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# Silica-Reinforced Deproteinized Natural Rubber

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## Abstract

Reinforcement effect of silica-silane system in deproteinized natural rubber (DPNR) is reported. The influence of mixing temperature and sulfur ranks in silane bis-triethoxysilylpropyl-polysulfide is compared between silica-DPNR and silica-natural rubber (NR). Dispersion morphology of silica and rubber-to-filler interaction in DPNR is visualized by atomic force microscopy and TEM network visualization, respectively. DPNR compound shows smaller influence of dump temperature and more constant mechanical properties as compared to NR compound. Establishment of the silica-silane-rubber coupling in DPNR tread compound results in an improvement in dynamic properties especially the lower  $\tan \delta$  at 60°C which indicates the lower rolling resistance of tire. DPNR shows better mechanical and dynamic properties as compared to NR.

**Keywords:** deproteinized natural rubber, silica, silane, tire, low rolling resistance

## 1. Introduction

The use of silica has become of growing importance in tires because of reduced fuel consumption in automotive transport and consequently preservation of the environment. The high-dispersion silica reinforcement was introduced in the early 1990, by Michelin in passenger tire tread rubbers, the so-called green tire [1], which offers approximately 30% lower rolling resistance, resulting in 5% fuel savings and lower carbon dioxide emission to the environment [2, 3].

The core of the high-dispersion silica technology is the nanoscale reaction of the 4–6 silanol groups per  $\text{nm}^2$  on the surface of the 20–30 nm diameter primary silica particles with a coupling agent. This reaction reduces the hydrophilic character of the filler and increases its compatibility with the rubber polymer [2, 4, 5]. This reaction is due to take place in the same processing step as mixing of the tire compound and is very difficult to lead to completion [6]. The coupling agent eventually creates a chemical link between the primary silica particles and the rubber molecules during the later processing steps of vulcanization [7, 8].

Silica technology as it is used today employs solution-polymerized synthetic elastomers like solution styrene-butadiene rubber (sSBR) and solution butadiene rubber (BR). On the other hand, the great majority of rubber polymers used for carbon-black reinforced tire applications are emulsion polymers such as natural rubber and emulsion styrene-butadiene rubber (E-SBR). Research on reinforcement of the silica-silane system has been extensively investigated, and most of the early silica compound development involved natural rubber as the base polymer [9]. Up until now, natural rubber is not fully utilized in silica technology due to

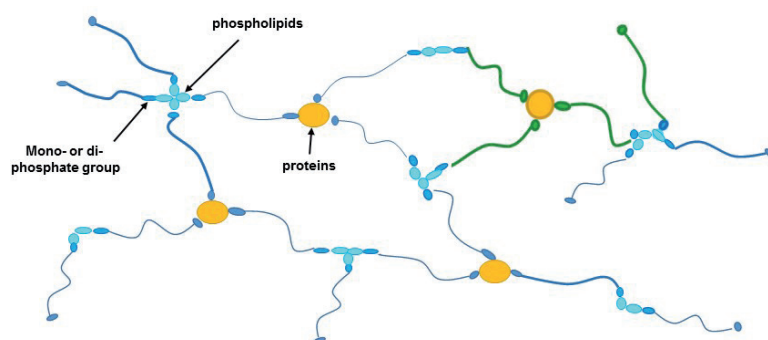
postulation of its ineffectiveness with silane coupling agent. An in-rubber study of the interaction of silica with proteins present in natural rubber shows that proteins compete with the coupling agents for reaction with the silica during mixing, making the silane less efficient for improving dispersion and filler-polymer coupling and consequently affecting the final properties of the compound [10].

Natural rubber is a linear, long-chain polymer with repeating isoprene units ( $C_5H_8$ ) [11]. It has a density of 0.913 at 20°C and glass transition temperature of -72°C [12]. The average molecular weight ( $M_w$ ) of commercial NR is  $1-1.5 \times 10^6$ , and number average molecular weights are  $3-5 \times 10^5$  [13]. The commercial NR is produced from coagulation of latex which is tapped from *Hevea brasiliensis* or rubber tree. The composition of Hevea latex is mainly rubber hydrocarbon of 30–45% weight; nonrubber components for 3–5% and the balance is water. The nonrubber components are proteins, lipids, amino acids, amine, carbohydrates, inorganic materials, and minerals [14].

