performance of plasticizers at low and high temperatures. The various molecular compositions of the oils are also reflected on the glass transition (T_g) temperatures, as described in Table 2.

An important tool often used in tyre industry for the evaluation of the processing oils aromaticity is the refractivity intercept (R.I.). This parameter is calculated based on the refractive index and the density at 20 °C. The higher the aromaticity of the oil, the higher the refractivity intercept.

The aniline point is another property which provides information about the structure of the processing oil. Low aniline points are characteristic for high aromatic structures. Paraffinic oils have high aniline points.

In order to predict the solvent power of the petroleum products, which are complex mixtures of unknown molecules varying by provenience and production technique, several approaches are used in the oil industry. These include, the solubility parameter (δ) concept [33], the relative content of aromatic (CA), naphthenic (CN) and paraffinic (CP) carbon atoms in oil [34], the aniline point and the kauri-butanol number (KBN) [35, 36]. The descriptor mostly used in practice is the solubility parameter model. If the δ values of two components are nearly equal, the substances are miscible. The dependence of the solubility parameter on the glass transi-

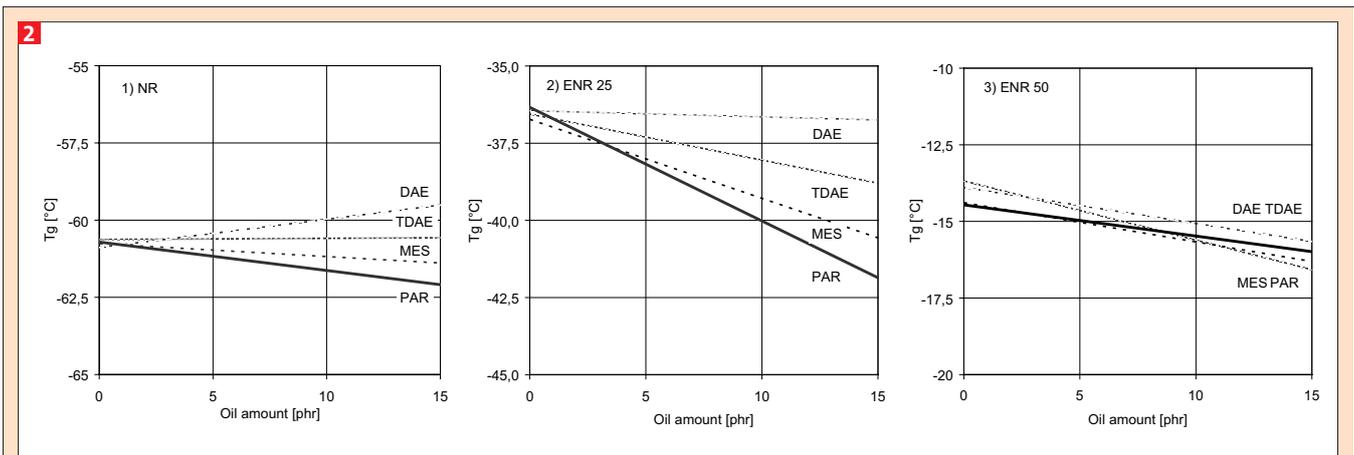


Fig. 2: Variation of T_g with plasticizer content: 1) NR, 2) ENR 25, 3) ENR 50

on of the processing oils and the polymers is depicted in Figure 1 [3, 37]. Increasing the aromatic content of the oils and the level of the epoxidation in NR, higher solubility parameters were noted. Additionally, the glass transitions increased due to the low mobility of the aromatic structures in oils and the epoxy units in the polymers. From the difference in the solubility parameters it can be predicted that the aromatic oil (DAE) will have great solvency and affinity to the polar polymer ENR 50 and the paraffinic oil (PAR) will show better affinity and therefore better compatibility with the unpolar polymer NR.

The compatibility of those plasticizers with the polymers was investigated by studying the impact of the oil addition on the glass transition temperature and the relationship between the oil incorporation time into the rubber matrix and the swelling degree.

By the addition of plasticizers in rubber matrix, the free volume in the system and the polymer chain mobility increase while the intermolecular forces between the chains decrease [38]. Therefore, a drop in glass transition and viscosity of the mixture will occur associated with changes in rheological and physical properties of the rubber melts as well as of the corresponding cured materials [24, 39, 40]. In Figure 2 the variations of the glass transition with the plasticizer content for NR and ENR compounds are plotted. The standard deviations of measuring the T_g are ± 0,6 °C for NR and ± 1,9 °C for ENR compounds. When the amount of plasticizer was increased, three different effects could be observed: i) a rise in T_g (for NR mix with DAE), ii) the T_g remains practically constant (for NR and ENR 25 compounds with TDAE and DAE respectively) and iii) a decrease in T_g (for NR with MES and PAR, for ENR 25

with TDAE, MES and PAR, and for ENR 50 with DAE, TDAE, MES and PAR). This behaviour is in accordance with the Flory-Fox equation and has also been discussed by other authors when studying the influence of oils on the properties of different polymers [41]. Namely, by mixing a plasticizer with a higher solidifying point than the T_g's polymer, an increase in the T_g of the compound has been noticed and vice versa. For the mixes containing polymer and plasticizer with comparable T_g and solidifying point, minimal variations on the T_g of the compound have been recorded.

