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Enhancing Filler-Rubber Compatibility of Silica-Reinforced Tire Tread Compounds by using Chemically Modified Natural Rubbers

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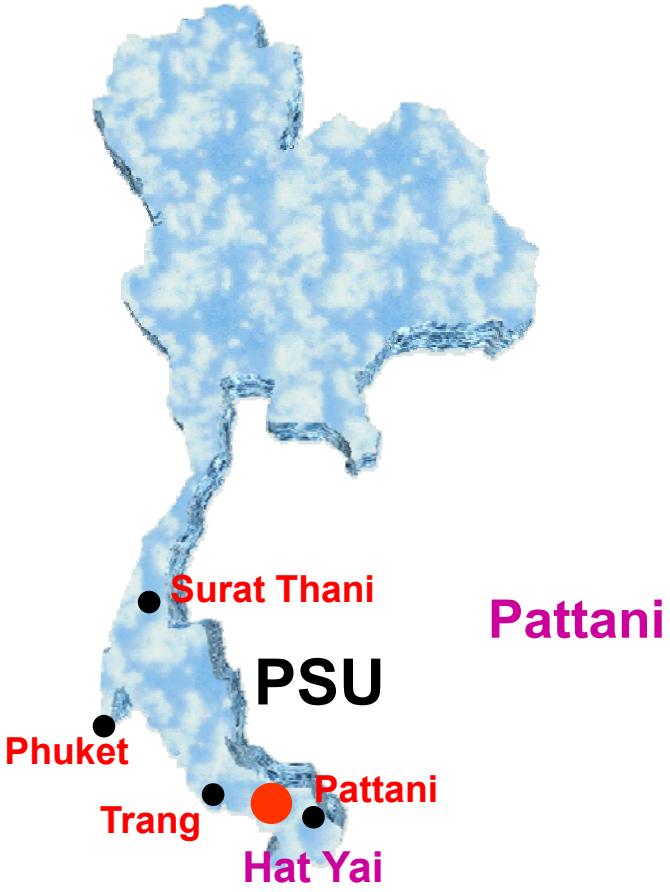

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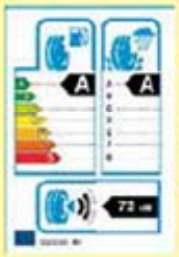
Introduction – Tire development

Japan	EU	Korea	Brazil	China	USA
					
PC summer replacement	All PC, LT, T&B	All PC, LT	All PC, LT, T&B	All PC, LT, T&B	PC replacement
January 2010	November 2012	December 2012	October 2016	2016, 2019 mandatory	Under discussion

A.Blume, F. Thibault-Starzyk. 2017. Rubber Fibres Plastics International 12(3), 152-157

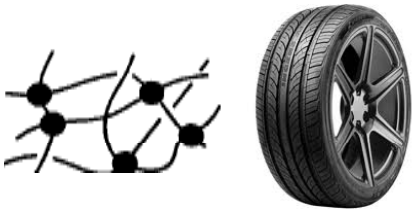
www.asdreports.com

Moving towards more "Green" tire industry

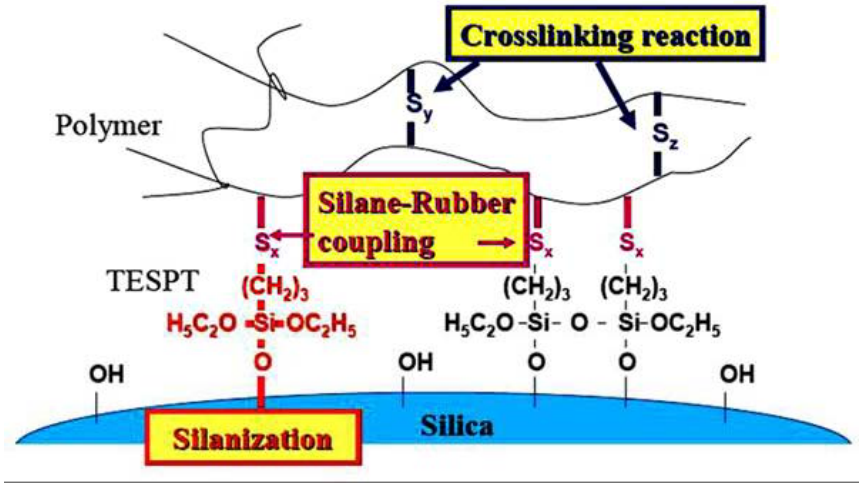
- **More energy-efficient and less CO_2 emission tires**
- **Use of safe compounding ingredients**
- **Less dependence on petroleum-based raw materials, but more dependence on biosources and sustainable supplies**

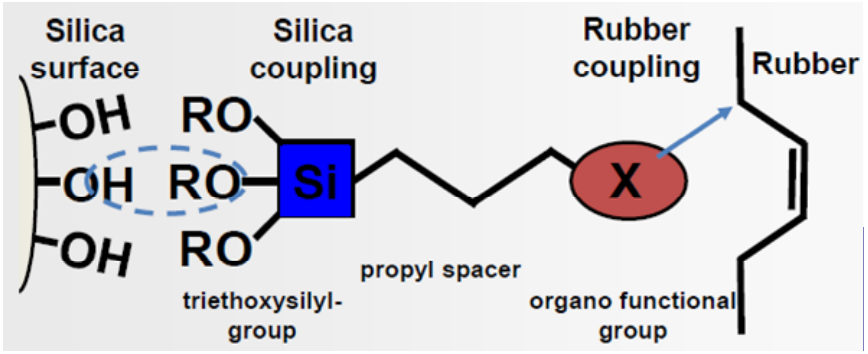
Introduction – Low rolling resistance tires

The basis for low rolling resistance tire treads



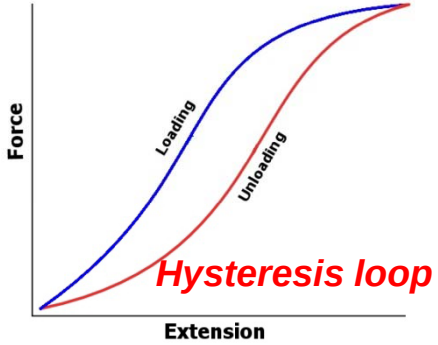
Enhanced Filler-Elastomer Interactions





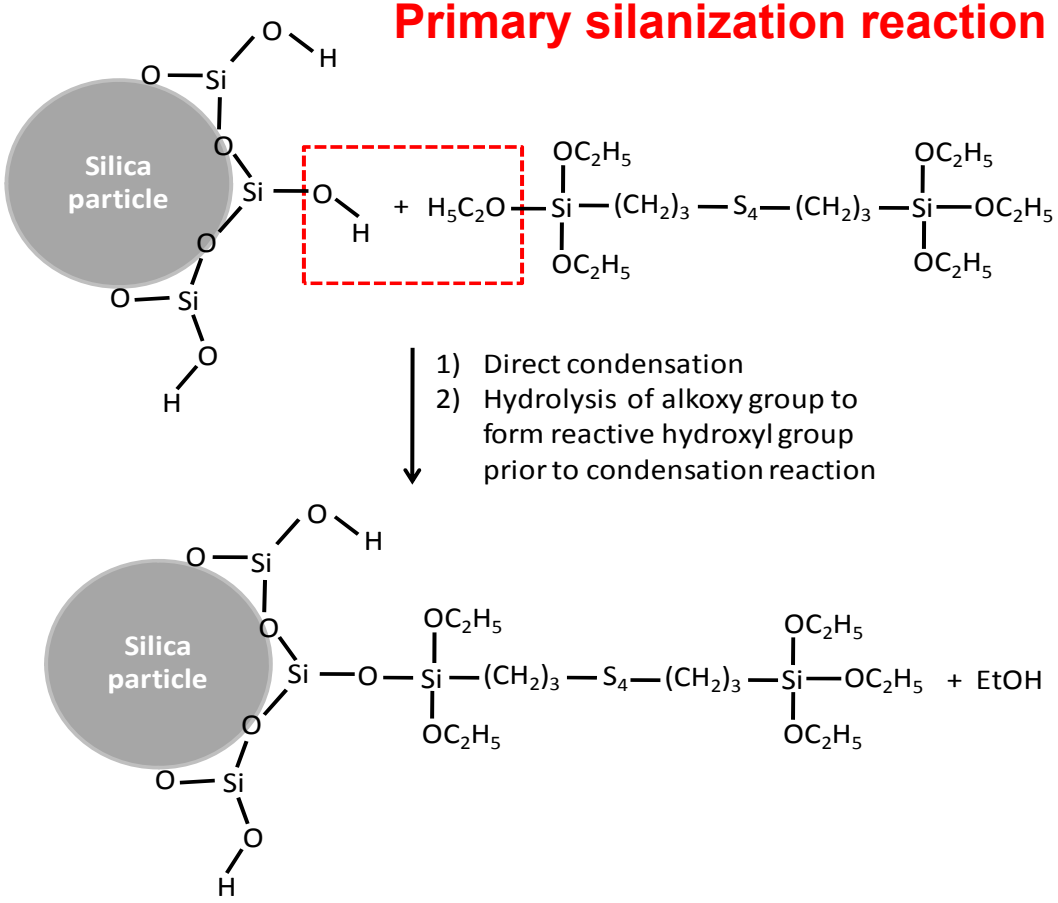
A.Blume. Reinforcement. In Elastomer Science and Engineering. University of Twente.

