Properties of Epoxidized Natural Rubber Tread Compound: The Hybrid Reinforcing Effect of Silica and Silane System

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SUMMARY

Modification of natural rubber via epoxidation process increases its compatibility with highly polar filler like silica. In this work, epoxidized natural rubber (ENR) reinforced with silica compound is evaluated for truck tire tread compound. The rheological, physical and dynamic properties as well as the bound rubber content of ENR-silica tread compound are discussed. The results show that ENR-silica compound has high chemically bound rubber indicating the good interaction and bonding between rubber and silica. In addition, the dynamic test shows the ENR-silica vulcanizate exhibit higher Tan delta at 0 °C and lower tan delta at 60 °C as compared to conventional natural rubber-carbon black vulcanizate, which gives indication of higher wet grip and lower rolling resistance of the ENR vulcanizate. The use of ENR reinforced with silica filler in tread compound is a unique combination that offers renewable material for greener tire application.

Keywords*:* Natural rubber, Epoxidized natural rubber, Silica, Tire, Rolling resistance

1. INTRODUCTION

Natural rubber (NR) is a renewable resource polymer which has been commercially available for over a hundred years. Modification of NR is used to alter the properties of NR so it can compete outside its conventional areas of applications[1]. The chemical modification of NR *via* epoxidation of natural rubber latex yield a specialty rubber called epoxidised natural rubber (ENR), that has improved properties depending on the degree of epoxidation[2,3]. Epoxidation increases the polarity of natural rubber[4]. The presence of polar epoxide groups in ENR, as shown in **Figure 1** results in the rubber compatible with highly polar filler like silica.

The strong interaction between ENR and silica results in unique properties[5,6]. ENR-25 which has 25 mole percent of epoxidation level is suitable for tire tread application[7]. The green tire concept introduced by Michelin in early nineties to give lower rolling resistance and better wet traction tire, which gives fuel benefit to consumer[8]. Silica-filled ENR-25 compound provides low rolling resistance together with high wet grip and offers the best balance required in green tire application[9].

A lot of studies have been dedicated to ENR with silica fillers due to its polarity compatibility[6-7,10]. However most of the work is using in the blend as reinforcement modifier or compatiblizer, with higher content of epoxidation[9-11] and using conventional silica.

The paper presents an investigation on the reinforcement of ENR-25 as base matrix with highly dispersible precipitated silica in tire tread compound. The ENR and silica system will be compared with a conventional black-filled natural rubber and butadiene (BR) blend compound commonly used in tread compound. The rheological properties, bound rubber content, physical and dynamic properties of ENR compound filled with silica are discussed.

2. MATERIALS AND METHODS

2.1 Materials

The rubber used for this study are epoxidized natural rubber (Ekoprena-25), with 25% epoxidation was produced by Felda Rubber Industries Sdn Bhd, Standard Malaysian Natural Rubber (SMR 20) supplied by the Malaysian Rubber Board and butadiene rubber (BR), Neo cis BR40 from Polimeri Europa. Highly dispersible silica, Zeosil 1165MP with CTAB surface area of 164 m^2/g, was obtained from

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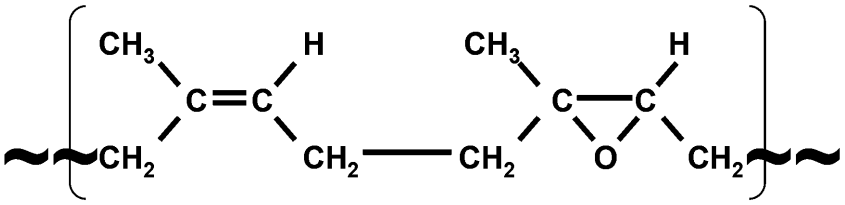
Figure 1. Structure of epoxidised natural rubber



Rhodia Solvay. Silane coupling agent, bis(triethoxysilylpropyl) tetrasulphide, X50S which is a dry blend with carbon black at 1:1 ratio from Evonik was used at 4% from silica wt. The rest of the ingredients were used as received.

2.2 Mixing of Compound

The compound was based on a truck tire tread composition. The formulation expressed based on parts per hundred of rubber (phr) is shown in **Table 1**. The NR/BR blend filled with carbon black is used as control as it is the common tread compound used by the industry.