The fundamental structure of NR has been revealed by NMR studies as a linear rubber chain consisting of initiating terminal ( $\omega$ -terminal), two trans-1,4 isoprene units, long sequence of 1000–3000 cis-1,4 isoprene units, and chain-end terminal ( $\alpha$ -terminal) as shown in **Figure 1** [15–17]. The  $\omega$ -terminal consists of mono- and diphosphate groups linked with phospholipids by hydrogen bond or ionic bond [18]. The  $\alpha$ -terminal is a modified dimethylallyl unit linked with functional groups, which is associated with proteins to form cross-linking via hydrogen bonding. These functional groups at both terminals are presumed to play a role in the branching and gel formation in NR [19, 20]. These secondary structures play a significant role in the strain-induced crystallization of unvulcanized and vulcanized natural rubber [21].

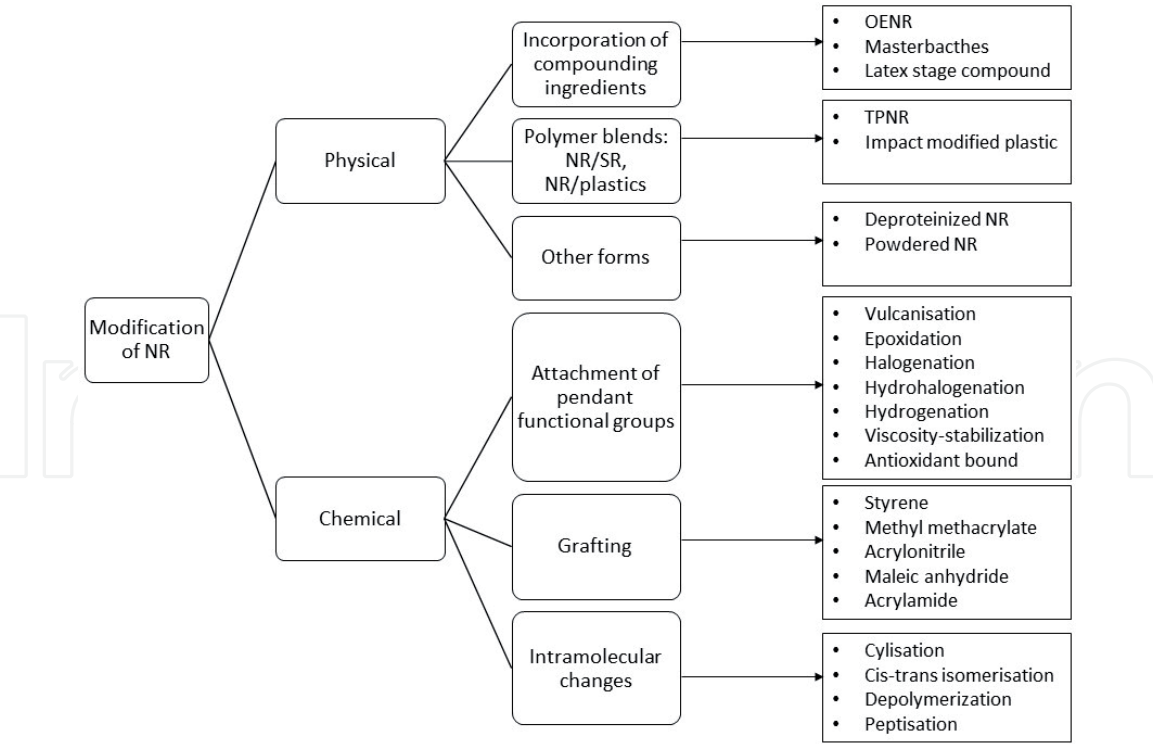
Modification of natural rubber is carried out to improve the behavior of NR during rubber product processing and to improve the in-service performance of the products which can be outside its traditional applications. NR is modified through physical and chemical processes. The major modifications of NR are outlined in **Figure 2** [12]. The physical modification of NR incorporates additives and other compounding ingredients which are not chemically reacting with rubber. Examples of physical-modified form of NR are oil extended NR, thermoplastic NR, powdered NR, and deproteinized NR. The chemical modification of NR involves reacting the NR chains chemically by attachment of pendant functional groups, grafting of different polymers along the rubber chains or through intramolecular changes and bond rearrangement. The chemical-modified form of NR includes epoxidized NR (ENR) [22], hydrogenated NR, and poly-methyl methacrylate (PMMA)-grafted NR.