Double network (crosslinking & coupling) reduces hysteresis, i.e. less energy loss during dynamic deformation



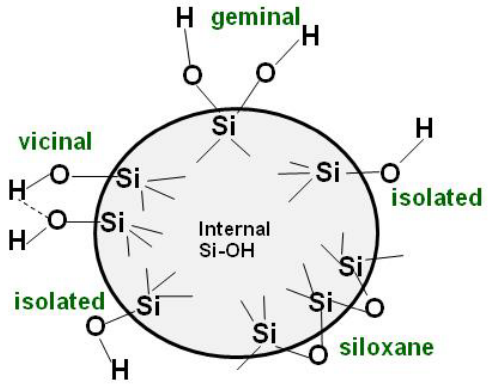
Introduction – Silica/silane technolgy

Primary silanization reaction



Mixing dump temperature is the key parameter.

C. Hayichelaeh et al. Polymers10(6), 584; doi:10.3390/polym1006058

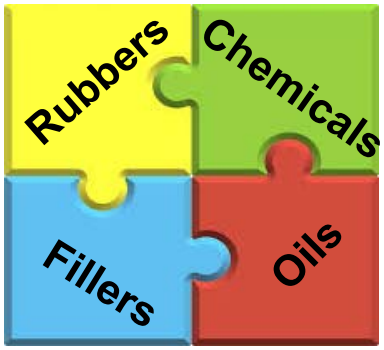


Based on model compound study,

- **Only isolated and geminal silanol groups react, and approx. 25% of the Si-OH groups react with silanes due to the accessibility;**
- **Small molecules such as alcohols or amines can further increase the hydrophobation of the silica surface.**

A.Blume, F. Thibault-Starzyk. 2017. Rubber Fibres Plastics International 12(3), 152-157

Introduction – Alternatives



Strategies to enhance filler-rubber interactions

- ✓ **Use of silane coupling agents**
- ✓ **Silica surface modification,e.g. by plasma treatment, silane pretreatment , admicellar polymerization, grafting of functional groups**
- ✓ **Use of polar rubber as compatibilizers, e.g. CR, NBR, ENR**

Natural rubber grafted with 3-octanoylthio-1-propyltriethoxysilane (NR-g-NXT)

Epoxidized natural rubber (ENR)

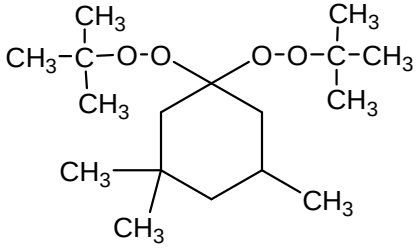
Epoxidized low molecular weight natural rubber (ELMWNR)