Supplementary information about the thermodynamic interaction between the plasticizers and polymers were acquired through swelling experiments. The results are plotted in Figure 3. Four conclusions can be drawn: i) superior solvent power of highly aromatic oil in ENR 25 and ENR 50. The swelling degrees

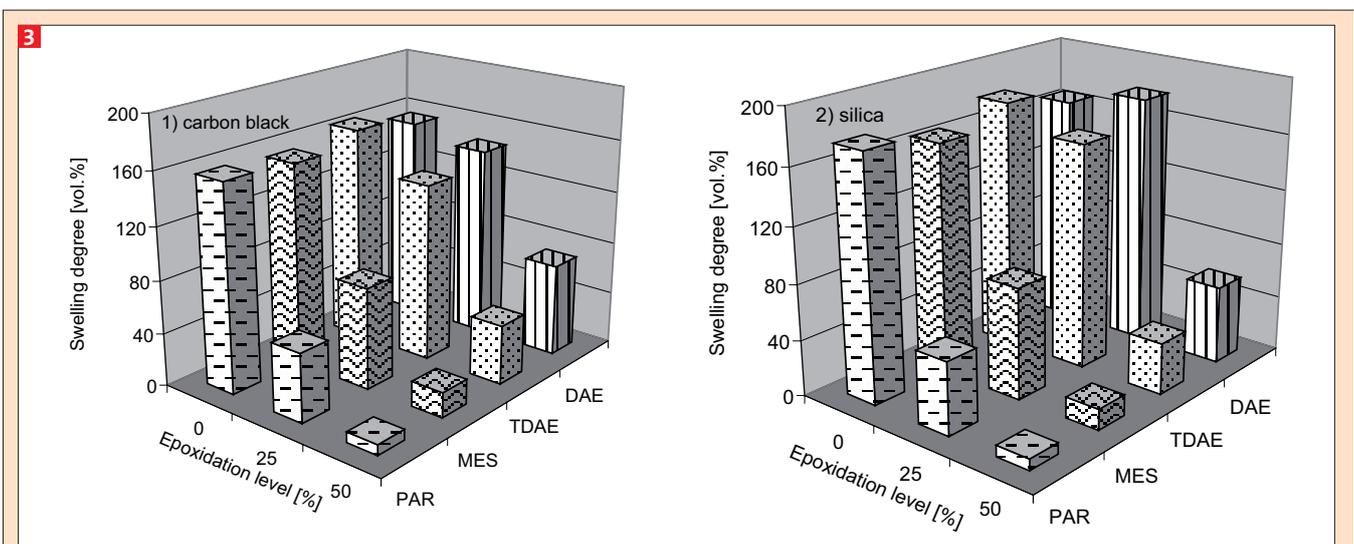


Fig. 3: Swelling degree as a function of epoxidation level at 100 °C: 1) carbon black, 2) silica

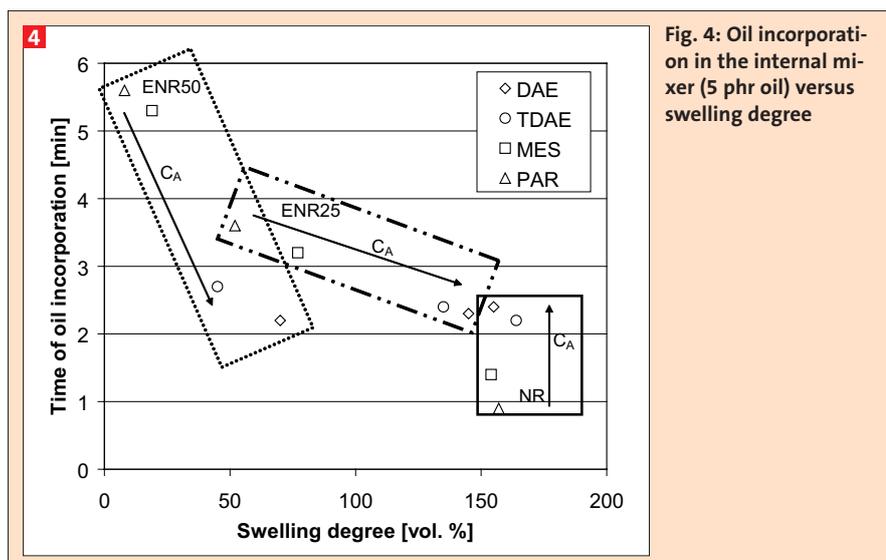


Fig. 4: Oil incorporation in the internal mixer (5 phr oil) versus swelling degree

of aromaticity were added to NR and ENR mixes.

Figure 5 displays the Mooney viscosities (ML (1+4), 100 °C) for (1) carbon black and (2) silica unfilled and filled compounds as a function of epoxidation degree. ENR does not need to be pre-mixed because of its higher breakdown rate compared to NR, which is pre-masticated before adding the other ingredients. Following ML were measured, 30 MU for NR, 31 MU for ENR 25 and 26 MU for ENR 50. By the addition of the filler a drastic increase in ML was noted. The polar surface of the silica is expected to show better wettability for the polar ENR polymers, and less for the nonpolar NR. The OH groups present on the surface of the silica lead to the formation of strong hydrogen bonds. These groups can react with the epoxide groups in ENR or by themselves enabling the filler to agglomerate. ENR 50 silica compounds displayed higher ML (110 MU - result not shown in Figure 5, 2) than ENR 25 (70 MU). NR matrix with silica-silane showed the lowest ML (65 MU). When silica filler was replaced by carbon black, ENR 25 and ENR 50 revealed similar Mooney viscosities (80 MU and 78 MU respectively), which were considerably higher than NR (64 MU).