The first step of mixing was done using an internal mixer GK70 with a capacity of 50 liters. The fill factor of the mixer was fixed at 0.7. The mixing procedure is shown in **Table 2**. After dumping, the batches were sheeted out on a two-roll mill. The re-milling stage of mixing was done on silica master batches in GK70 due to high Mooney viscosity. The curatives were mixed in the finalizing stage of mixing in GK70 with the batch temperature is kept controlled below 110 °C.

2.3 Testing

The cure characteristics at 150 ºC were measured using a MDR2000 from Alpha Technologies, under the conditions of 0.5° arc over 30 min at temperature of 150 °C. Mooney viscosity and scorch were tested using Alpha Technologies MV200 viscometer at 100 and 120 °C respectively.

The bound rubber content (BRC) measurements were performed on uncured samples by extracting the unbound rubber with toluene at room temperature for seven days in both normal and ammonia environment. The ammonia treatment of BRC was done to obtain the chemically bound rubber as ammonia cleaves the physical linkages between rubber and silica[9,10]. The amount of BRC (g/g filler) was calculated by:

$$BRC(\%) = \frac{w_{dry} - w_{insol}}{w_o \times \frac{w_{filler,phr}}{w_{total,phr}}} x100\% \quad (1)$$

Where w_o is the initial weight of the sample, w_{dry} is the dry weight of the extracted sample, w_{insol} is the weight of insoluble (mainly filler) in the sample, $w_{filler,phr}$ is the total filler weight in phr and $w_{total,\ phr}$ is the total compound weight in phr. The total BRC is referred to BRC obtained from normal atmosphere while chemically BRC is the data obtained from ammonia treated BRC measurement.

Vulcanizates were prepared by curing the compounds for their respective t_{95} (time to reach 95% of torque difference in the curemeter) at 150 ºC using an electrical press at 100 bar. Tensile properties of the vulcanizates were measured according to ISO-37. The hardness of the cured samples was determined according to DIN-53505. The abrasion resistance was conducted according to ISO4649 as well as Akron abrasion test.

The dynamic properties of vulcanizates: storage modulus, loss modulus and glass transition temperature were measured using a Mettler Toledo Dynamic Mechanical Analyzer (DMA1 Start system). The samples were cut from the vulcanized sheets of 2 mm thickness. A temperature sweep measurement from -100 to +100 °C was performed in tension mode at a frequency of 10Hz and dynamic strain of 0.1%.

Table 1. Formulation of the compound

Ingredients *	NR/BR-CB	ENR-silica	ENR-silica-CB
NR	70	-	-
BR	30	-	-
ENR (Ekoprena 25)	-	100	100
Silica	-	55	50
TESPT (X50S)	-	4.4	4.0
Carbon black, N234	53	5	10
**Mixes also contain the ingredients ZnO 3, stearic acid 3, calcium stearate 2, 6PPD 1, TMQ 1, TDAE oil 8, wax 1, sulphur 0.7, TBBS 1.5 and TBzTD 0.25*			

Table 2. Mixing procedure

Time (min)	Ingredients
0	Rubber
1	½ filler, ½ silane**
2	½ filler, ½ silane**, oil
3	sweep
4	powder
5	dump
***Only for silica compound*	

3. RESULTS AND DISCUSSION

3.1 Cure Characteristics

The rheometer curves at 175 °C of ENR-silica compounds as compared to NR/BR-carbon black compound are shown in **Figure 2**. The scorch time (t2) and cure time (t90) of ENR-silica systems are faster than NR/BR-CB compound. The interaction of epoxy group of ENR with silanol groups and the presence of silane coupling agent decrease the silanol groups. This also leads to less of accelerators and other compounding ingredients interact with silanol group of silica and results in the faster cure of the compound[11]. Delta torque is higher for NR/BR-carbon black compound as compared to ENR compounds indicating different crosslinking system in both compound. Flocculation sign or agglomeration of silica is not presence in the rheometer curve for all compounds giving indication of good dispersion of fillers is obtained in the compounds[16-17]. Cure reversion is only seen for ENR-silica, very small in ENR-silica-CB but not seen at all for NR/BR-CB compound.