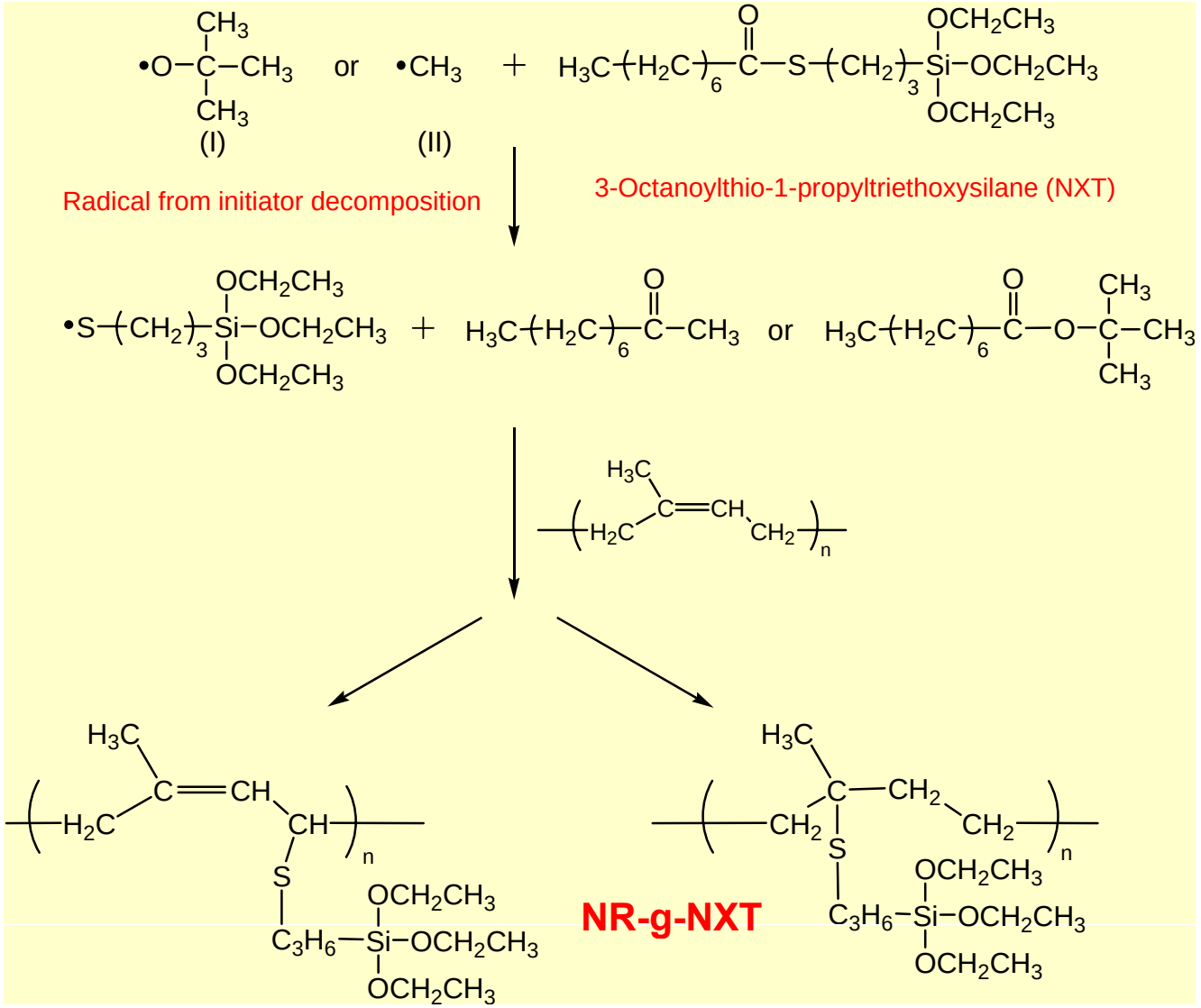
Preparation of NR-g-NXT

Melt mixing at 140°C for 12 mins

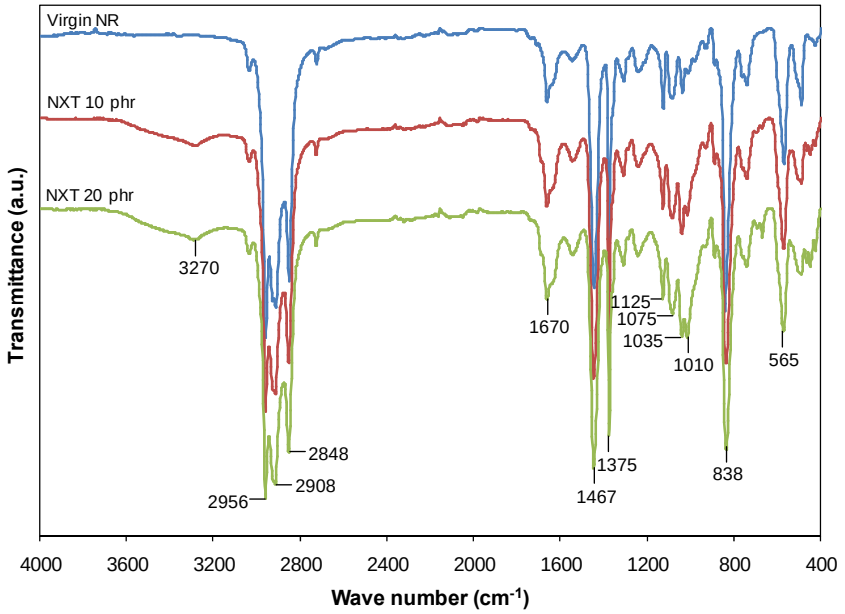
Initiator: 1,1′-di(tert-butylperoxy)-3,3,5-trimethylcyclohexane (Luperox® 231XL40)

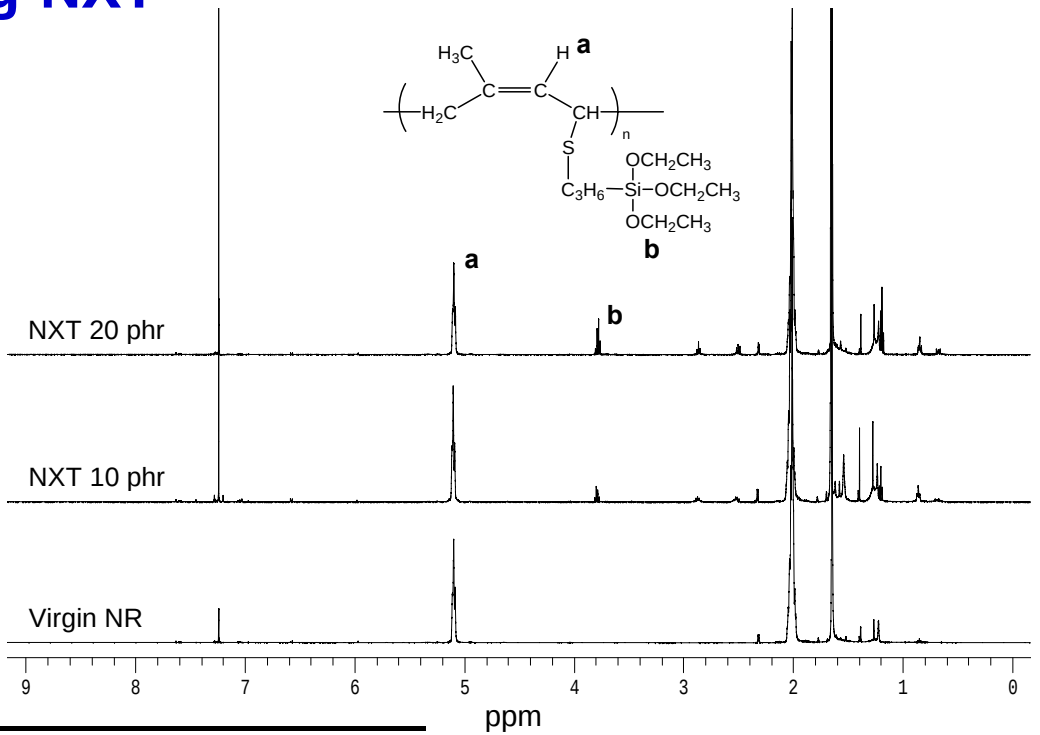
NXT 10, 20 phr
Initiator 0.1 phr





Characterization of NR-g-NXT

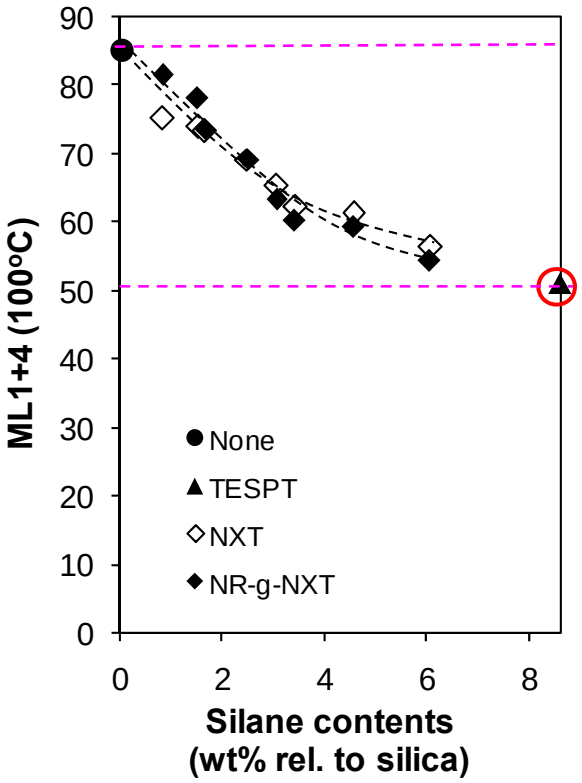


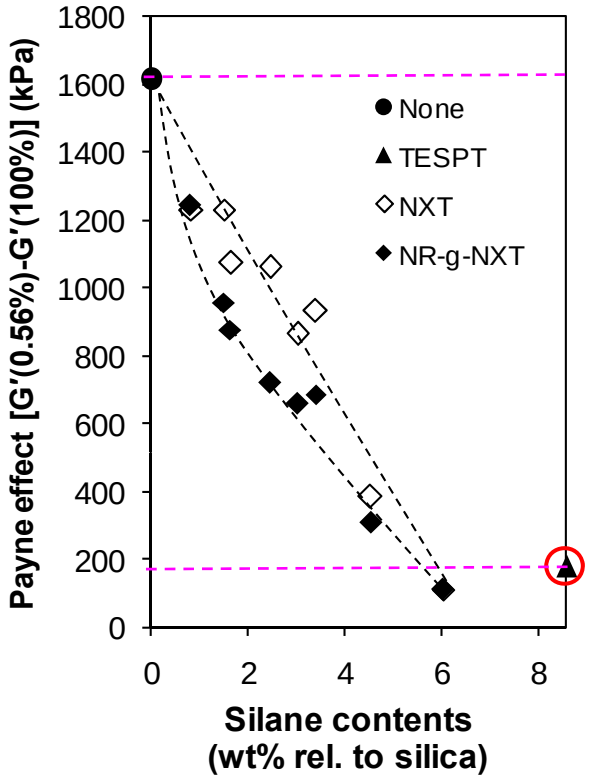


Analysis results	Amount of NXT (phr)		
	virgin NR	10	20
R value from ATR-FTIR			
$R_{1075}=A_{1075}/A_{1375}$	0.31	0.49	0.55
$R_{1035}=A_{1035}/A_{1375}$	0.22	0.42	0.49
Mol% of NXTfrom ^{1}H NMR	0.00	0.66	1.32
Amount of grafted NXT (wt%)	-	3.43	6.68
Amount of NXT used (wt%)	-	9.09	16.67
Grafting efficiency (%)	-	37.7	40.1

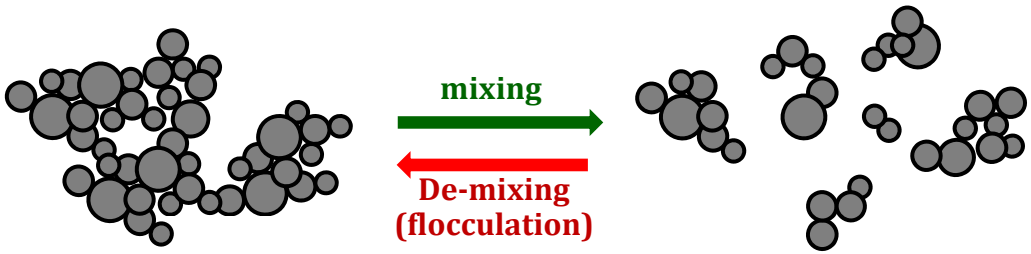
Peaks at 1075 and 1035 cm^{-1} are assigned to Si-O-C and Si-OSi deformations.