By the addition of plasticizers, the ML decreases considerably for all compounds as a result of the plasticising effect of the oils. For black mixes reductions in viscosity of about 30% for NR and of about 50% for ENR were noticed. A comparison between all three polymers revealed almost the same Mooney viscosities for NR, ENR 25 and ENR 50 if contained DAE and TDAE and a moderate drop in ML especially for ENR 25 and ENR 50 if PAR and MES oils were used. This

of plasticizers in both polymers increased in the sequence: PAR < MES < TDAE < DAE; ii) Greater solubility of all oils in NR if compared with the ENR compounds. The lower oil swelling degrees in ENR mixes can be attributed to the bulkier epoxide groups which reduce the mobility of the rubber molecules and accordingly reduce the interaction between the polymer and plasticizers. Comparable swelling degrees were measured in NR: PAR ≈ MES ≈ TDAE ≈ DAE; iii) the swelling degree is a function of the Tg of the rubber and iv) the filler does not influence the absorption of mineral oils in NR and ENR.

The relationship between the swelling degree and the oil incorporation time into the rubber matrix is graphically presented in Figure 4. The experimental results show that the time of incorporation of plasticizers into epoxidized natural rubbers is shorter if the aromatic content in the oil increases. This is associated

with a great compatibility of DAE and TDAE with polar ENR rubbers. On the opposite side, paraffin-rich oils demonstrated a marked effect on the time of incorporation. Namely, longer times were assessed for PAR followed by MES. In natural rubber, the incorporation times of the plasticizers varied moderately, the shortest time was registered for PAR and the longest time was measured for DAE. Enhancing the oil amount (15 phr), the time needed to incorporate the plasticizers becomes longer, but the same tendency as stated above was observed.

Processability

Aside from the influence of plasticizers on the phase compatibility and the low temperature properties of the polymers, the impact of the oils on the processability during mixing is relevant for obtaining high quality compounds with low viscosity and power consumption. Petroleum derived softeners of varying degree

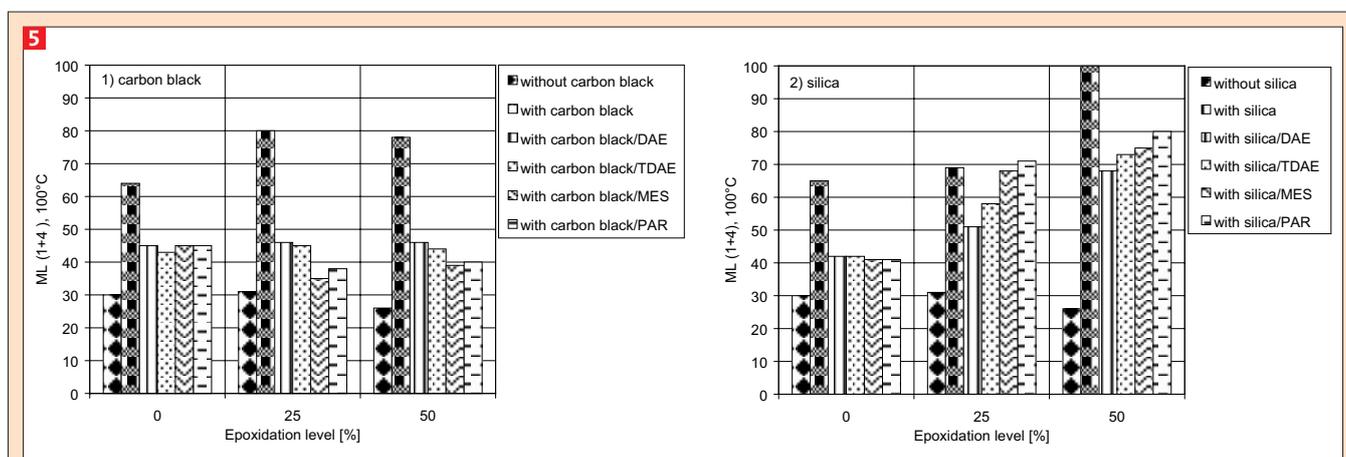


Fig. 5: Influence of type of filler and oil (15 phr) on Mooney viscosity: 1) carbon black, 2) silica

