Petroleum-based Safe Process Oils: From Solubility Aspects to Practical Use in Carbon Black-Reinforced Rubber Compounds

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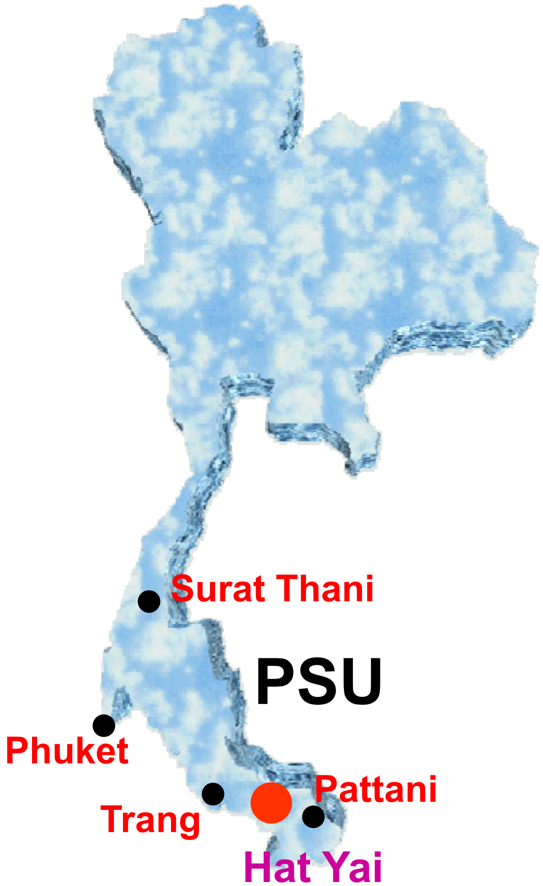
Talk outline

- **Introduction: PAHs and safe rubber process oils**
- **TDAE and MES safe process oils in a replacement of highly aromatic DAE oil**
    - **Solubility aspects**
    - **Their influence on unfilled rubber compounds**
    - **Their influence on practical carbon black-filled compounds**
- **Summary**



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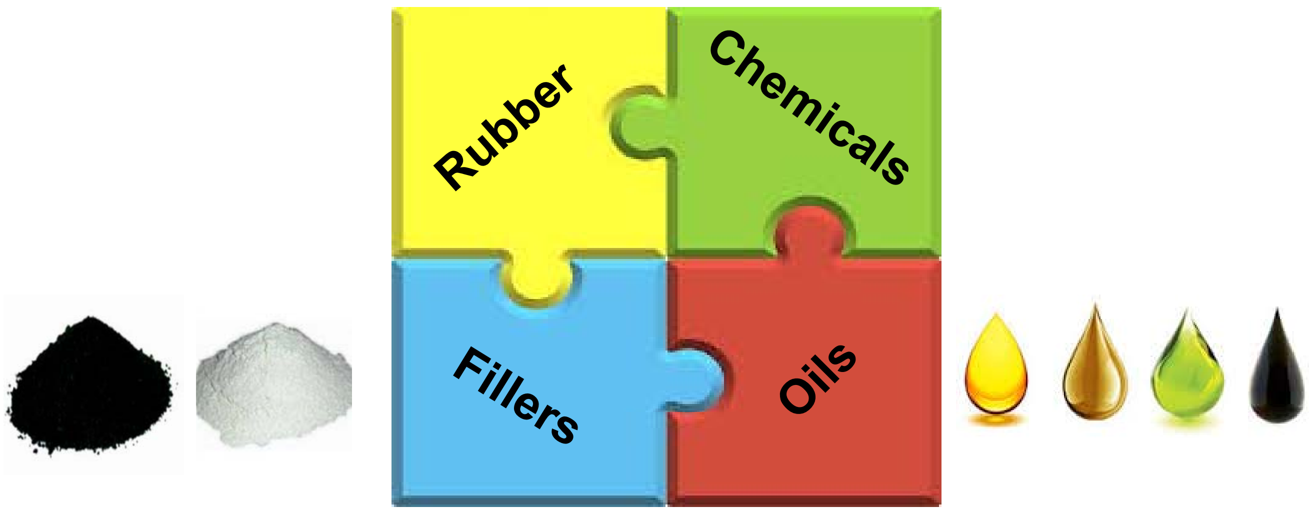
Rubber process oils

Rubber process oils are added in the compounds to improve processing properties, low temperature flexibility, dispersion of fillers, and to reduce cost.

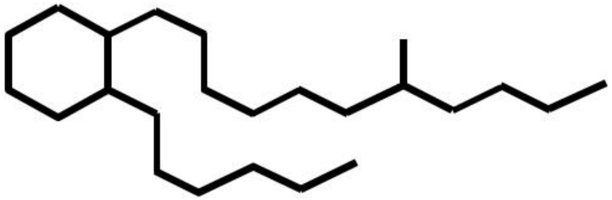
3 Basic types: aromatic, naphthenic and paraffinic.

The conventional oils commonly used in tire compounds are Highly Aromatic (HA) oils.

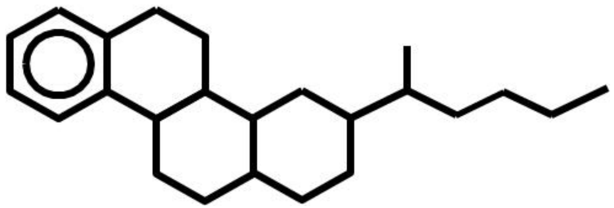


Simplified structures of oils

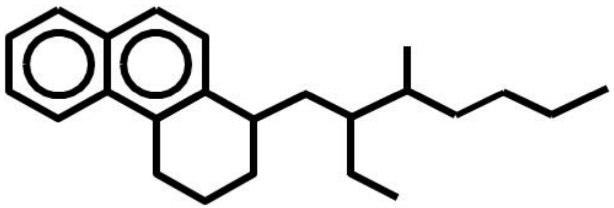
paraffinic

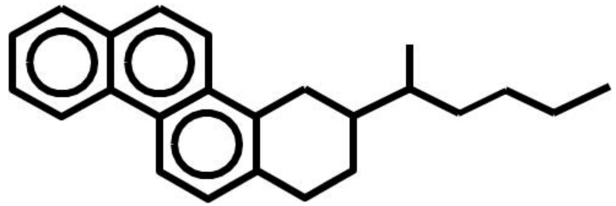


naphthenic

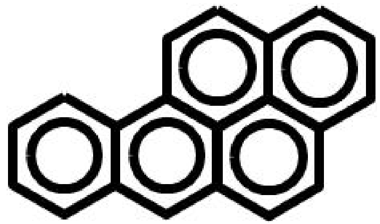


aromatic





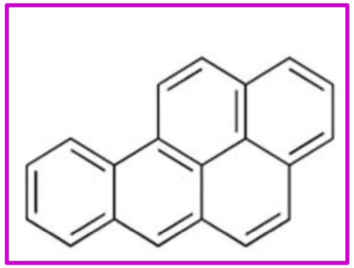
Very aromatic



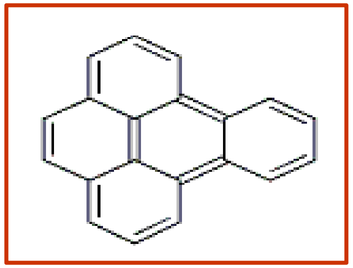
Highly aromatic

PAHs in highly aromatic oils

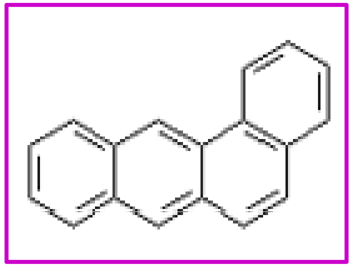
According to EU, 8 of PAHs (Polycyclic aromatic hydrocarbons) have been classified as carcinogens.