Effect of NR-g-NXT on silica-filled NR compounds



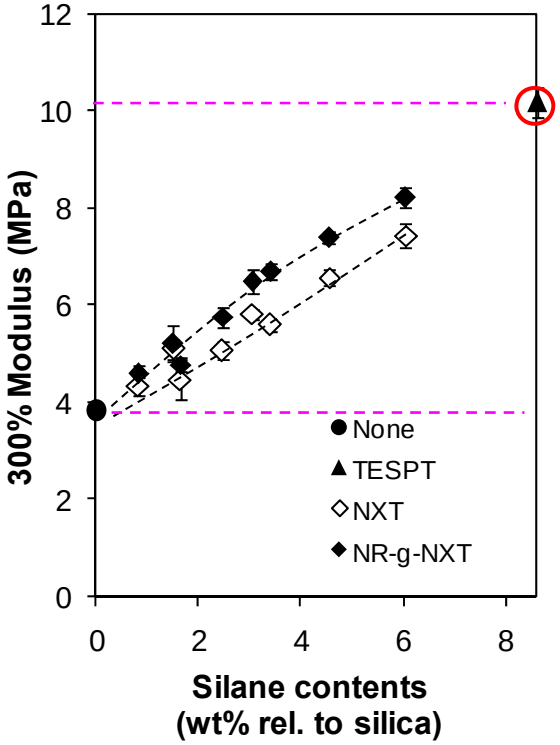


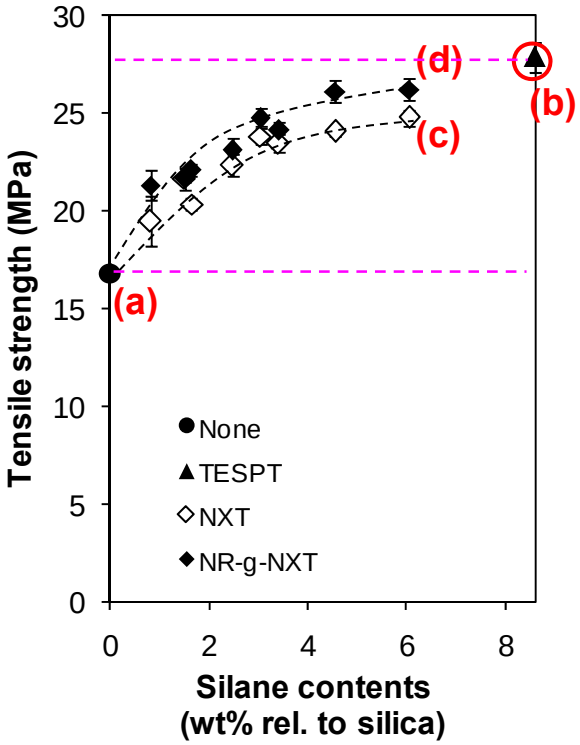
Zeosil 1165MP	55
TDAE	8
ZnO	3
Stearic acid	1
TMQ	1
DPG	1
CBS	1.5
Sulfur	1.5