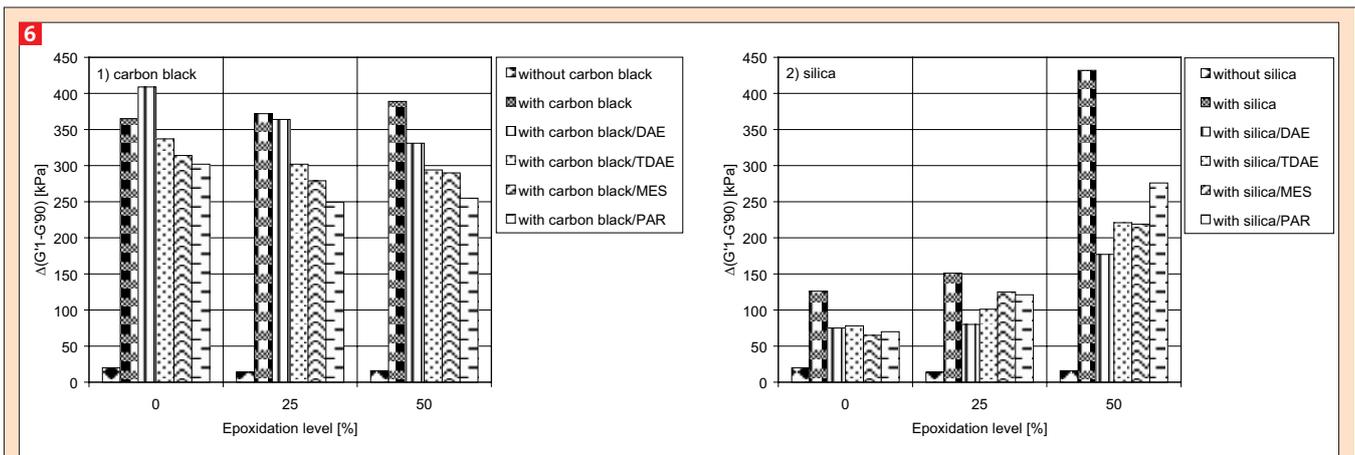


Fig. 6: Influence of type of oil (15 phr) on Payne effect: 1) carbon black, 2) silica

can be explained by the poor compatibility of PAR and MES with the polar polymers ENR, the oils acting more as lubricants than as plasticizers.

By changing the filler, the effect of the plasticizers on the Mooney viscosity of the silica compounds is well noticeable in ENR and less in NR. For ENR 25 and ENR 50, the ML showed the following course: PAR > MES > TDAE > DAE. However, the influence of DAE in epoxidized natural rubbers is remarkable. DAE drops the ML by 28% for ENR 25 and 15% for

ENR 50 if compared to the performance of paraffinic oil. The results highlight the good plasticizing efficiency of DAE and TDAE in ENR polymers compared to the MES and PAR.

In view of filler-polymer interaction, strain sweep measurements were performed in order to study the influence of the type of oil on the Payne effect (Figure 6). The Payne effect is defined as the elastic modulus (G') which decreases with increasing the strain amplitude [$\Delta(G' - G'_{90})$]. The higher the difference in G' bet-

ween the low and high strain ($\Delta(G' - G'_{90})$), the better the filler-filler interaction and the worse the filler dispersion.

In absence of filler, the difference in elastic moduli was very low (around 20 kPa), comparable for all mixes. By the addition of both fillers, the Payne effect became higher and increased by increasing the polarity of the polymer. For carbon black was measured 365 kPa for NR, 372 kPa for ENR 25 and 389 kPa for ENR 50. In the case of silica, the following values were found: 2000 kPa for NR silica

5 Cure characteristics

1) carbon black

Properties	Polymer	Oil [phr]			DAE [phr]			TDAE [phr]			MES [phr]			PAR [phr]		
		0	5	10	15	5	10	15	5	10	15	5	10	15		
$S_{max} - S_{min}$ [Nm]	NR	2.0	1.9	1.7	1.6	1.9	1.7	1.6	1.9	1.8	1.6	1.9	1.7	1.6		
	ENR25	2.2	2.0	1.8	1.6	2.0	1.8	1.6	2.0	1.8	1.6	2.0	1.8	1.6		
	ENR 50	2.3	2.0	1.8	1.6	2.0	1.9	1.7	2.0	1.8	1.7	2.0	1.9	1.7		
t_{s2} [min] ^{d)}	NR	4.2	4.4	4.8	5.2	4.5	4.9	5.3	4.5	4.8	5.2	4.5	4.8	5.2		
	ENR25	3.0	3.2	3.5	3.7	3.4	3.6	3.9	3.2	3.5	3.8	3.4	3.7	4.0		
	ENR 50	3.1	3.7	3.3	3.8	3.7	3.6	4.1	3.6	3.7	4.0	3.3	3.5	4.2		
CRI [min ⁻¹] ^{e)}	NR	20.4	23.3	23.7	24.6	22.0	22.5	22.9	21.6	22.1	17.3	21.6	21.9	16.7		
	ENR25	36.8	36.8	37.0	37.2	35.7	35.5	35.0	35.8	36.0	29.1	34.8	33.7	27.1		
	ENR 50	23.9	28.2	28.4	28.7	27.2	26.2	26.0	26.8	26.3	25.0	26.6	25.8	25.3		

d) Scorch time, e) Cure rate index ($100/(t_{90} - t_{s2})$) [43]

2) silica

Properties	Polymer	Oil [phr]			DAE [phr]			TDAE [phr]			MES [phr]			PAR [phr]		
		0	5	10	15	5	10	15	5	10	15	5	10	15		
$S_{max} - S_{min}$ [Nm]	NR	2.4	2.1	1.8	1.6	2.1	1.9	1.7	2.0	1.9	1.6	1.9	1.9	1.6		
	ENR25	1.9	1.7	1.6	1.5	1.7	1.7	1.5	1.7	1.5	1.5	1.6	1.3	1.3		
	ENR 50	2.8	2.3	2.1	2.0	2.3	2.2	2.0	2.3	2.1	1.9	2.4	2.2	1.8		
t_{s2} [min] ^{d)}	NR	4.8	5.8	6.9	7.5	5.7	6.8	7.7	6.0	7.1	8.0	6.5	6.5	7.8		
	ENR25	8.1	8.8	9.2	10.6	9.0	8.8	10.0	8.5	9.1	9.2	6.2	7.5	7.2		
	ENR 50	3.1	3.9	4.2	4.9	4.0	4.6	5.1	4.0	4.9	5.3	3.8	4.4	5.0		
CRI [min ⁻¹] ^{e)}	NR	11.5	14.6	14.1	15.2	14.5	13.8	13.8	15.2	14.4	15.6	15.0	14.9	14.6		
	ENR25	10.4	12.3	12.5	14.2	12.9	10.4	11.8	12.7	11.6	10.5	9.7	10.0	10.4		
	ENR 50	16.5	17.5	17.0	16.6	17.3	16.3	16.0	18.2	15.6	16.6	16.9	14.9	13.8		