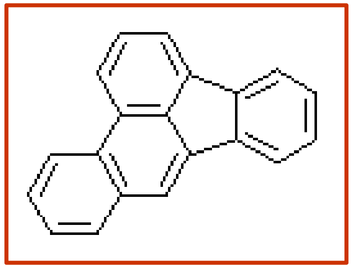
Benzo[a]pyrene (BaP)



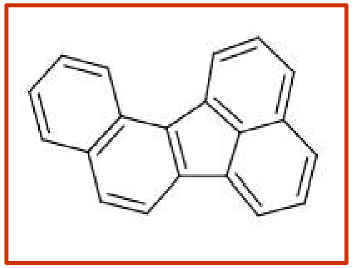
Benzo[e]pyrene (BeP)



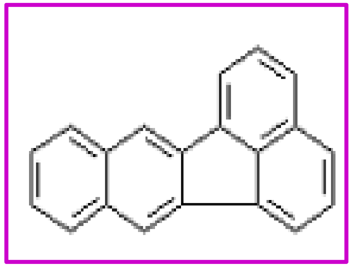
Benzo[a]anthracene (BaA)



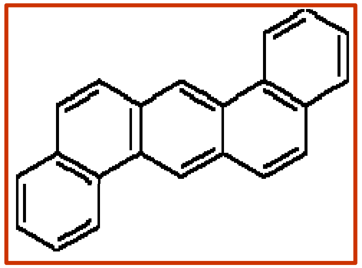
Benzo[b]fluoranthene (BbFA)



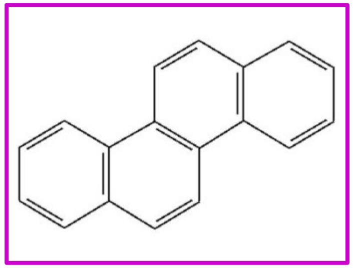
Benzo[j]fluoranthene (BjFA)



Benzo[k]fluoranthene (BkFA)



Dibenzo[a,h]anthracene (DBahA)



Chrysene (CHR)

Regulation (EC) No 552/2009, *Official Journal of the European Union*, **L164**, 25 (2009).

Commission Regulation (EC) No 552/2009:

"From 1 January 2010, extender oils shall not be placed on the market, or used for the production of tyres or parts of tyres if they contain:

— more than 1 mg/kg (0,0001 % by weight) BaP, or,

— more than 10 mg/kg (0,001 % by weight) of the sum of all listed PAHs.

These limits shall be regarded as kept, if the polycyclic aromatics (PCA) extract is less than 3 % by weight as measured by the Institute of Petroleum standard IP346"

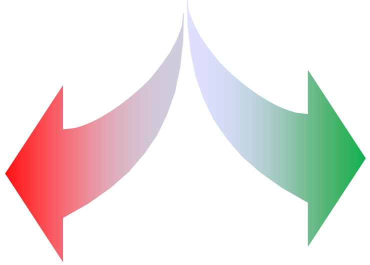
26.6.2009 EN Official Journal of the European Union L 164/7

COMMISSION REGULATION (EC) No 552/2009

of 22 June 2009

amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards Annex XVII

Alternatives for DAE



Mineral oils

- **Treated distillate aromatic extract (TDAE)**
- **Mild extracted solvates (MES)**
- **Naphthenic process oil (NAP)**

Natural oils

- **Epoxidized palm oil (EPO)**
- **Epoxidized soybean oil (ESBO)**
- **Other vegetable based-oils**
- **Natural oil derivatives**

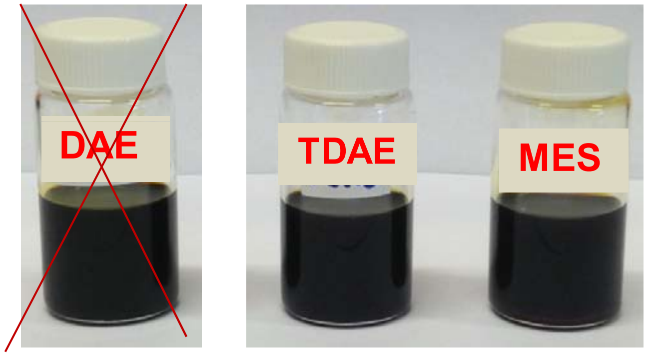
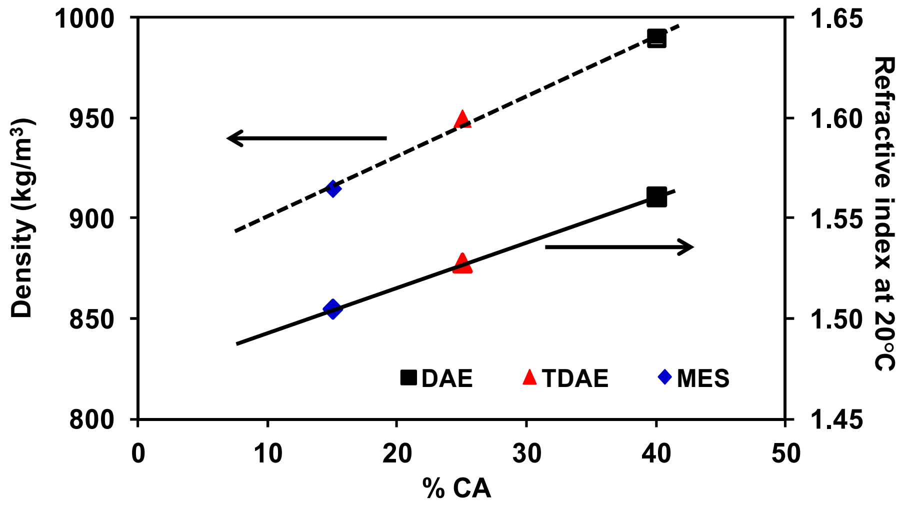
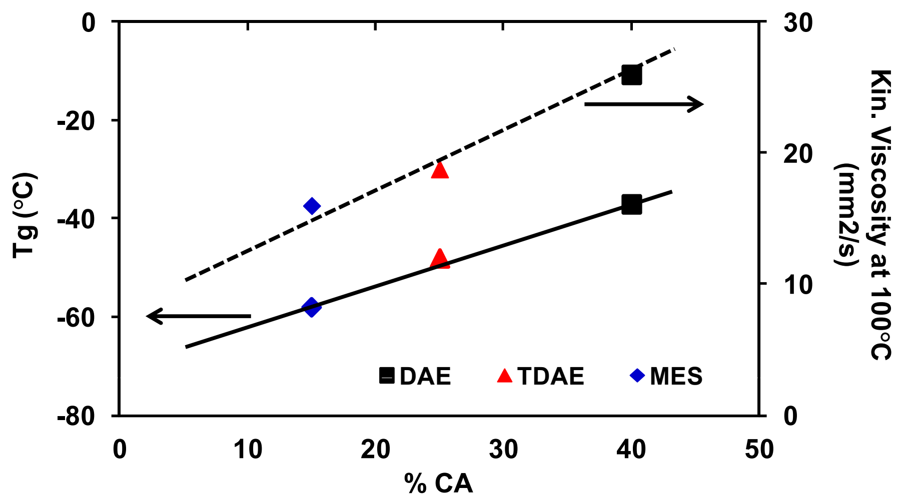


Table 1: Some characteristics of DAE, TDAE and MES oils.