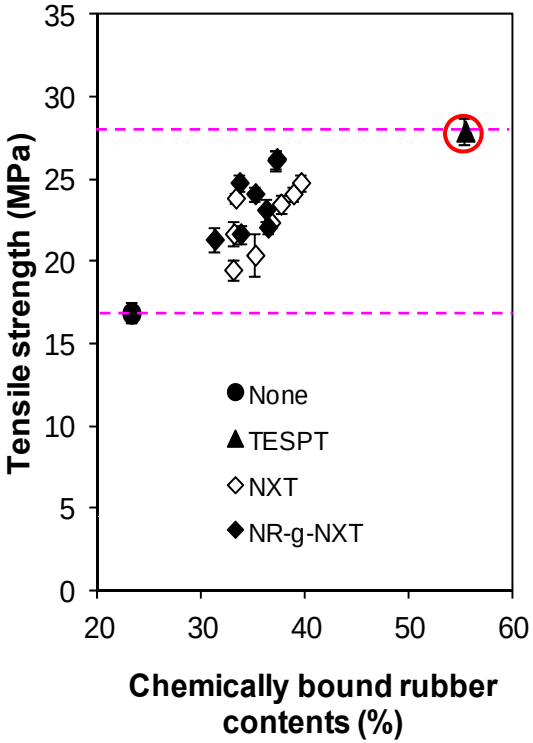


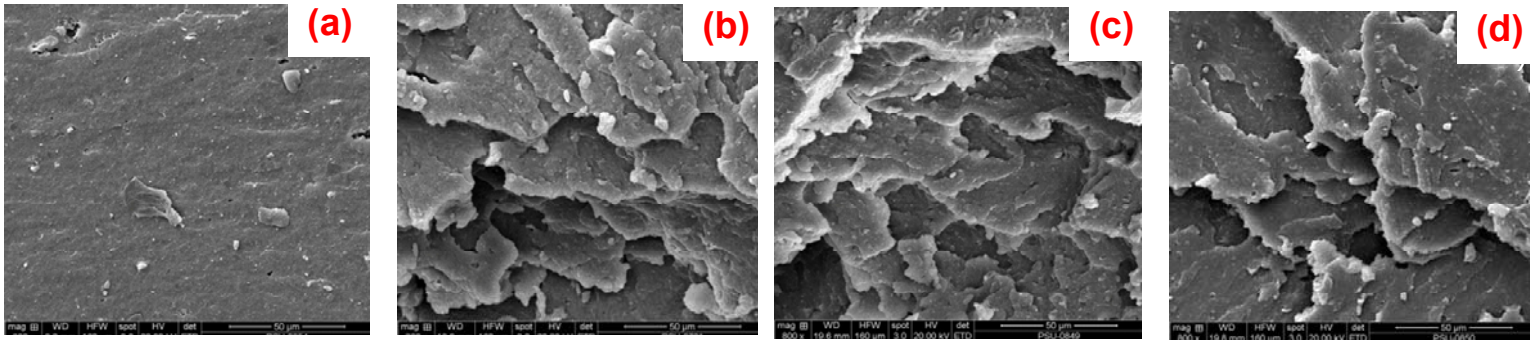
agglomerates aggregates

Effect of NR-g-NXT on silica-filled NR vulcanizates



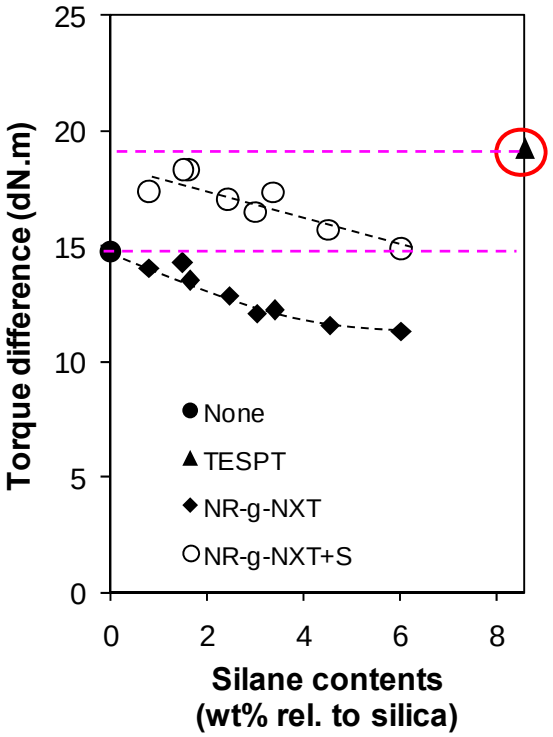


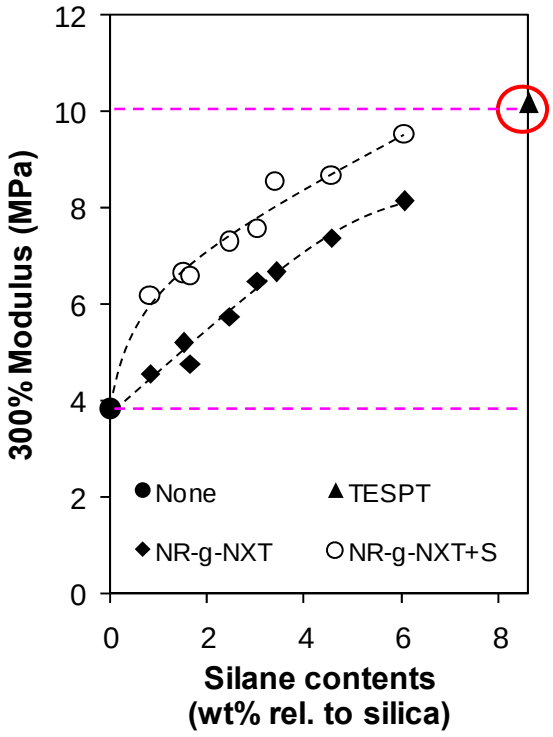


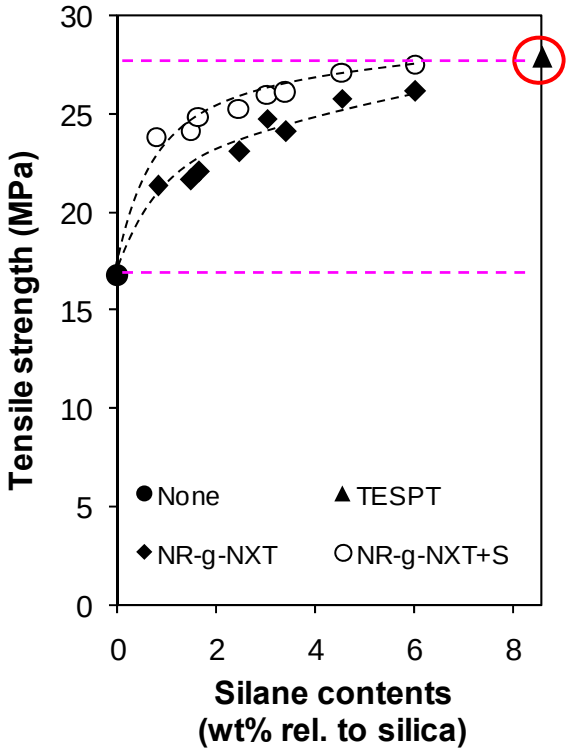


SEM micrographs of tensile fractured surfaces at 800x

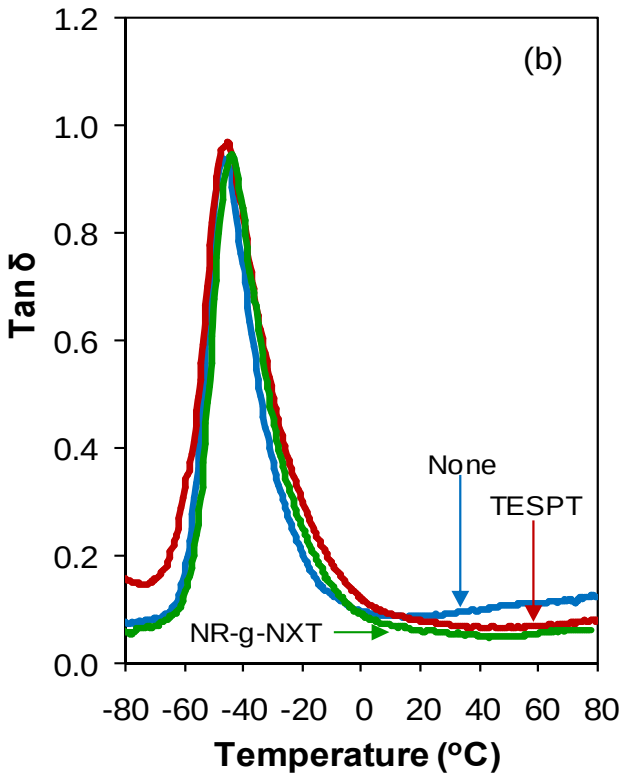
Effect of NR-g-NXT & sulfur compensation on the properties

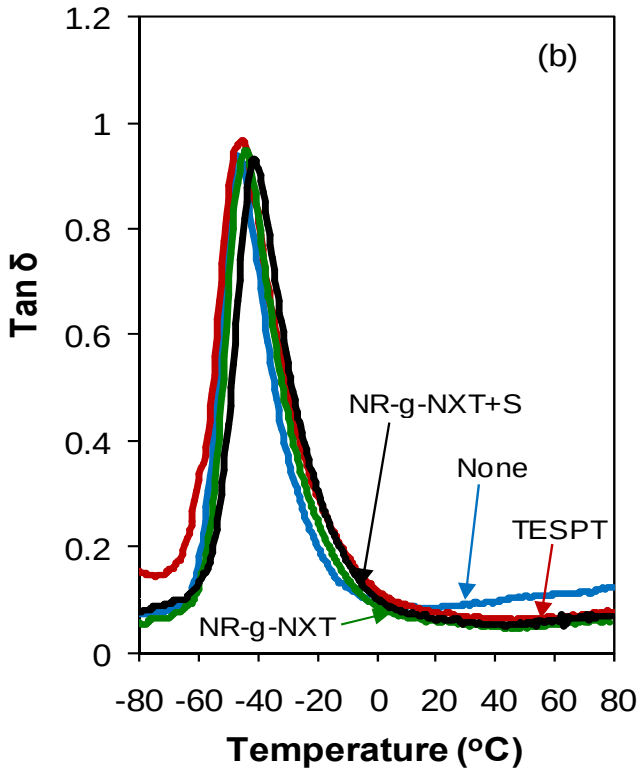






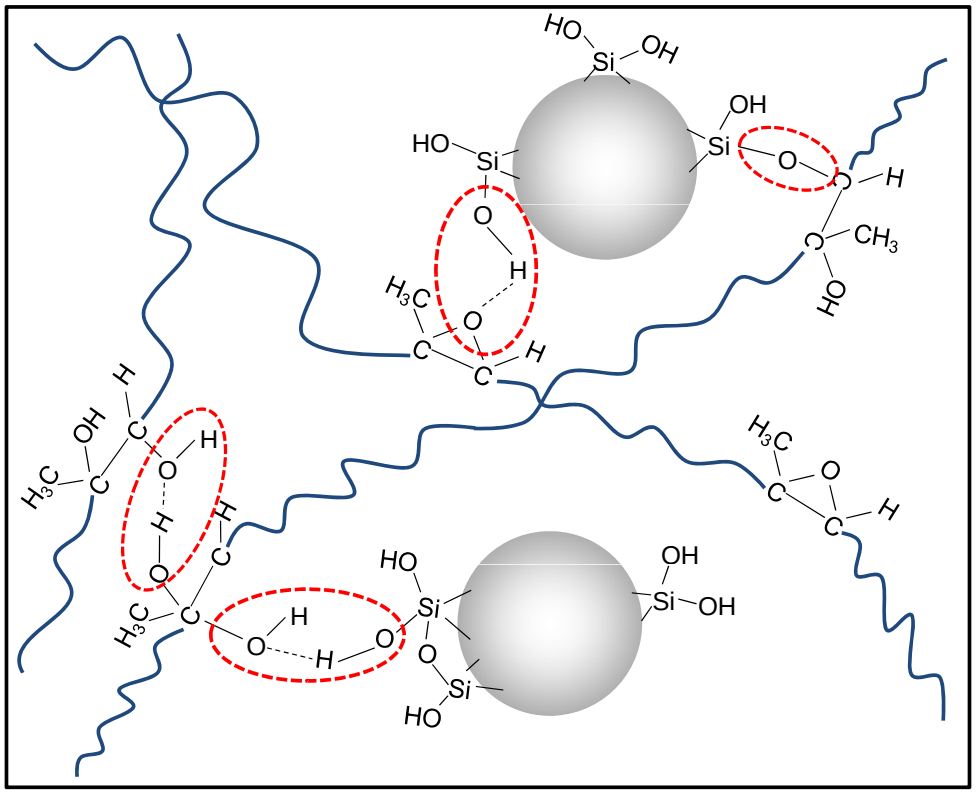
Sulfur compensation for the system having NR-g-NXT by taking the compound with TESPT as reference results in enhanced modulus and tensile strength.