The Mooney viscosity and scorch of the compounds are presented in **Table 3**. Both ENR-silica and ENR-silica-CB compounds show very high viscosity after the first mixing and re-milling stages. The ENR-silica and ENR-silica-CB compounds need to go for extra re-milling stage at two roll mill in order to reduce the viscosity. After finalizing stage, all compounds have acceptable Mooney viscosity.

3.2 Bound Rubber Content

Rubber to filler interaction can be described from the bound rubber content. **Figure 3** shows the bound rubber content of the compounds. Ammonia treatment on the bound rubber of the compound separates the physically bound rubber and only chemically bound rubber was obtained. ENR-silica compounds have higher total bound rubber content than NR/BR-CB compound. Chapman[18] have reported the high level of ENR-25 is bound to silica (>1 g ENR per g of silica) and ENR-25 binds more strongly to silica than NR based on volume swelling (Vr). With ammonia treatment, the chemically bound rubber content of ENR-silica compounds are still high and only showing very slight reduction which is due to breaking of hydrogen bonding between ENR and silica. This indicates the strong interaction of rubber to filler in ENR-silica compounds which derived from the coupling of ENR and silica and also the enhancement of interaction with the use of coupling agent. The theory of this strong interaction has been elucidated using model compound by Kaewsakul

Figure 2. The cure characteristics of ENR-silica compounds compared to NR/BR-CB compounds

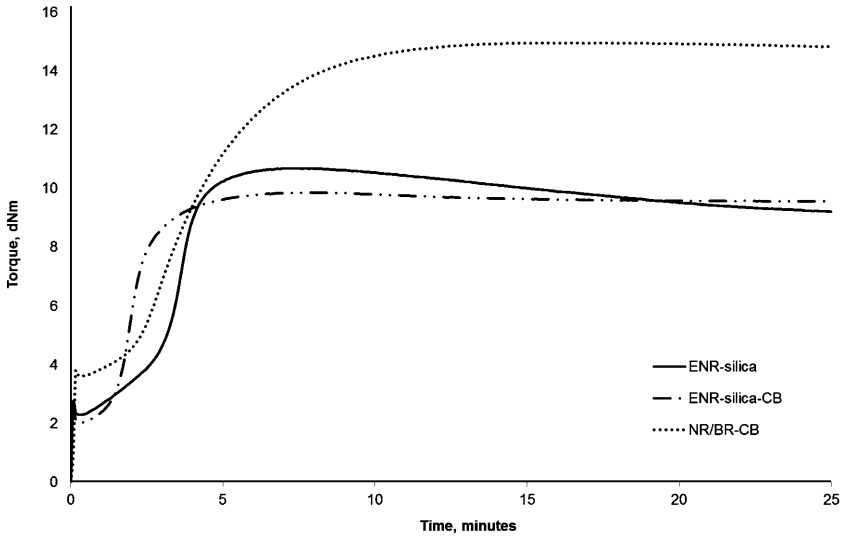


Figure 3. The total and chemically bound rubber content of ENR compound as compared to NR-CB compound

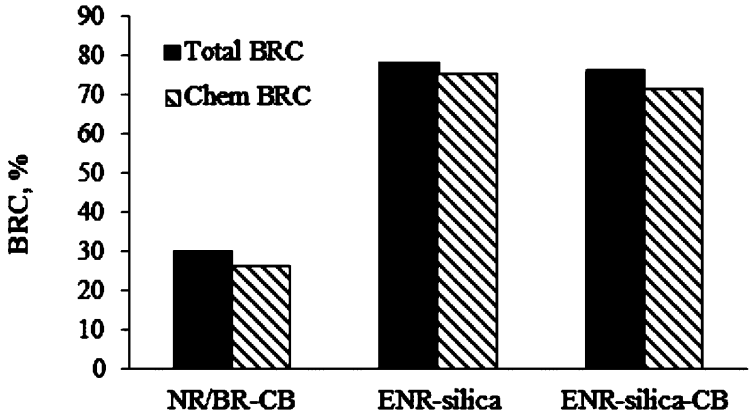


Table 3. Mooney viscosity and scorch of compounds

	NR/BR-CB	ENR-silica	ENR-silica-CB
Master batch (1st stage), ML(1+4)@100 °C	84	135	101
Compound (final stage), ML(1+4)@100 °C	61	58	52
Mooney scorch, t_5, min	46	63	54

et al.[19]. This synergistic effect is resulted from hybrid reinforcement of ENR with silica and silane system. The proposed mechanism for the hybrid interactions consist of combination of interaction and coupling between ENR and silica as illustrated in **Figure 4**. The interaction of ENR and silica comes from hydrogen bonding between the silanol groups of silica with epoxide group in ENR. The stronger interactions between ENR and silica derived from bonding of silica with ring opening of ENR; as well as coupling of silica with ENR through silane coupling bonding.