Properties	DAE	TDAE	MES
Density at 20°C, kg/m^3	987	947	912
Kin. Viscosity at 40°C, mm^2/s	1240	410	210
Kin. Viscosity at 100°C, mm^2/s	26.0	18.8	16.0
Sulfur, wt%	1.2	0.8	0.5
Aniline point, °C	41	68	97
C distribution: C_A, wt%	40	25	15
C_N, wt%	25	30	27
C_P, wt%	35	45	58
DMSO extract, wt%	20	<2.9	<2
Tg, °C	-37	-48	-58





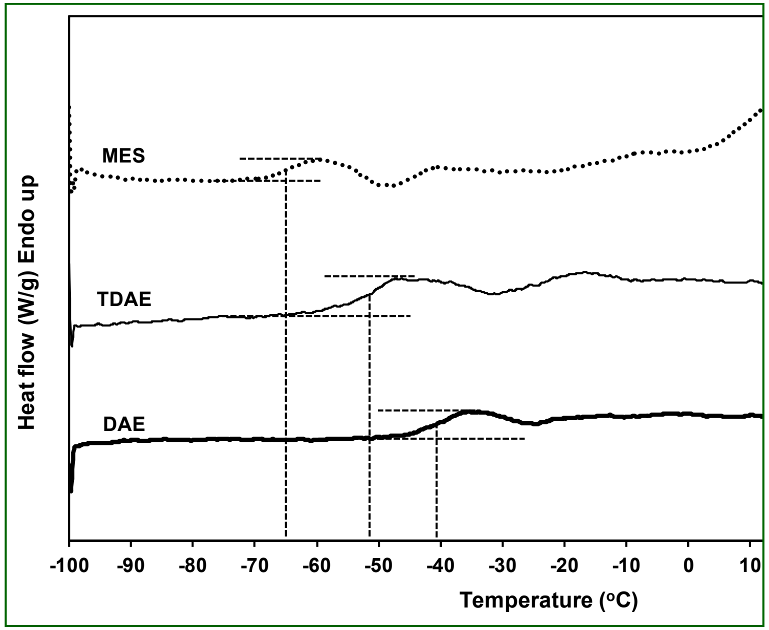


Fig. 1 – Correlations between oil characteristics with C_A content of the process oil.

Solubility parameters (δ) of oils and rubbers

Theoretical prediction of δ based on group contribution method:

$$\delta = \frac{\sum_j F_j}{V}$$

Fj = molar attraction constant for group j
V = unit volume

δ values of DAE, TDAE and MES oils were estimated based on the mol% of methylene, cyclohexane and benzene structural groups, representing paraffinic, naphthenic and aromatic groups, respectively.

Solubility parameters at higher temperature

For oils at the liquid state : $\ln \delta_T = \ln \delta_{298} - 1.25\alpha(T - 298)$

For rubbers above T_g: $\ln \delta_T = \ln \delta_{298} - \alpha(T - 298)$

α= the coefficient of linear thermal expansion of the oils and rubbers

P.A. Small, J. Appl. Chem. **3** (1953) 71; D.W. Van Krevelen, Properties of Polymer, Elsevier, Amsterdam, (2009) 189.
H.G. Weyland, P.J. Hoftyzer and D.W. van Krevelen, Polymer **11** (1970) 79.
J.H. Hildebrand and R.L. Scott. The Solubility of Non-electrolytes, Dover Publications, New York, (1964) 432.
A.N. Gent, Engineering with Rubber: How to Design Rubber Components, Hanser-Verlag, Munich, (2001) 5.

Solubility parameters (δ) of oils and rubbers

Table 2 Calculated solubility parameters (δ) of rubbers and process oils based on molar attraction constant (F)

Rubber and oil type	δ ($J^{1/2}/cm^{3/2}$)			
	25 °C	60 °C	100 °C	140 °C
NR	16.9	16.6	16.3	16.0
SBR	17.5	17.2	16.8	16.5
DAE	17.5	17.0	16.5	15.9
TDAE	17.2	16.7	16.1	15.6
MES	17.1	16.5	15.9	15.3

Table 3 Calculated absolute Δδ of rubbers and process oils ($J^{1/2}/cm^{3/2}$)

	25 °C		60 °C		100 °C		140 °C	
	NR	SBR	NR	SBR	NR	SBR	NR	SBR
DAE	0.6	0	0.4	0.2	0.2	0.3	0.1	0.6
TDAE	0.3	0.3	0.1	0.5	0.2	0.7	0.4	0.9
MES	0.2	0.4	0.1	0.7	0.4	0.9	0.7	1.2

Swelling of rubbers in oils

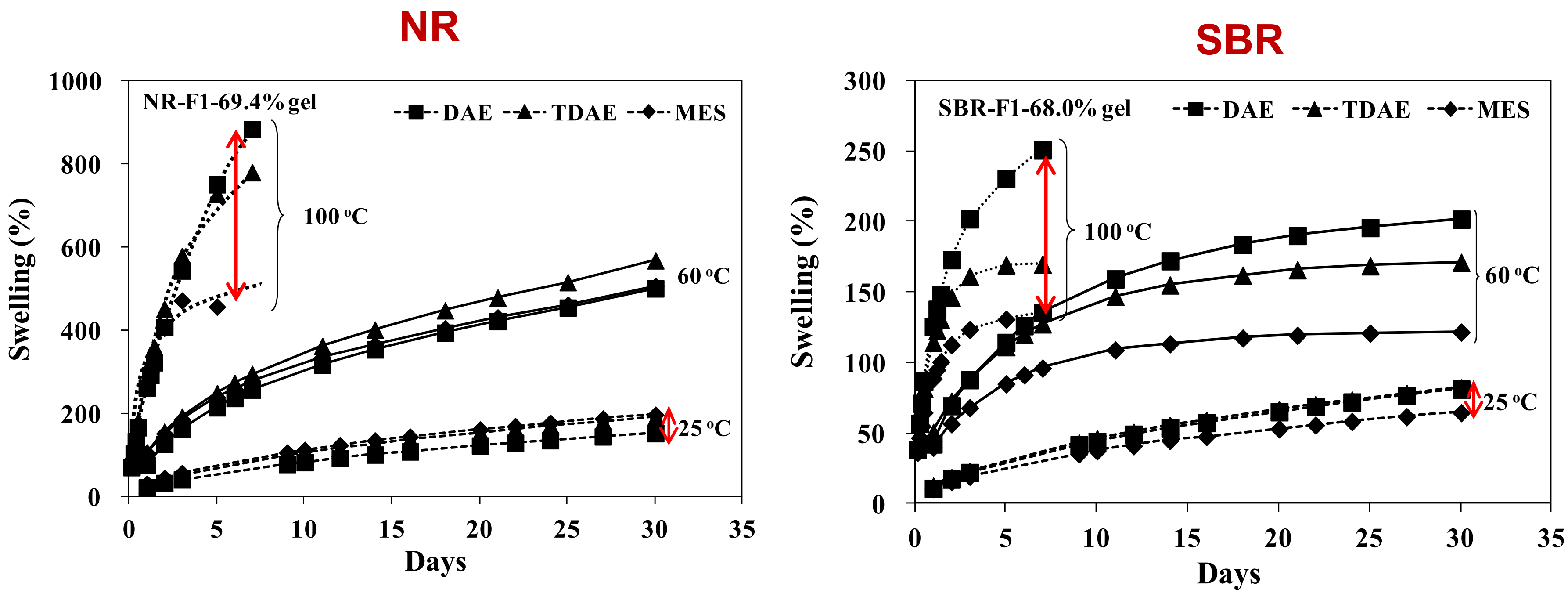


Fig. 2 – Swelling of NR and SBR having gel content ~ 70 % in different oils at 25, 60 and 100°C.