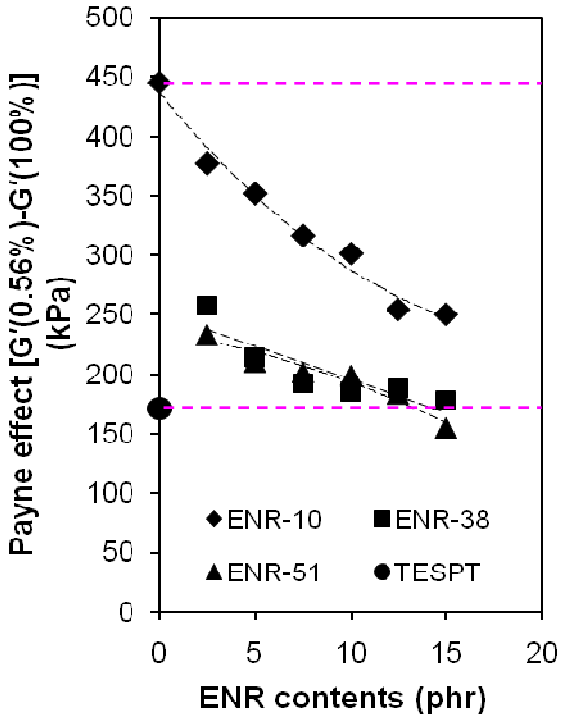


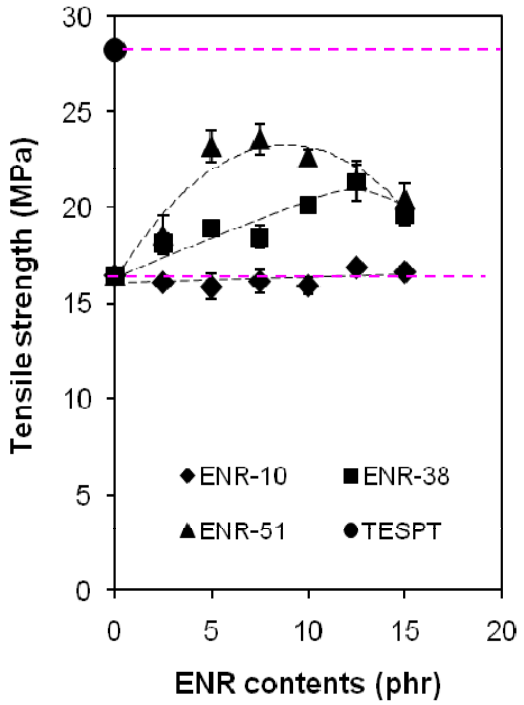


Compatibilizer types	T_g (°C)	Values of Tan δ	
		at 5°C	at 60°C
Without	-47	0.09	0.11
TESPT	-45	0.10	0.07
NR-g-NXT	-44	0.08	0.05
NR-g-NXT + sulfur	-42	0.08	0.06

Use of ENR as compatibilizer





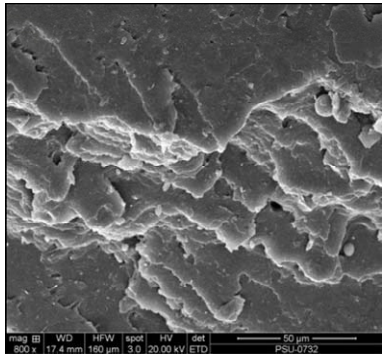


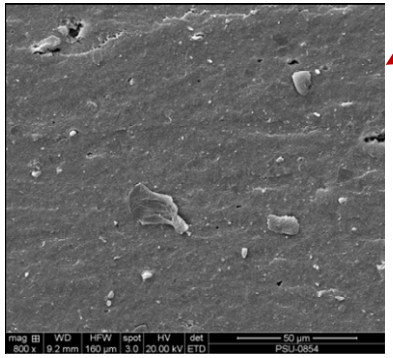
K. Sengloyluan et al. 2014. European Polymer Journal. 51, 69-79.

K. Sengloyluan et al. 2016. Rubber Chemistry and Technology. 89(3), 419-435.

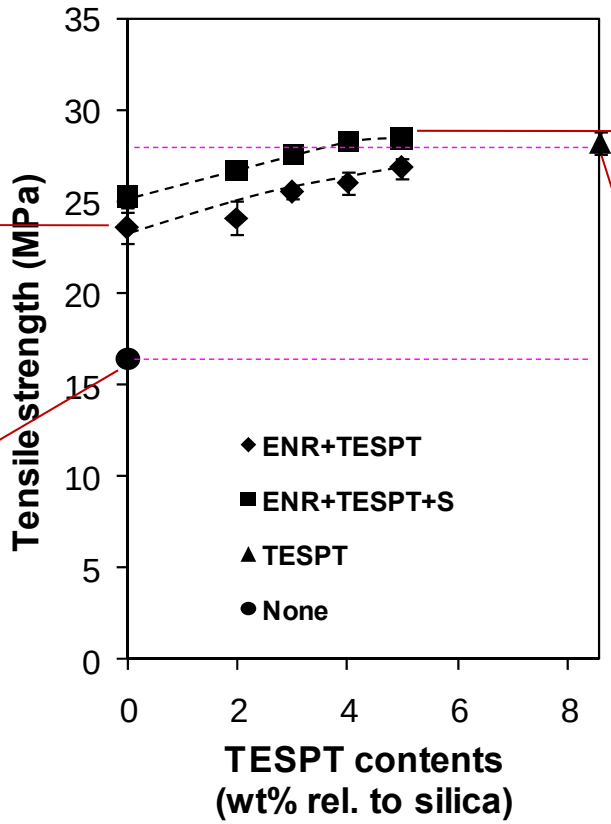
Use of ENR as compatibilizer + TESPT + sulfur compensation