The first use of silica in truck tire treads based on NR had shown an improvement in tear properties in terms of cut and chip behavior, but the amount used was limited to 25 phr in order to avoid negative effects on tread wear [2]. Higher amounts of silica require coupling agents, which at that time were not used for



**Figure 1.**

*A linear rubber chain structure with naturally occurring network associated with proteins and phospholipids.*



**Figure 2.**  
*Modification of natural rubber.*

silica. From a study on optimization of the mixing conditions of silica-filled NR compounds with silane, an increase of mixing temperature and time for the silica modification with silane enhances the compatibility between silica and NR through a chemical bond between bis-triethoxysilylpropyl-tetrasulfide (TESPT) and the rubber [23]. The overall properties are dependent on the extent of this interaction [23]. The field tests with truck treads demonstrated that the rolling resistance can be improved by 30% when TESPT-modified silica is used in comparison to N220 carbon black. The tread wear index (abrasion resistance) decreases by no more than 5%, and wet traction shows little changes [24].

High reinforcement of properties for silica in NR and other rubbers needs to employ silane coupling agent [2, 7, 9, 25]. High reinforcing effect of silica is obtained with ENR without the use of coupling agents [26, 27] or reduced amount of coupling agent [28]. The vulcanizate properties of silica-filled ENR are comparable to carbon black compound at similar loading and are superior to a silica-filled NR without silane coupling agent (**Table 1**) [26, 29]. A comparison of physical properties of ENR-25—silica tread compound without coupling agent to sSBR/BR—silica compound is shown in **Table 2** [30]. In contrast with sSBR/BR, the ENR compound shows better reinforcement with silica without coupling agent. ENR exhibits both excellent wet grip and very low rolling resistance properties which is an attractive choice for tire tread compound for both passenger car and bus/truck applications [22, 31, 32].

Alternative approaches in incorporating silica into NR as nanocomposites are via in situ sol-gel technique, admicellar polymerization, and polymer-encapsulated silica [33]. Using sol-gel process, solid rubber is swollen in a silica precursor, e.g., tetraethyl orthosilicate (TEOS), followed by the sol-gel reaction, and silica content in the range of 15–22 wt % is achievable with stiffer and stronger tensile strength of 24 MPa. The in situ sol-gel technique on ENR with 3-aminopropyltriethoxysilane (APS) has been reported [34]. The ENR-APS sol-gel system with 28% sol-gel silica has higher tensile properties compared to a conventional ENR-sulfur-cured silica vulcanizate at 27% silica content with no silane coupling agent (**Table 3**) [35]. In

Properties	50 phr carbon black <sup>a</sup>			50 phr silica <sup>b</sup>		
	NR	ENR25	ENR50	NR	ENR25	ENR50
Tensile strength, MPa	29	26	25	24	21	27
Elongation at break, %	495	435	500	720	405	435
M300, MPa	12	12	13	6	13	13
Hardness, IRHD	65	69	73	69	67	68
Compression set 24 h/70°C, %	18	17	21	32	18	22
Akron abrasion (mm <sup>3</sup> /500 rev)	21	14	11	63	15	14
Heat buildup, ΔT, °C	7	7	23	47	7	19
<sup>a</sup> Rubber formulation in phr: rubber 100, filler, oil 5, ZnO 5, StA 2, antioxidant 2, S 2, MBS 1.5.						
<sup>b</sup> Rubber formulation in phr: rubber 100, filler, oil 5, ZnO 5, StA 2, antioxidant 2, S 2, MBS 1.5, DPG 0.5.						

**Table 1.**  
*Comparison of physical properties of black and silica-filled ENR vulcanizates.*

Properties	sSBR/BR*		sSBR/BR*	ENR
	Silica	Silica-TESPT	Black N234	Silica
Filler (phr)	80	80	67.5	50
Tensile strength, MPa	16	20	19	24
Elongation at break, %	780	515	600	550
M300, MPa	3.9	8.4	7.6	9.5
Hardness, IRHD	82	62	65	63
Angle tear, N/mm	39	36	43	40
Akron abrasion, vol loss, mm <sup>3</sup>	41	13	12	<20
Dunlop resilience, %	44	55	38	67
*70/30.				