d) Scorch time, e) Cure rate index ($100/(t_{90} - t_{s2})$) [43]

(result not shown in Figure 6, 2), 95 kPa for NR silica-silane, 220 kPa for ENR 25 silica and 398 kPa for ENR 50 silica. The absence of the coupling agent in NR and ENR silica compounds leads to strong filler-filler interactions which lead to silica flocculation and therefore the hardening of the material reflected in higher ML.

Additional changes in the Payne effect were recorded by mixing the plasticizer into the compounds. For the black mixtures, a lowering of $\Delta(G'1 - G'90)$ by extending the epoxide amount in NR was monitored, while $\Delta(G'1 - G'90)$ was improved by decreasing the aromatic content of the oil. This behaviour may be explained by the poor compatibility of paraffinic oils with the polar ENR polymers. The PAR and MES oils reduced the polymer-filler interaction by adsorption of the oil on the carbon black surface, resulting in compounds with lower viscosity as before shown. Another trend could be noticed for the silica compounds. The Payne effect improved with enhancing the aromatic content of the oil and worsens with increasing the epoxide units in NR. In NR silica-silane compounds, the Payne effect remains practically unchanged by varying the aromatic content of the oil. In ENR, the polymer-filler interaction is promoted by the DAE and depressed by the PAR oil. TDAE and MES displayed values in between the DAE and PAR oils.

Cure characteristics

Table 5 shows the effect of loading and structure of oils on several vulcanisation parameters, like Δ torque ($S_{max} - S_{min}$), scorch time (t_{s2}) and cure rate index (CRI) for NR and ENR filled carbon black (Table 5, 1) and silica (Table 5, 2) compounds.

Generally, a drop in Δ torque for both filled rubbers was noticed by adding plasticizers up to 15 phr. For the carbon black systems extended with DAE, TDAE, MES and PAR, the maximum change in torque was comparable for all NR and ENR mixtures and decreased up to 20% and around 27%, respectively. For the silica systems it could be seen that the PAR oil exhibited the highest reduction in Δ torque around 32% for ENR 25, and almost 36% for ENR 50, followed by the MES with 21% for ENR 25 and 32% for ENR 50. DAE and TDAE showed the same performance in ENR 25 and ENR 50 with 21% and 28% losses. This implies that the DAE and TDAE contribute to higher crosslinking efficiency than the MES and PAR plasticisers.

Dependent on the rubber type, the torque differences exhibited higher values for ENR 50 matrix than those obtained for ENR 25 and NR, which is explained by the chemical structure of the polymer that lead to different network structures. For carbon black mixtures, the Δ torque shows similar values, unlike for silica compounds where the Δ torque is signifi-

cantly higher due to the contribution of the reinforcing effect of the silica filler.

The scorch time, known as t_{s2} , gives an indication of the time needed until the cross-linking process starts. Higher loading levels of oil prolonged the scorch times for both filled systems when compared to the non-oil extended compound, as a result of the plasticizing effect. At high oil content in black compounds (e.g. 15 phr oil), DAE extended the t_{s2} in ENR 50 with 22% while PAR prolonged significantly the t_{s2} with 35%. For ENR 25, the enhancement in t_{s2} is rather analogous. The lowest changes in t_{s2} were recorded for NR and are comparable for all types of oil plasticizers. For the silica systems, extensive t_{s2} were acquired by increasing the oil concentration.

At low oil concentration (e.g. 5 phr) the t_{s2} is practically not affected for NR, ENR 25 and ENR 50 black compounds as well as for ENR 50 silica mixes by increasing the aromatic content of the oil. For NR silica-silane mixes, the t_{s2} shortened by the incorporation of plasticizer with increased aromatic structures. It can be concluded that, DAE and TDAE can accelerate the vulcanization adjacent to the curing agents, which might be due to the heterocyclic components present in those oils. In view of the curing process of the epoxidized rubbers, these heterocyclic compounds may also participate besi-