Swelling of rubbers in oils

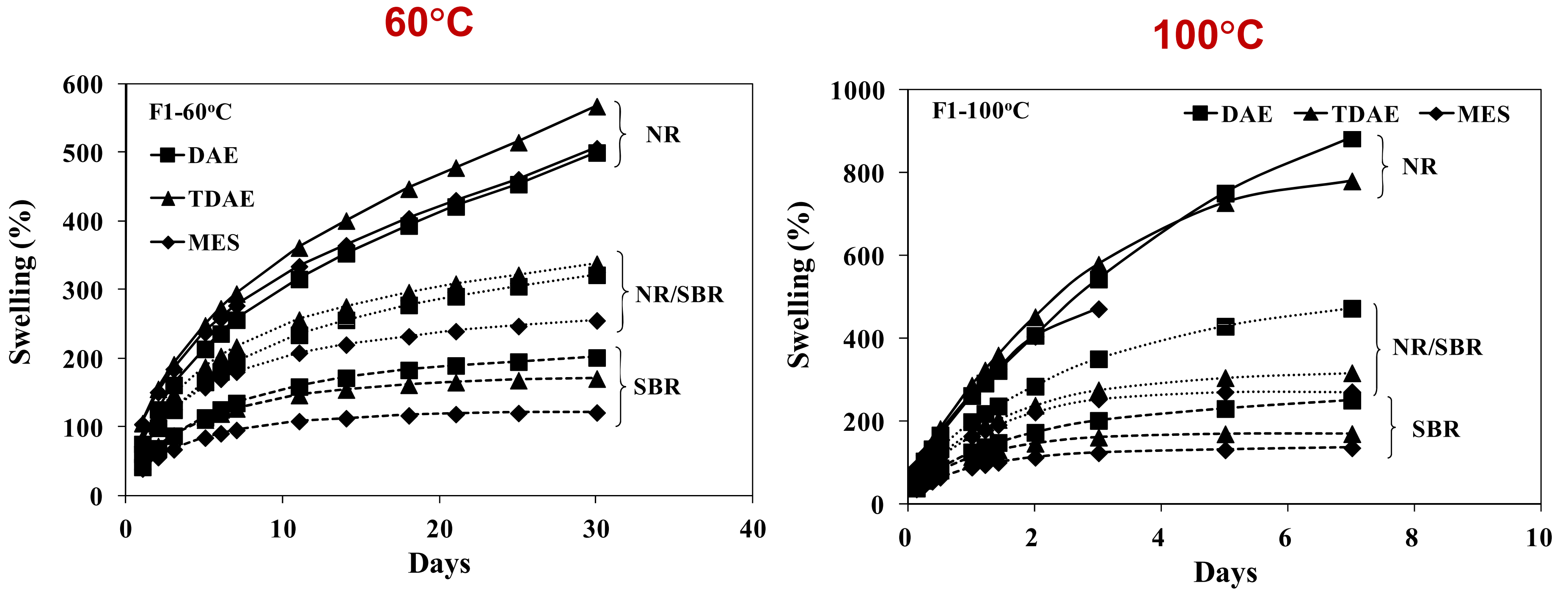


Fig. 3 –Swelling of NR, NR/SBR blend, and SBR (gel contents ~ 70%) in different oils at 60 and 100°C.

Unfilled NR, SBR and NR/SBR compounds

Table 3 Formulations for the compound study.

Ingredients	Amount (phr)		
NR (RSS 3)	100.0	50.0	-
SBR 1502	-	50.0	100.0
Oil	Varying types and loadings		
Zinc oxide	3.0	3.0	3.0
Stearic acid	1.0	1.0	1.0
CBS	1.2	1.2	1.2
DPG	0.3	0.3	0.3
Sulfur	1.5	1.5	1.5

Mixing conditions: Internal mixer (500 cm^3), mixer temperature setting 60°C, rotor speed 60 rpm.

Oil contents were varied from 0, 5, 10, 15 to 20 phr.