3.3 Physical Properties

Physical properties of the ENR vulcanizates as compared to NR vulcanizate are shown in **Figures 5** and **6**. The tensile strength of ENR-silica and ENR-silica-CB vulcanizates are comparable but slightly lower than NR/BR-CB vulcanizate. ENR-silica and ENR-silica-CB vulcanizates show higher modulus and lower elongation at break than NR/BR-CB vulcanizate. The modulus M300 of NR/BR-CB vulcanizate is slightly low than normally expected. Hardness of ENR-silica vulcanizates is comparable to NR/BR-CB vulcanizate. For abrasion resistance, DIN abrasion resistance index (ARI) is higher for NR/BR-CB vulcanizate but inversely the Akron abrasion resistance index is higher for ENR-silica-CB vulcanizate.

The ageing properties of the vulcanizate after accelerated ageing at 70 °C for 7 days are shown in **Table 4**. The tensile strength and elongation at break of all vulcanizates reduce slightly after ageing. Only NR/BR-CB vulcanizate shows an increase in hardness after ageing, while for ENR-silica vulcanizates is either no change or reduce slightly.

3.4 Dynamic Properties

The dynamic properties of the vulcanizates from the DMTA measurement can be used to predict the important tire tread rubber properties[20]. For high wet skid resistance of a tire, a high tan delta at temperature around 0 °C is required. However, for low rolling resistance tire, a lower tan δ at 60 ºC is needed. Comparison of temperature dependence of tan delta at

Figure 4. The proposed mechanism for the hybrid reinforcement of ENR with silica through combination of (a); interaction between the silanol group of silica with epoxide group in ENR, (b) coupling of silica with ENR through ring opening of ENR and

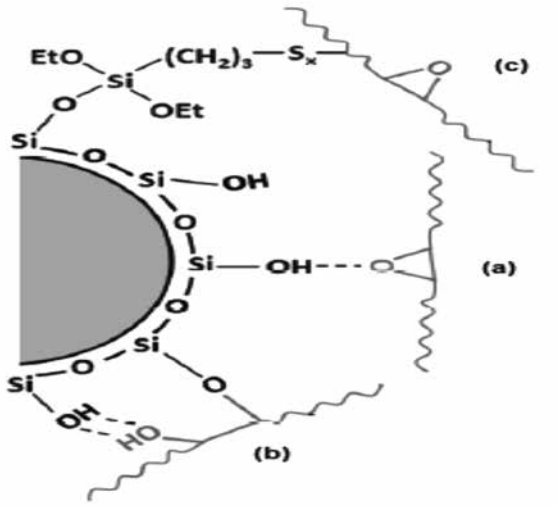
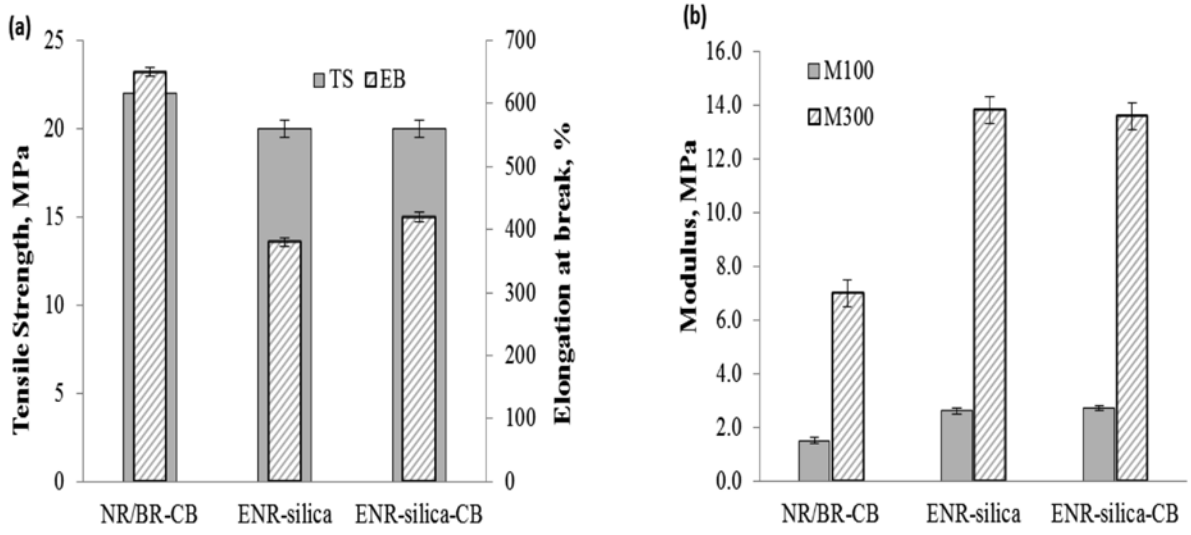