6 Dynamic mechanical properties															
1) carbon black															
Properties	Polymer	Oil [phr]	DAE				TDAE			MES			PAR		
		0	5	10	15	5	10	15	5	10	15	5	10	15	
Rolling resistance															
Tan Delta Max at 60 °C	NR	0.157	0.150	0.150	0.169	0.144	0.140	0.144	0.139	0.140	0.139	0.135	0.132	0.134	
	ENR 25	0.164	0.167	0.179	0.188	0.167	0.167	0.182	0.182	0.183	0.170	0.170	0.169	0.163	
	ENR 50	0.216	0.240	0.232	0.238	0.236	0.210	0.231	0.233	0.220	0.236	0.230	0.224	0.228	
Wet grip															
Tan Delta Max at 0 °C	NR	0.196	0.211	0.230	0.233	0.202	0.214	0.205	0.193	0.208	0.196	0.205	0.202	0.191	
	ENR 25	0.296	0.322	0.322	0.340	0.312	0.316	0.318	0.307	0.306	0.318	0.298	0.292	0.300	
	ENR 50	0.823	0.888	0.853	0.825	0.888	0.886	0.883	0.808	0.801	0.778	0.859	0.831	0.868	
2) silica															
Properties	Polymer	Oil [phr]	DAE				TDAE			MES			PAR		
		0	5	10	15	5	10	15	5	10	15	5	10	15	
Rolling resistance															
Tan Delta Max at 60 °C	NR	0.094	0.086	0.083	0.076	0.085	0.080	0.078	0.090	0.091	0.080	0.093	0.083	0.084	
	ENR 25	0.110	0.110	0.100	0.090	0.110	0.110	0.100	0.110	0.110	0.110	0.110	0.110	0.110	
	ENR 50	0.100	0.100	0.100	0.090	0.100	0.090	0.090	0.110	0.100	0.090	0.100	0.100	0.100	
Wet grip															
Tan Delta Max at 0 °C	NR	0.146	0.152	0.150	0.147	0.168	0.167	0.140	0.140	0.146	0.142	0.144	0.146	0.142	
	ENR 25	0.240	0.250	0.240	0.250	0.250	0.230	0.230	0.210	0.220	0.230	0.230	0.220	0.220	
	ENR 50	1.100	1.130	1.120	1.000	1.100	1.030	0.987	1.052	0.955	0.950	0.971	0.962	0.990	

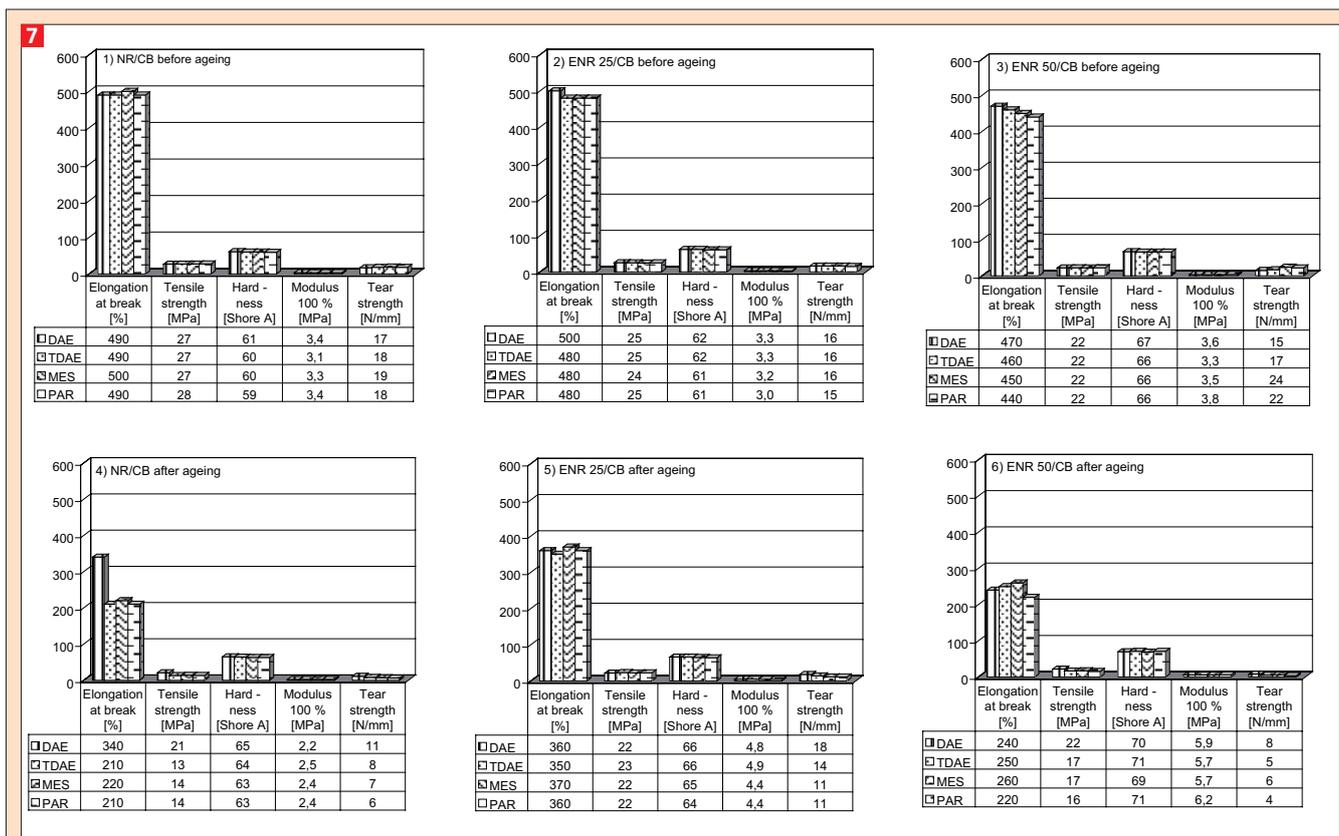


Fig. 7: Influence of type of oil (15 phr oil) on physical properties before and after ageing 72 h at 100 °C of carbon black compounds

de the vulcanizing system in the vulcanization of ENR by ring opening through the reaction with the nitrogen based components. This may explain the longer t_{s2} for ENR 25 silica compounds with DAE and TDAE if compared with ENR 50.