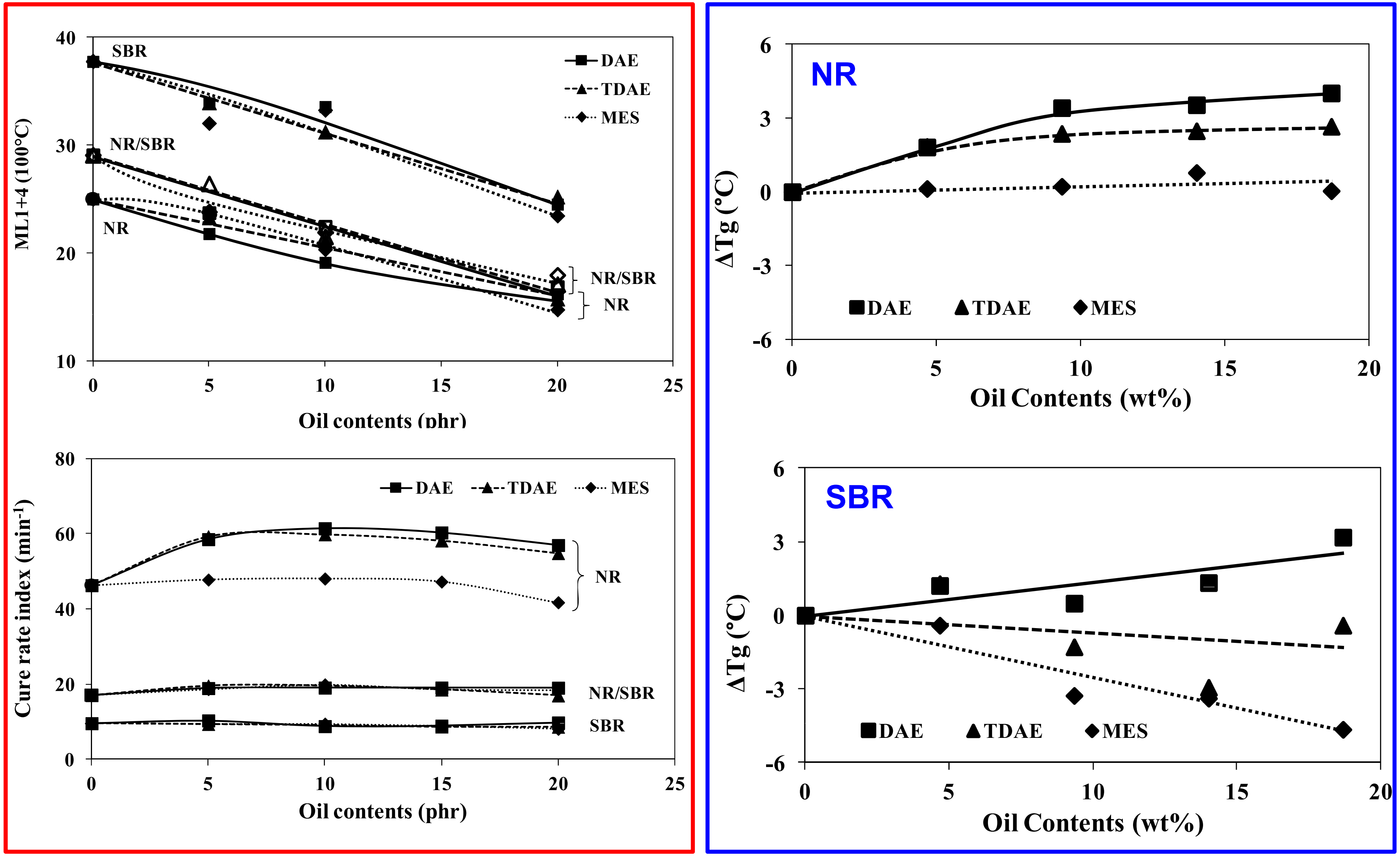
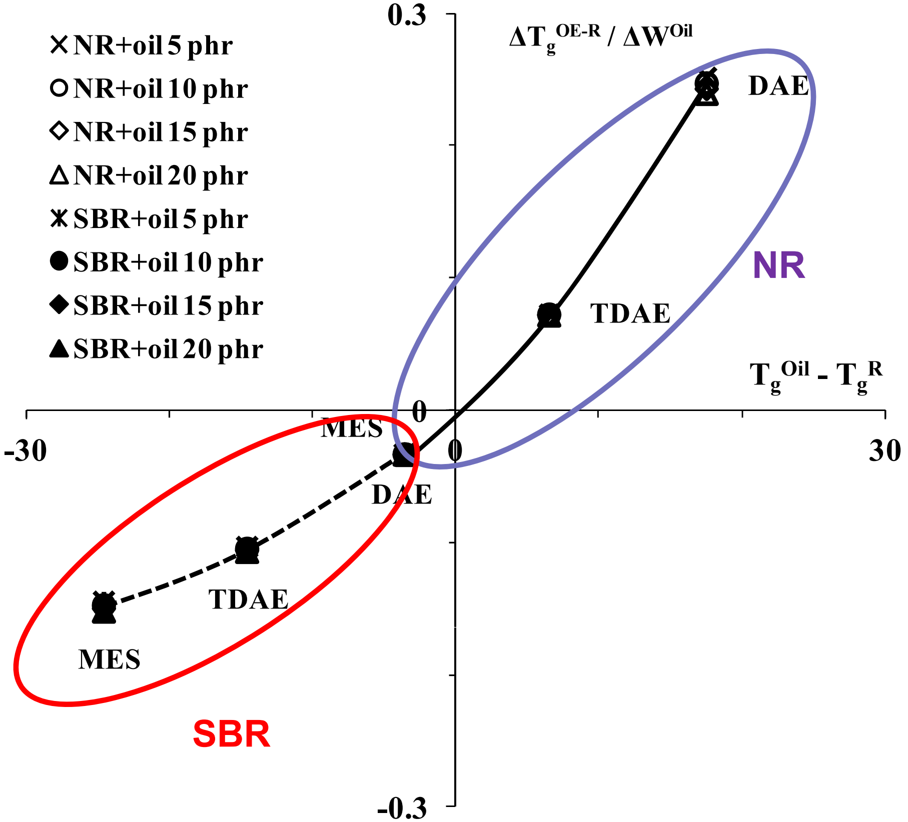


Fig. 4 – Mooney viscosity, cure rate index at 150°C and ΔTg of NR and SBR with different oil types/contents.



T_g of OE-R is calculated from the weight average of the T_g of its components using the inverse rule of mixtures, according to the Fox equation

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

The derivation of Tg with respect to W_{oil} can be used to define a measure for the plasticizer efficiency of the process oil:

$$\frac{\Delta T_g^{OE-R}}{\Delta W_{oil}} = T_g^{oil} - T_g^R$$

Fig. 5 – Shift by weight of the T_g of oil-extended NR and SBR vs. the differences in T_g of the pure components. (Theoretical prediction)

J.R. Fried, "Polymer Science and Technology", Pearson Education Inc., New Jersey, (2003).

Unfilled NR, SBR and NR/SBR compounds

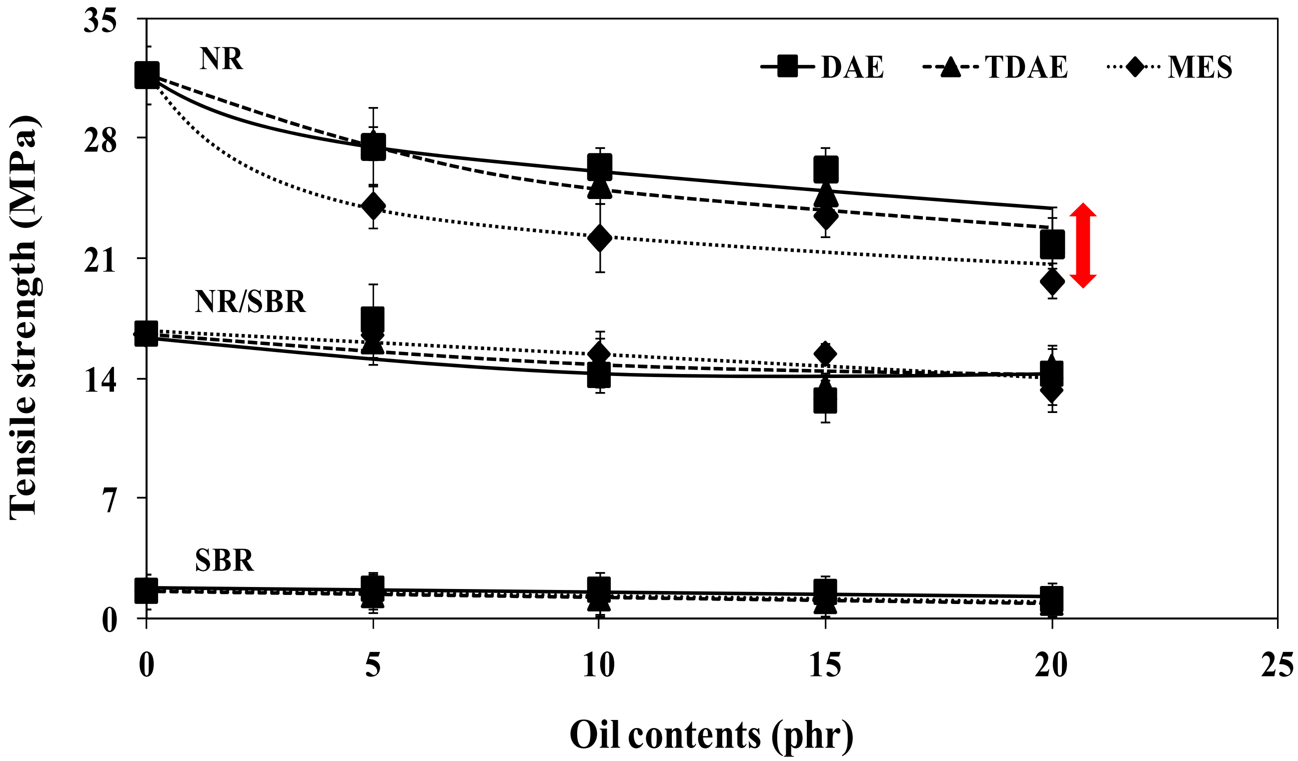


Fig. 6 – Tensile strength of the vulcanizates containing different oil types/contents.