Figure 5. Tensile properties of ENR vulcanizates (a) Tensile strength and elongation at break and (b) modulus M100 and M300



10Hz for ENR and NR/BR vulcanizates is shown in **Figure 7** and **Table 5**. From the tan delta curve, it is observed that the ENR-silica vulcanizates has higher tan delta peak than control NR/BR-CB vulcanizate. The results show that ENR-silica vulcanizates exhibit higher tan delta at 0 °C and lower tan delta at 60 °C as compared to control NR/BR-CB vulcanizate. This gives an indication that the use of silica filler contributes to the higher wet grip and lower rolling resistance of the ENR vulcanizates. It also confirms the unique properties of silica-filled ENR-25 compound that provide low rolling resistance together with high wet grip.

The tan delta peak from DMTA measurement also corresponds to T_g

Figure 7. Tan delta curve of ENR vulcanizates, DMTA -100 °C to 100 °C at 10 Hz

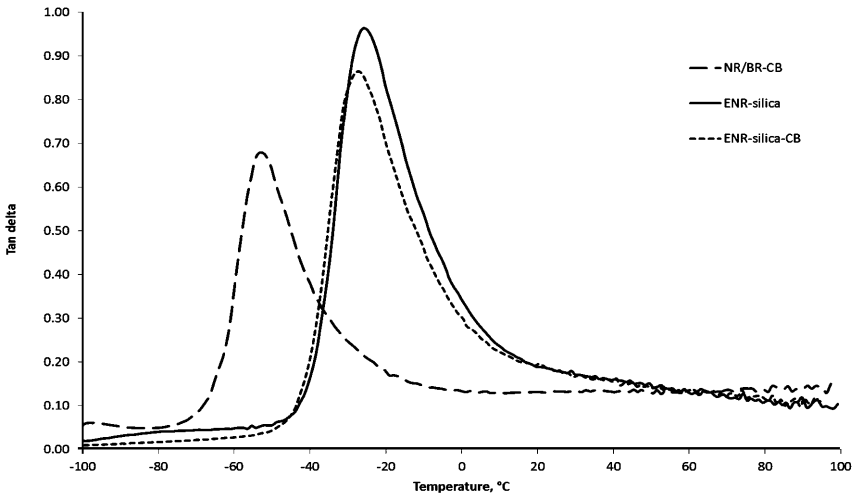


Figure 6. Comparison of ENR vulcanizates with NR vulcanizate in: (a) Hardness; (b) Abrasion resistance index (DIN ARI) and Akron abrasion index