**Table 2.**  
*Comparison of physical properties of ENR-silica and sSBR/BR tread compounds.*

Properties	ENR-sulfur vulcanizate (no silane)	ENR-APS sol-gel	ENR-APS sol-gel
Silica content (%)	27	28	27
Tensile strength, MPa	12	19	16
Elongation at break, %	390	290	300
M100, MPa	2	7	5

**Table 3.**  
*Comparison of tensile properties of ENR-silica sulfur cured with ENR-APS sol-gel system.*

admicellar polymerization, a bilayer of surfactant (admicelle) is formed on the surface of silica and polymerization of the monomer in the admicelle resulting in an ultrathin layer of polymer covering the silica [33, 36, 37]. The silica modified with admicellar polymerization has superior performance compared to those reinforced with unmodified or silica modified with typical coupling agents [37].



2. Deproteinized natural rubber

Purification of natural rubbers from nonrubber components is possible especially the protein removal. The deproteinization process of natural rubber yields a rubber with reduced protein content significantly as well as low ash and volatile matter which is known as deproteinized natural rubber (DPNR). The deproteinization process can be carried out with natural rubber latex via enzymatic treatment [38–40] or urea treatment [41, 42]. The principle of deproteinization with enzymatic treatment is to hydrolyze the proteins in the natural rubber latex into water soluble which will be removed during washing process of manufacturing the rubber [41, 42].

Structural changes of NR branch points are proposed to occur with the deproteinization process [15]. This is based on the findings that a linear rubber chain contains two types of functional groups at both terminals. After deproteinization, the branch points formed by the functional groups associated with proteins at the  $\alpha$ -terminal through hydrogen bonding decompose and leave the branch points from phospholipid at the  $\alpha$ -terminal. The long-chain branching in the purified NR originated from the interaction of phospholipids which link the rubber chain together [43–45]. The phospholipids are associated together by the formation of a micelle structure.

The commercially available DPNR is Pureprena, which is produced by the Malaysian Rubber Board and licensed to Felda Rubber Industries Sdn Bhd. Pureprena is a purified form of natural rubber and has a very-low-nitrogen, ash, and volatile matter contents as well as being lighter in color (**Table 4**). DPNR is less prone to storage hardening than a normal NR grade. When compounded using an efficient vulcanization (EV) system, DPNR has low creep and stress relaxation, low water absorption, low compression set, and a more consistent modulus when subjected to variable humidity conditions [46]. DPNR gives superior rubber compounds with excellent dynamic properties which are suitable for engineering applications (**Table 5**) [46].

Properties	Specification of SMR 20	Specification of Pureprena
Dirt retained on 44 $\mu$ m aperture (% wt)	0.20 max	0.01 max
Ash content, (% wt)	1.00 max	0.15 max
Nitrogen content, (% wt)	0.60 max	0.12 max
Volatile matter content, (% wt)	0.80 max	0.30 max

**Table 4.**  
*Comparison of raw rubber properties specification of DPNR (Pureprena) and natural rubber (SMR20).*

Features	Applications
Low stress relaxation and low creep	Hydromounts, seals, joint rings, large shock absorbers, suspension bushes, helicopter rotor bearings
Low water absorption	Underwater applications, large shock absorbers
Good dynamic properties	Anti-vibration mountings, surge fenders
Low protein and low ash	Medical, pharmaceutical, and food applications

**Table 5.**  
*Areas of application of DPNR.*

3. Carbon black reinforcement of DPNR

The reinforcing of DPNR by carbon black has been studied in the past [46, 47]. For mixing carbon black and natural rubber, a high reinforcement can be obtained with good dispersion of filler as there is strong physical interaction between the carbon black and the rubber. DPNR-CV is a grade of viscosity stabilized at between 60 and 70 Mooney units. The typical vulcanizate properties of DPNR-CV in comparable to SMR CV is shown in **Table 6** [46]. DPNR-CV gives lower water absorption and compression stress relaxation. **Table 7** shows the physical properties of DPNR filled with carbon black at 50 phr loading and cure using EV system [46]. Similar results are observed where DPNR gives lower water absorption and compression stress relaxation.

The recent evaluation of DPNR (Pureprena) shows that its physical properties are comparable to SMR CV and SMR 10 (**Table 8**). Comparison of DPNR with synthetic polyisoprene (IR) is reported where DPNR shows similar tensile properties and low water absorption to IR (**Table 9**) [48]. The rubber compound using DPNR with total nitrogen content adjusted in the range of 0.12–0.3% by weight exhibits an improved low hysteresis loss property, excellent abrasion resistance, and remarkably excellent tear resistance which is advantageous to be used for tire tread [49].