Table 4 Carbon black-filled compound formulations.

Ingredients	Amount (phr)	
NR (RSS 3)	100.0	50.0
SBR (1502)	-	50.0
Carbon black (N330)	60.0	60.0
Oil (DAE, TDAE, MES)	Varying types and loadings	
6PPD	1.5	1.5
TMQ	2.0	2.0
Microcrystalline wax	0.5	0.5
Zinc oxide	3.0	3.0
Stearic acid	1.0	1.0
CBS	1.2	1.2
DPG	0.3	0.3
Sulfur	1.5	1.5

Two step-mixing procedure

1st Step: Mixing of masterbatch in internal mixer (Werner & Pfleiderer GK5E)
- chamber volume 5 L;
- intermeshing rotor system;
- mixer temp.setting 50°C;
- fill factor 0.70;
- rotor speed 40 rpm

2nd step: Addition of curatives on two-roll mill

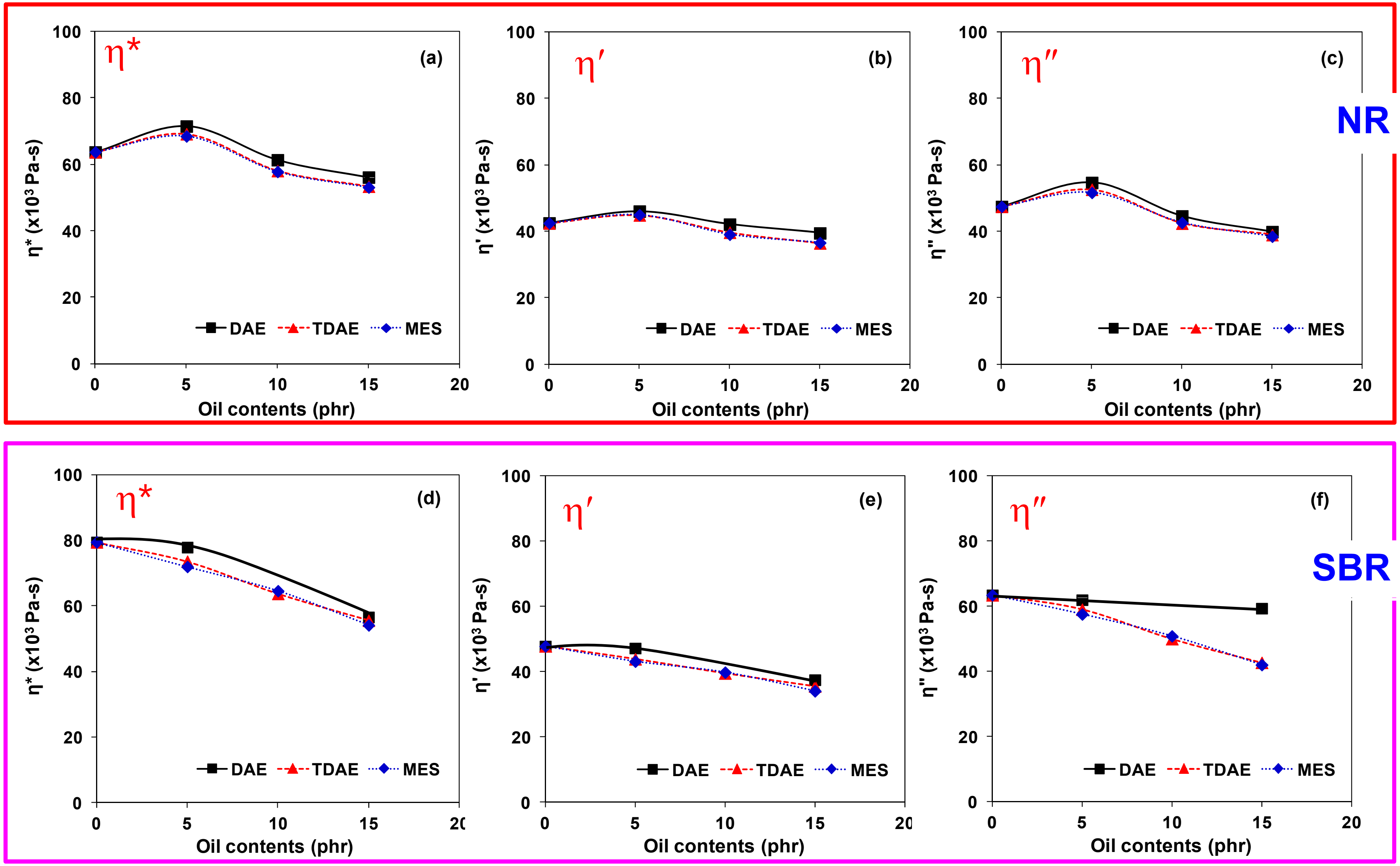
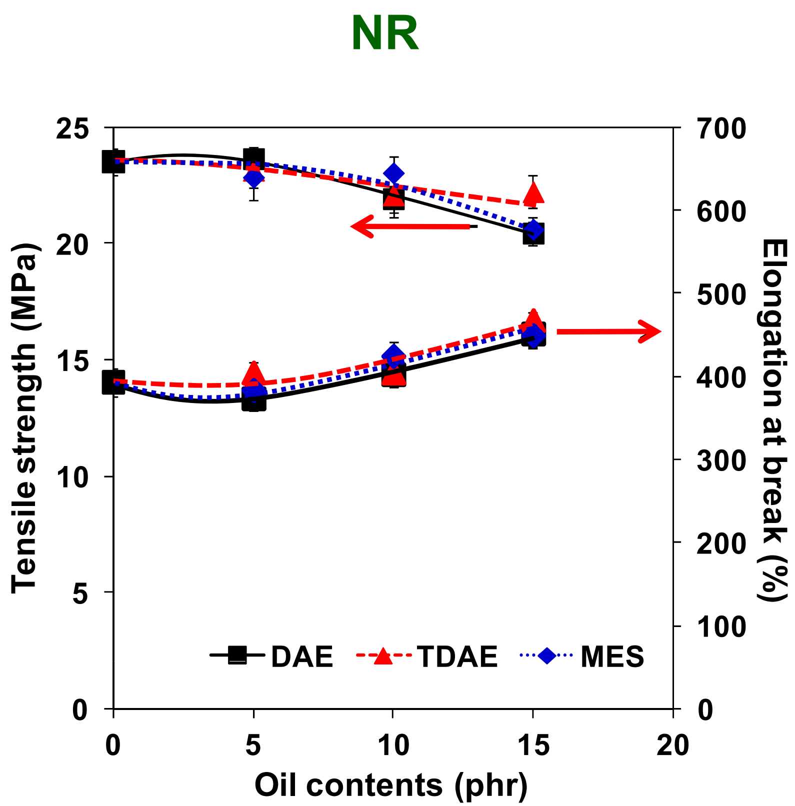


Fig. 7 – Complex viscosities (η*), real (η') and imaginary (η") parts at 0.5 Hz at 7% strain and 100°C