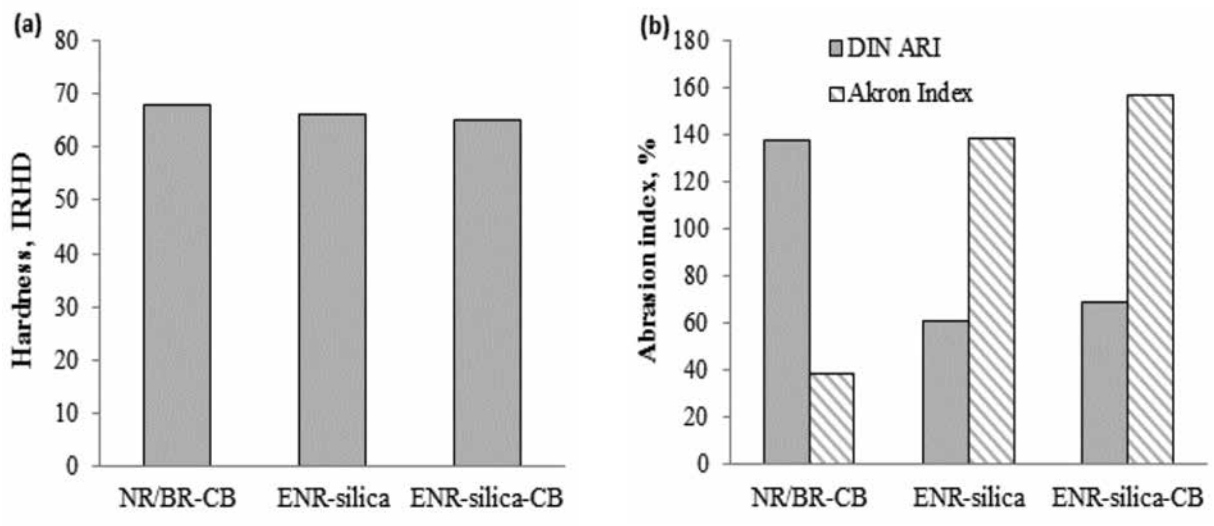


Table 4. Physical properties of ENR vulcanizates after ageing for 7 days at 70 °C

	NR/BR-CB	ENR-silica	ENR-silica-CB
Tensile strength	95% retained	89% retained	98% retained
Elongation at break	91% retained	86% retained	87% retained
Hardness	+3	+0	-1

Table 5. Tan delta at 0 °C and 60 °C of ENR (DMTA, 10Hz)

Tan Delta	NR/BR-CB	ENR-silica	ENR-silica-CB
Tan delta at 0 °C	0.1325	0.3567	0.2790
Tan delta at 60 °C	0.1361	0.1207	0.1152
Tan delta peak,	-53.5 °C	-26.4 °C	-27.9 °C

Table 6. Glass transition temperature, T_g and decomposition temperature of Ekoprena vulcanizates

Parameters	NR/BR-CB	ENR-silica	ENR-silica-CB
T_g (DSC), °C	-64.1	-40.1	-40.1
T_g (DMTA), °C	-53.5	-26.4	-27.9
Decomposition Temp (TGA), °C	392 &459	388	394

of the vulcanizates. The T_g of ENR-silica vulcanizates is about 25 degree higher than NR/BR-CB vulcanizates due to the 25% epoxidation level in ENR. The T_g from DSC measurement is about 10 degree lower for NR/BR-CB vulcanizate and 15 degree lower for Ekoprena vulcanizates as shown in **Table 6**. Abrasion resistance of a rubber is dependent on its T_g[20]. From the value of T_g in **Table 6**, it is expected that the abrasion resistance of ENR is inferior to that of NR. This is in agreement with DIN Abrasion resistance discussed earlier and previous work reported by Gelling *et al*.[1] and Varkey *et al*.[11]. On the other hand, the decomposition temperature of the vulcanizate can be used as indicator for tire wear. The ranking of decomposition temperature is ENR-silica < ENR-silica-CB< NR/BR-CB, indicating NR/BR-CB has better wear resistance than ENR-silica vulcanizates. However, some improvement in the tire wear of ENR-silica can be provided to match the level of control NR/BR by incorporating some level of carbon black in ENR-silica compound.

4. CONCLUSIONS

Reinforcement of modified natural rubber, epoxidized natural rubber with silica fillers was evaluated. The bound rubber content of ENR-silica compounds is higher than NR/BR-CB compound indicating strong rubber-to-filler interaction between ENR and silica. In term of physical properties, the ENR-silica and ENR-silica-CB compounds have inferior tensile strength, lower elongation at break, and higher modulus than NR/BR-CB compound. In addition, the ENR-silica and ENR-silica-CB has higher Akron abrasion index as compared to NR/BR-CB compound. The dynamic test shows the ENR-silica vulcanizate exhibit higher tan delta at 0°C and lower tan delta at 60°C as compared to NR/BR-CB vulcanizate, which gives indication of higher wet grip and lower rolling resistance of the ENR vulcanizates.

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