Properties	DPNR-CV	SMR CV	SMRL
Tensile strength, MPa	33	32	33
Elongation at break, %	570	550	520
M100, MPa	2.4	2.9	2.7
M300, MPa	11.5	13.3	14.5
Hardness, IRHD	60	63	59
Resilience, %	69	68	70
Volume swell in water: 7 day/23°C, %	0.6	0.9	0.9
Compression stress relaxation: 25% strain, 7 day/23°C, %	10.5	12.4	11.5

*\*Rubber formulation: rubber 100, N330 35, ZnO 5, StA 2, TBBS 0.7, S 2.25. Cheang KT, Rais AR, Basir KB. Deproteinised Natural Rubber (DPNR), Malaysian Rubber Board (MRB) Monograph No. 10, C&D Trading, Kuala Lumpur, (2003).*

**Table 6.**  
Typical vulcanizate properties of DPNR-CV.

Properties	DPNR CV	SMR CV
Tensile strength, MPa	26	27
Elongation at break, %	520	480
M300, MPa	11.3	13.5
Resilience, %	63	67
Hardness, shore A	52	55
Volume swell in water: 7 day/23°C, %	0.9	1.3
Compression stress relaxation: %, 25% strain, 7 day/23°C	8.6	11.7

*\*Rubber formulation: rubber 100, N774 50, ZnO 5, ZEH 2, Permanex TQ 2, MOR 1.44, TBTD 0.6, S 0.6, cured at 150°C for 20 min. Cheang KT, Rais AR, Basir KB. Deproteinised Natural Rubber (DPNR), Malaysian Rubber Board (MRB) Monograph No. 10, C&D Trading, Kuala Lumpur, (2003).*

**Table 7.**  
Physical properties of DPNR.

Properties	DPNR	SMR CV	SMR L	SMR10
Tensile strength, MPa	28	26	27	27
Elongation at break, %	590	560	570	570
M100, MPa	2.4	2.4	2.4	2.5
M300, MPa	12.0	12.3	12.4	12.3
Hardness, IRHD	71	68	69	70
Resilience, %	55	57	58	55
Abrasion resistance index (ARI), %	109	106	110	114
<i>*Rubber formulation: rubber 100, N234 60, ZnO 3, StA 2, 6PPD 2, Wax 1, TDAE 8, CBS 1.5, S 1.5, cured at 150°C for 6 min.</i>				

**Table 8.**  
*Physical properties of DPNR (Pureprena).*

Properties	DPNR <sup>#</sup>	IR <sup>##</sup>	SMR CV
Tensile strength, MPa	24	23	26
Elongation at break, %	700	730	700
M100, MPa	0.8	0.8	0.8
M300, MPa	2.6	2.5	2.6
Hardness, IRHD	42	40	41
Resilience, %	84	84	85
Compression set, 22 h 70°C, %	12	5	11
Volume swell in water: 7 day/23°C, %	0.1	0.2	0.4
3 day/100°C, %	1.7	1.5	3.8

*\*Rubber formulation: rubber 100, N774 20, ZnO 4, ZEH 2, TMQ 2, accelerator 1.44, accelerator 2 0.7, S 0.7.*

*<sup>#</sup>Pureprena.*

*<sup>##</sup>SK1-3.*

*Abd Rahim R, Zaeimoedin TZ, Muhamad AK, Sarkawi SS. New Process Deproteinised Natural Rubber (Pureprena): Raw Rubber, Processability and Basic Physical Properties, Malaysian J. Analytical Sciences. 2016; 20(5):1145-1152.*

**Table 9.**  
*Comparison of physical properties of DPNR with IR.*

#### 4. Silica reinforcement of DPNR

The reinforcement of rubber by silica is different from the reinforcement by carbon black. The use of conventional silica has been limited to a white filler for colored rubber compounds [2] such as shoe soles, until the introduction of bifunctional silanes as coupling agents back in the 1970s [50]. In 1992, Michelin patented the silica-filled rubber compound for the production of all-season high-performance tires [1], which provide an excellent compromise of low rolling resistance, good traction on wet and snow-covered roads, as well as noise reduction. The rubber compound is a blend of high-vinyl solution SBR and high-cis BR filled with highly dispersible silica [51] at a loading of 80 phr and an organosilane coupling agent. Since then, a lot of work on reinforcement of silica in SBR-based passenger car tires has been investigated [2, 7, 24, 52–54].