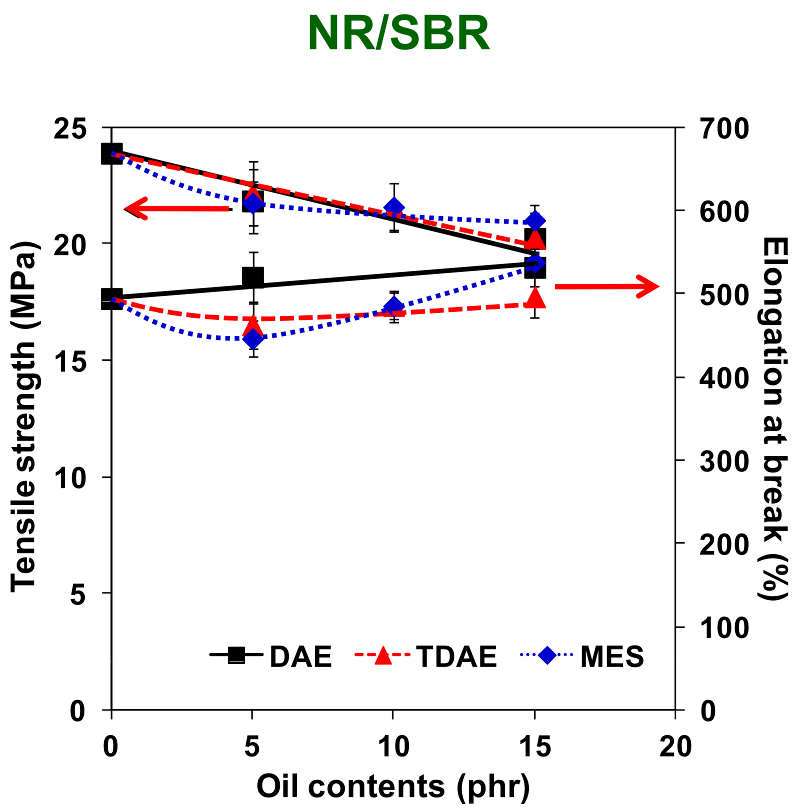


Fig. 8 – Tensile strength and elongation at break.

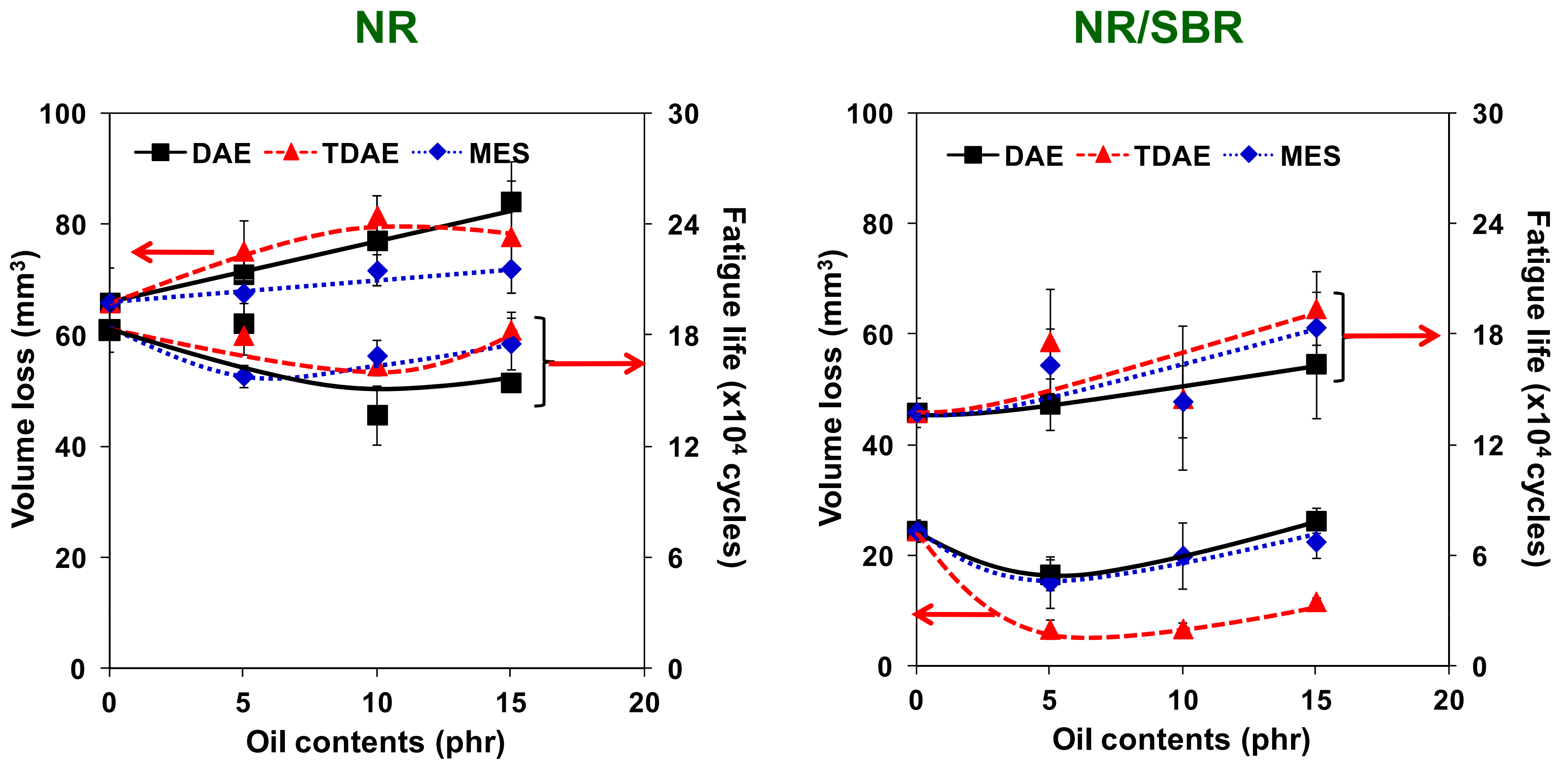


Fig. 9 – DIN abrasion loss and fatigue life.