Finally the cure rate index was studied. This parameter changed by varying the concentration and the type of the plasticizers and the chemical structure of the polymer. Generally, it was seen that DAE and TDAE accelerated the vulcanisation reaction at higher levels than MES and PAR. Increasing the oil loading, a drastic deactivation of the CRI especially for PAR and MES was noted because of an increase of the optimum cure time (t_{90}), which suggests a poor compatibility of the oils with the polymer matrix.

Dynamic mechanical properties

Table 6 shows the comparison between two key parameters often used in the tire industry to predict compound performance, rolling resistance and wet grip. Lower $\tan \delta$ at 60 °C is translated in lower rolling resistance and higher $\tan \delta$ at 0 °C is indicative of better wet grip. Aside from the ENR 25 and ENR 50 silica systems, which showed comparable rolling

resistance, all oil extended and non-extended compounds displayed increased $\tan \delta$ at 60 °C and at 0 °C with increasing epoxide content in NR compounds. Thus, the best rolling resistance was accomplished by using natural rubber and the best wet grip was reached by employing epoxidized natural rubber.

As oil was added to the NR black compounds, the rolling resistance improved with reducing the glass transition of the plasticizers. At 5 phr oil, the paraffinic oil demonstrated the lowest $\tan \delta$ at 60 °C, which means 14% improvement in rolling resistance. The other oils upgraded the $\tan \delta$ at 60 °C at lower levels, MES with 11%, TDAE with 8% and DAE with 4%. At higher levels of plasticizers, e.g. 15 phr, $\tan \delta$ at 60 °C was not further improved. On the other side, the incorporation of plasticizers in ENR black compounds resulted in no major improvement of the rolling resistance. As by NR, the influence of glass transition of the oil on the rolling resistance could be also recognized in ENR 25 matrixes. The $\tan \delta$ at 60 °C decreased by the addition of the oils in the sequence: DAE < TDAE < MES < PAR, which is inline with the T_g of these oils. For ENR 50, this property varied not so much.

The $\tan \delta$ at 60 °C of the NR silica-silane compounds is promoted by DAE and TDAE at the same level, independent of the oil concentration. For the silica filled epoxidized natural rubber compounds, the rolling resistance is not influenced by both loading and composition of the oils. With regard to the wet grip, all compounds extended with DAE and TDAE achieved better wet grip than those using MES and PAR.

Physical properties before and after ageing

It was generally noticed that increasing of the oil amount in NR, ENR 25 or ENR 50 carbon black or silica compounds, the elongation increased, the hardness and the modulus at 100% decreased. The changes in physical properties of rubber compounds with different types of oils before and after ageing 72 hours at 100 °C are documented in Figure 7 (carbon black compounds) and Figure 8 (silica compounds).

The results presented in Figure 7 indicate that ENR 25 shows similar physical properties combined with excellent heat resistance for all types of oils to the NR compound with DAE, and superior result, compared to all other compounds. Gene-