ENR-51 7.5 phr + TESPT

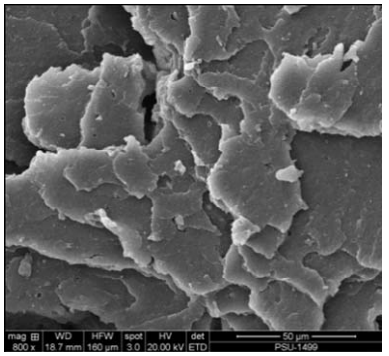


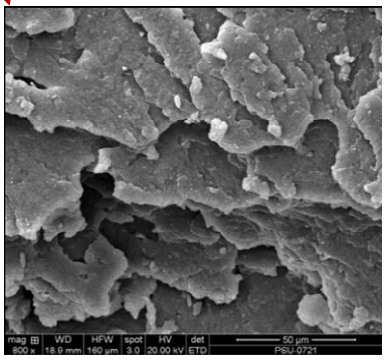


Without



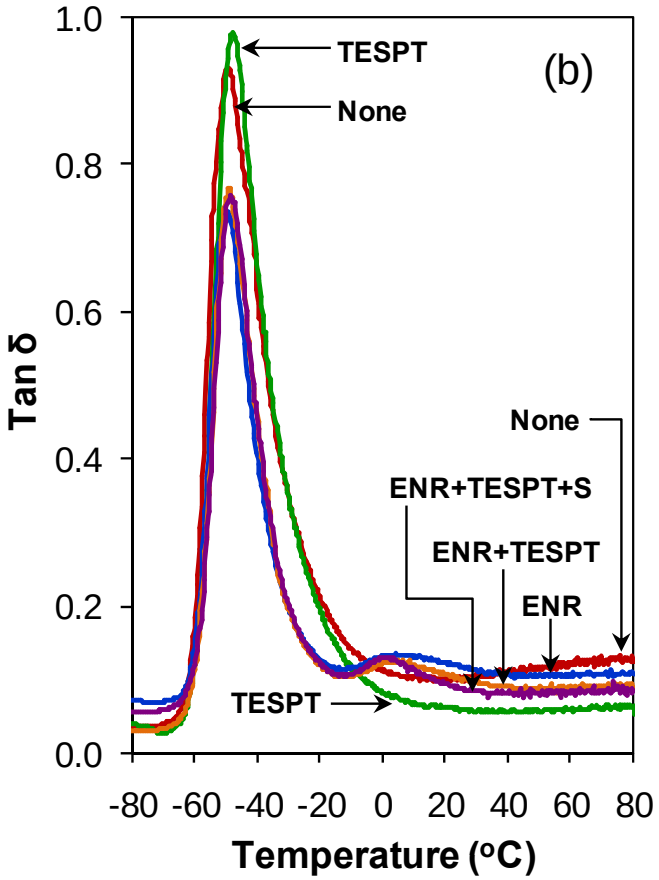
ENR-51 7.5 phr + TESPT+S

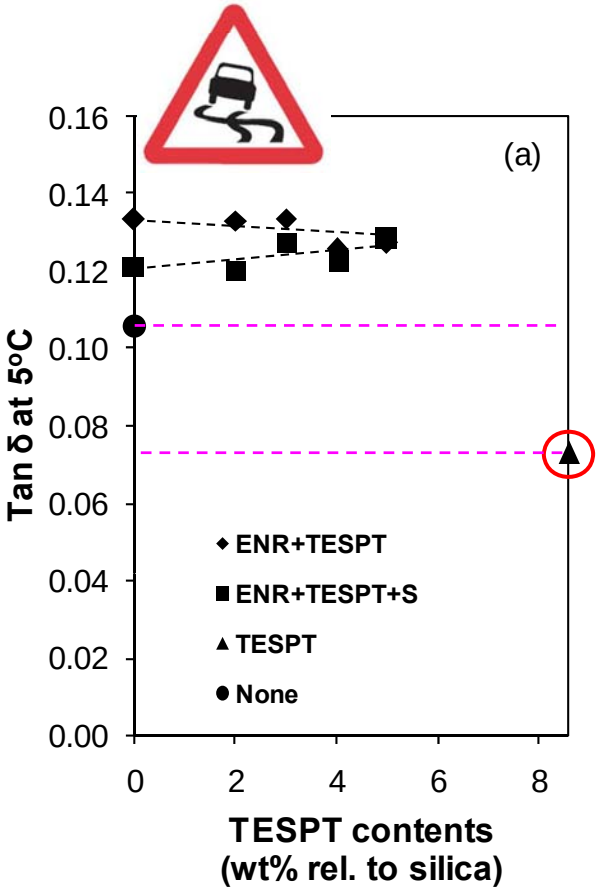


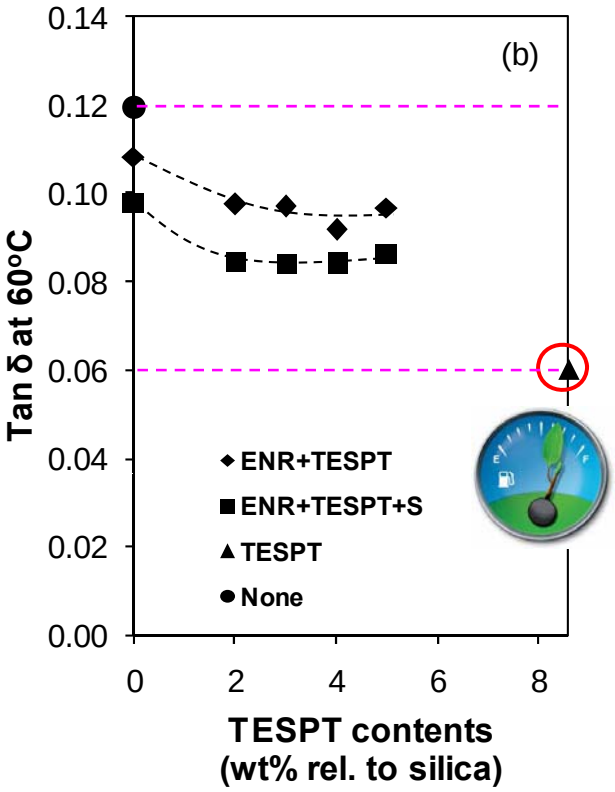


TESPT 8.6 wt% rel.to silica

- **With only half or smaller amount of TESPT is needed when ENR-51 is included, so the amounts of ethanol released can be substantially reduced.**

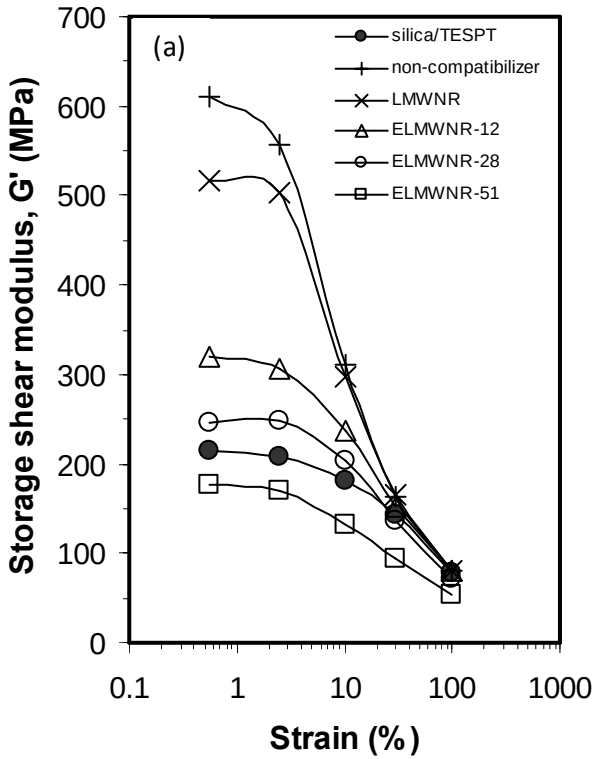


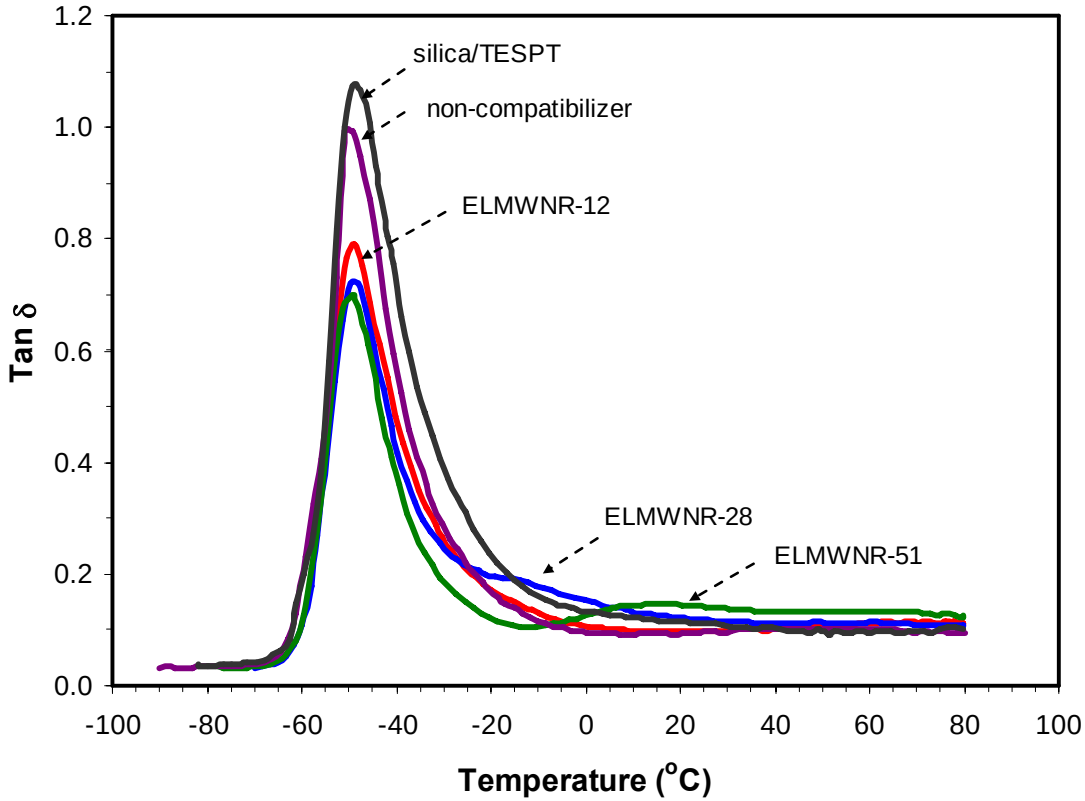




From the perspective of the "Magic Triangle of Tire Technology", when the wet skid resistance needs to be boosted, e.g. for "Winter Tires", the combination of ENR-51, TESPT and sulfur compensation presents itself as a better option.