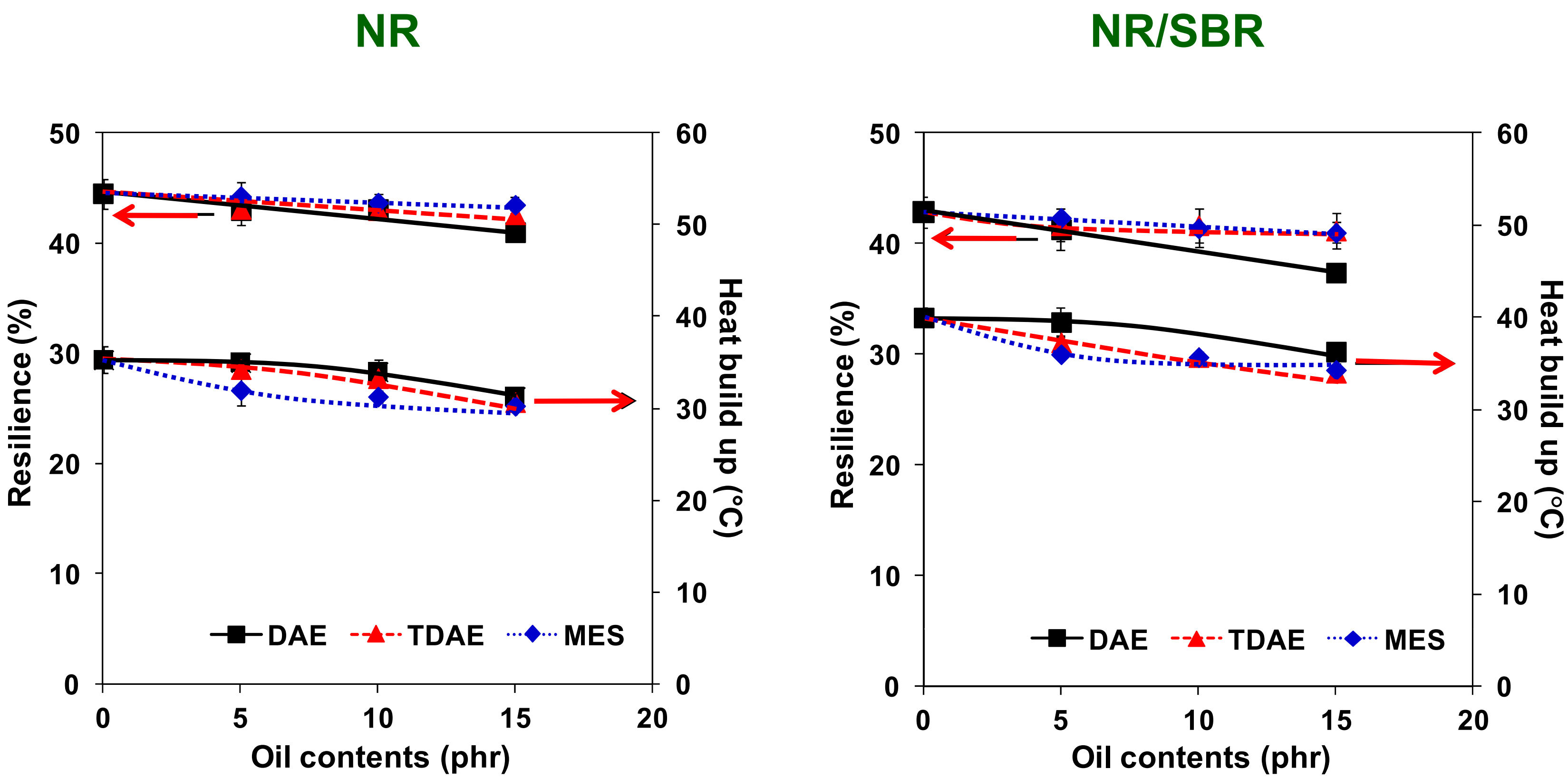


Fig. 10 – Resilience and heat build-up.

NR

NR/SBR

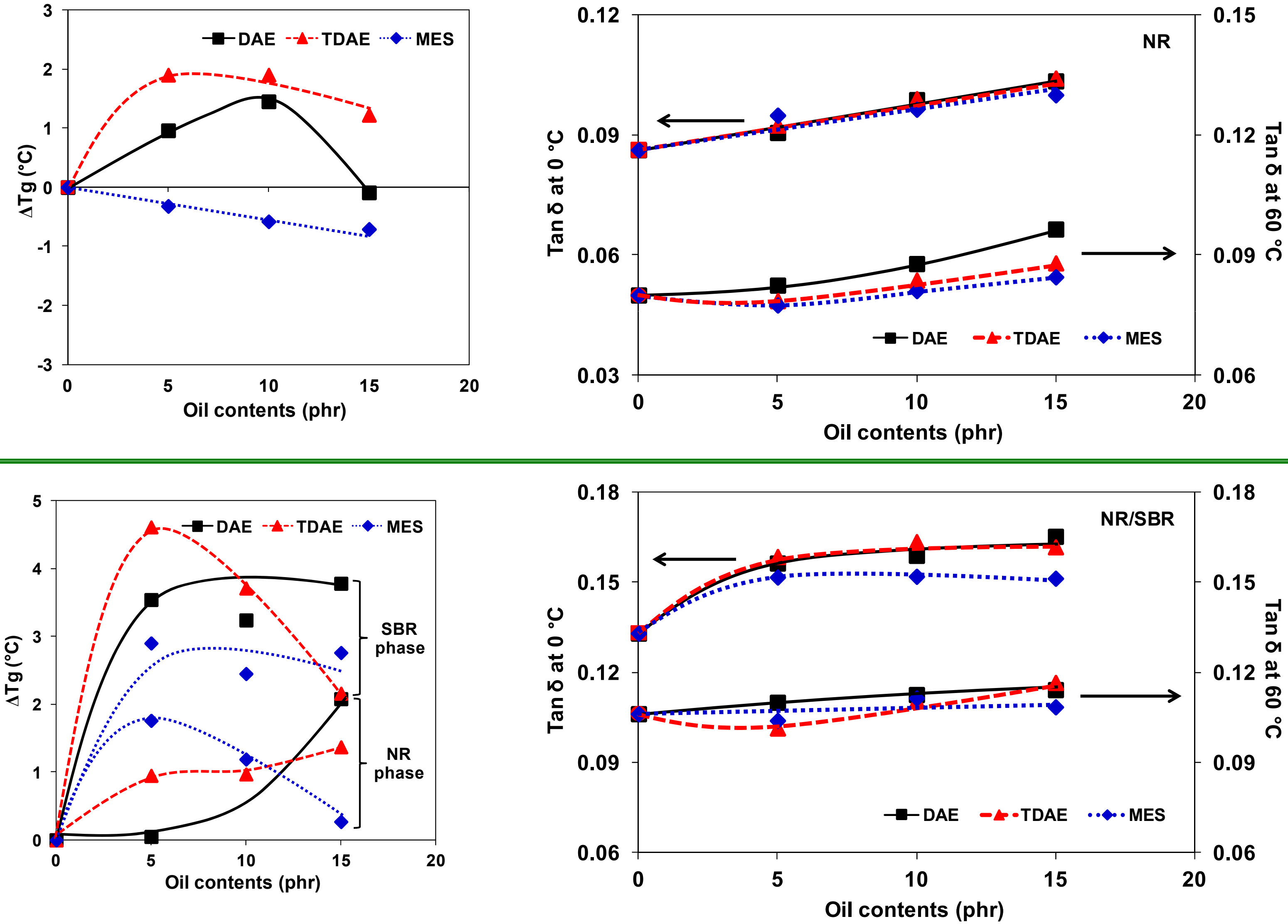


Fig. 11 – ΔTg in relation to the unplasticized compound, and loss tangent at 0 and 60°C at 10 Hz.

Summary

- $\Delta\delta$ between oil and rubber and % swelling become larger at higher temperature. MES has less compatibility than TDAE and DAE in both NR and SBR.
- For unfilled compounds, oil types have only minor effect on the properties of uncured and cured rubber, except for the NR compounds in which MES shows lower cure rate index and tensile strength compared to DAE and TDAE.
- For filled compounds, the compounds with DAE show the highest complex viscosities. The replacement of DAE- with TDAE- and MES-oils has no significant effect on the mechanical properties, but does influence the dynamic mechanical properties due to Tg-shift. The use of TDAE and MES improves the elastic properties.
- Based on the dynamic mechanical properties, the use of TDAE-oil provides the best balance of wet grip and rolling resistance for tire treads.

Acknowledgement

My former PhD Student under this project:

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