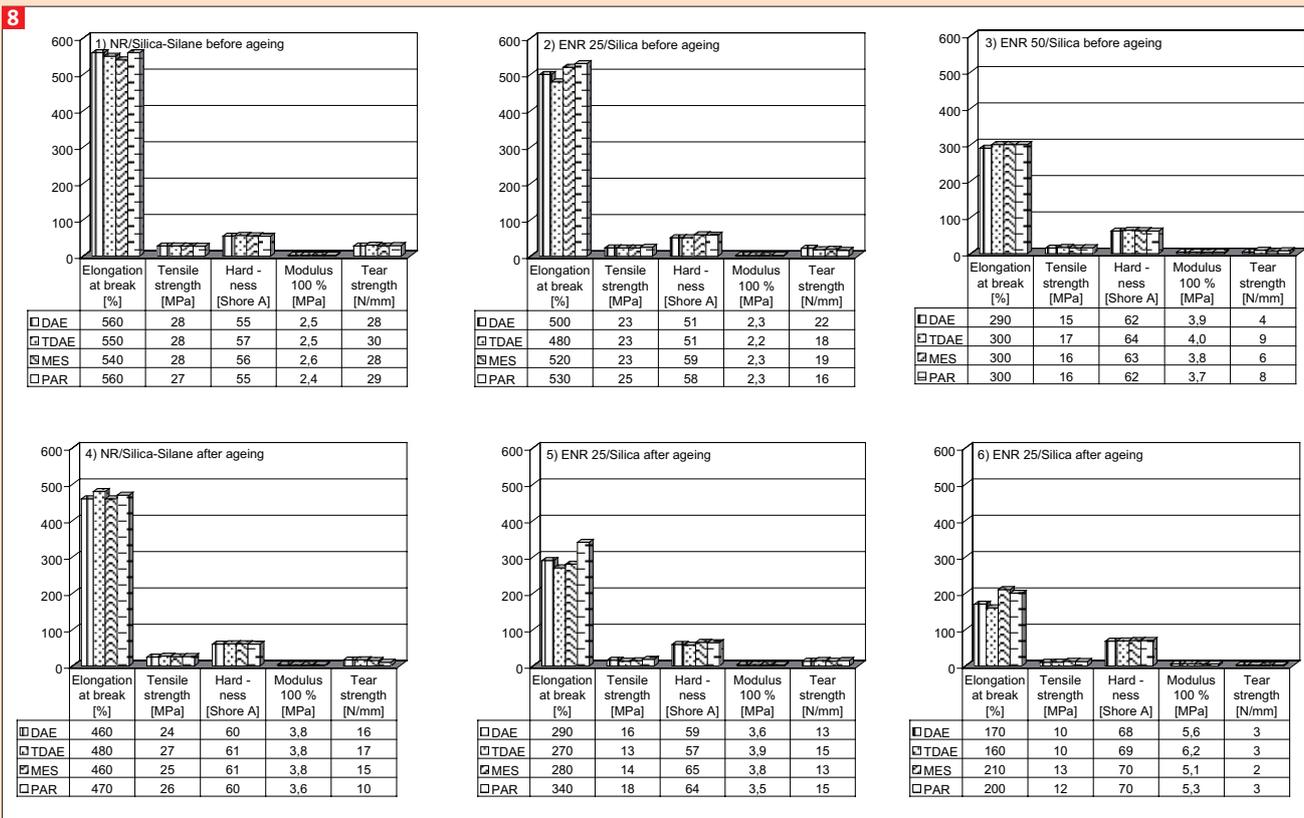


Fig. 8: Influence of type of oil (15 phr oil) on physical properties before and after ageing 72 h at 100 °C of silica compounds

rally, the elongation at break and modulus at 100% were only slightly affected by the variation of the aromatic content of the oil. Both parameters increased marginally with increased aromaticity. Hardness is less influenced by the composition of the oil but is apparently higher for aromatic oils. Before ageing, tensile strength and tear strength were comparable for all compounds. After ageing, enhanced values for both properties were noted when the aromatic oils were used.

Figure 8 highlights the physical properties of the silica oil extended compounds. The elongation at break, tensile strength, the hardness and the modulus at 100% changed marginally by varying the composition of the plasticizers before and after storage in hot air. The comparison of tear strength between the carbon black and silica compounds before and after ageing shows that the filler dispersion and implicates the filler-polymer interaction are the driving forces for this trend in physical properties. The following sequence was recorded: NR silica-silane > ENR 25 silica > ENR 25 carbon black > NR carbon black ≈ ENR 50 carbon black > ENR 50 silica. The results are sustained by the Mooney

viscosity and Payne effect experiments discussed before.

Summary and conclusions

As a response to the legislation debates over the last years, the rubber industry has been forced to substitute the labelled oils due to their carcinogenic potential with unlabelled oils. Several rubber processing oils can be seen as replacement for DAE, like TDAE, NAP and MES. The performance of those alternative plasticizers in NR and ENR compounds was evaluated in this work.

The correlation between the time of oil incorporation and the swelling degrees demonstrated that plasticizers with more similar solubility parameter values to the rubbers were faster incorporated (DAE > TDAE > MES > PAR in ENR and DAE < TDAE < MES < PAR in NR) and absorbed in higher amount into the rubber matrixes. In NR, all plasticizers showed the same solvency power, while in ENR the following sequence was obtained: DAE > TDAE > MES > PAR.

The strain sweep measurements evidenced, that DAE oil promotes the filler-polymer interaction in silica based compounds due to a strong interaction of the oil with the polymer which implies a

good compatibility of this plasticizer with the rubber matrix. In carbon black compounds, PAR oil reduced the polymer-filler interaction by adsorption of the oil on the carbon black surface, resulting in compounds with lower viscosity. The oil is acting here more as a lubricant than as plasticizer in ENR systems.

The changes in cure characteristics were more pronounced for silica compounds than for carbon black by the addition of plasticizers with different polarity, especially for epoxidized natural rubbers. Increasing the oil content, the Δ torque ($S_{max} - S_{min}$) decreased, scorch time (t_{s2}) enhanced and cure rate index (CRI) decreased due to the plasticising effect. DAE and TDAE accelerated the vulcanisation reaction and displayed higher cure rate indexes than the extended rubber compounds with MES and PAR. This might be due to the heterocyclic components present in those oils which can accelerate the vulcanization adjacent to the curing agents.

With respect to the chemical structure, the investigated polymers exhibited different dynamic properties. NR crystallises under strain and has very low hysteresis providing a good rolling resistance. Through epoxidation of NR,

the glass transition increases and the ability to strain crystallise is reduced, which affects the dynamic properties of ENR.

Both filled natural rubber compounds are most sensitive to the changes of the plasticizer on the rolling resistance. The $\tan \delta$ at 60 °C decreased by the addition of the oils in the sequence: DAE < TDAE < MES < PAR, which is inline with the Tg of these oils. With regard to the wet grip, all compounds extended with DAE and TDAE achieved better wet grip than those using MES and PAR. The effect of the oils on both properties in the ENR compounds was lower.

Slightly lower levels of physical properties (e. g. elongation, tensile and tear strength) of MES and PAR extended compounds compared to the TDAE and DAE mixes were measured due to lower contents of polar and aromatic components in these oils.

The overall conclusion is that TDAE demonstrated similar or even equal results to DAE in NR and ENR filled compounds, which indicates that this oil is a suitable substitute for the classified DAE.

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