Use of ELMWNR as compatibilizer





ELMWNR (mole% epoxide)	M_w (g/mol)
0	65,000
12	55,000
28	49,000
51*	N/A

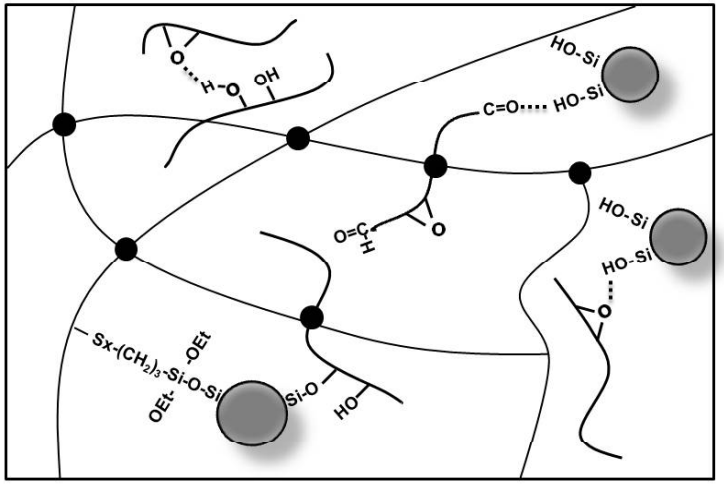
With 10 phr of low molecular weight rubber

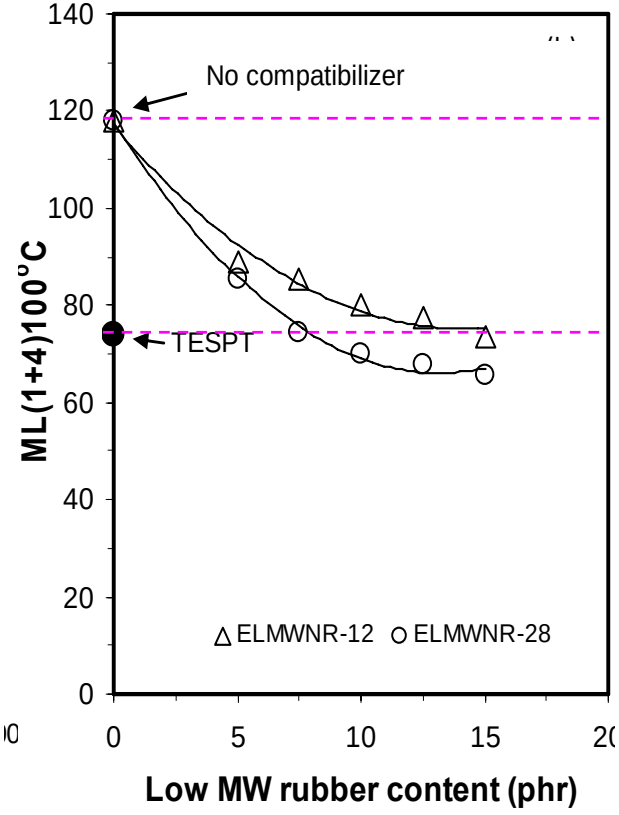
P. Saramolee et al. 2016 . Journal of Rubber Research. 19(1), 28-42.

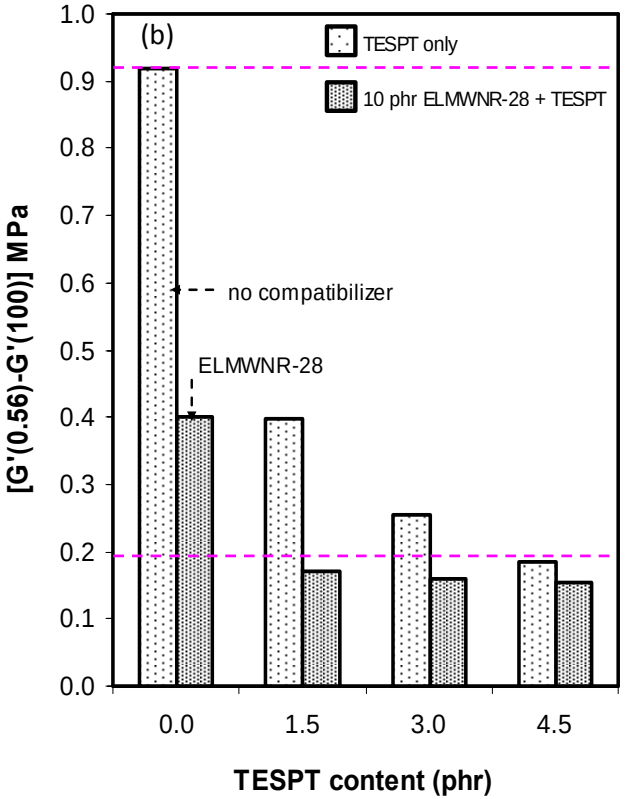
P. Saramolee et al. 2016 . Journal of Elastomers and Plastics. 48(2), 145-163.

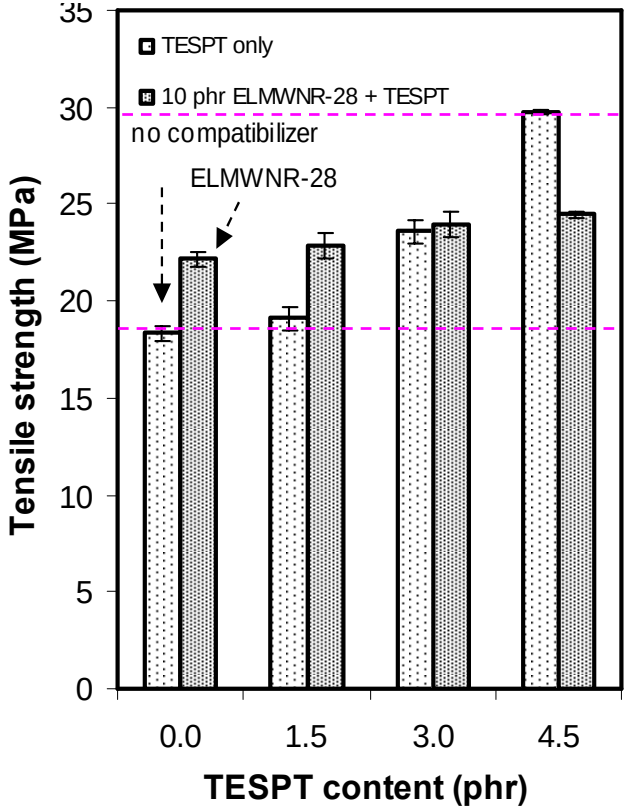
Use of ELMWNR as compatibilizer

+small amount of TESPT









Conclusions

NR-g-NXT, ENR and ELMWNR show their potential to be used as compatibilizers for silica-reinforced rubber compounds as observed by the improved processability and enhanced mechanical & dynamic properties compared to the system without compatibilizer.

The use of state-of-the-art TESPT at its optimum loading remains superior but the application of these modified rubbers with a small amount of TESPT and sulfur compensation results in properties that close to the levels obtained with TESPT.

NR-based compatibilizer/TESPT combinations provide environmental benefits from the use of renewable material and a reduced amount of ethanol emitted from TESPT silane coupling agent during processing.

Acknowledgement

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