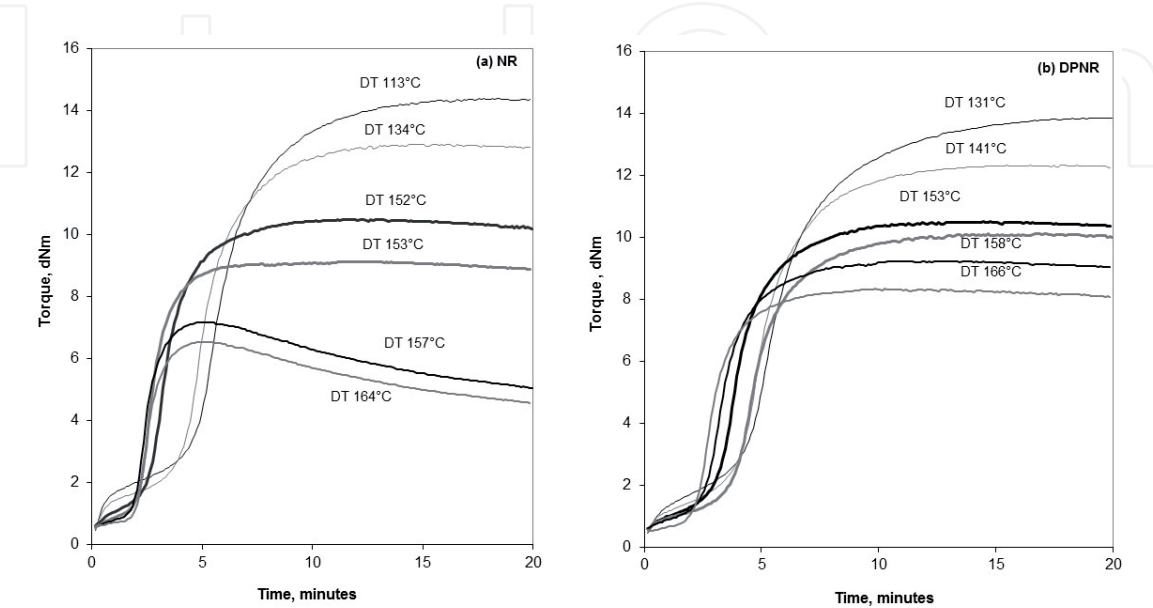
The in situ treatment of silica with silane is commonly adopted for mixing silica with rubber rather than the use of pre-reacted silica-silane. Compared to mixing carbon black, the in situ mixing of silica-silane in rubber requires optimal



silanization to be completed to obtain high reinforcement [7]. The silanization is influenced by the temperature as it is a chemical reaction. Hence, mixing temperature is the parameter of paramount importance in mixing silica and rubber in the presence of coupling agent such as TESPT [55, 56]. The temperature has a more dominant effect than time in the silica-TESPT reaction [23]. In order to achieve a sufficient degree of silanization, the temperature during mixing should be between 150 and 160°C. However, above 160°C either the coupling agent starts to prematurely react with the rubber matrix or the TESPT starts to donate sulfur; both result in pre-scorch of the compound. A mixing time of at least 10 minutes at 150°C is necessary to ensure complete coupling of the silica and the silane and that the reaction between the silica and the silane takes place primarily during the first mixing step [50]. In an investigation of cure characteristics of NR and TESPT in comparison with SBR, it clearly shows that NR starts to react with TESPT at a temperature of 120°C but SBR only reacts with TESPT at a higher temperature of 150°C [56].

4.1 Influence of mixing dump temperature in silica-DPNR compound

The properties of silica-filled compounds show a strong dependence on mixing temperature, since the silanization reaction and silica dispersion are key parameters in this system [25]. The optimal mixing conditions for silica-filled NR compounds with TESPT as a coupling agent are required to obtain high reinforcement in NR [56]. The influence of the dump temperature of the first mixing step on the vulcanization behavior of the DPNR-silica compounds as compared to the NR-silica compounds is illustrated in **Figure 3**. Dump temperature is the final temperature reached when the compound is discharged from the internal mixer. The compound formulation is described in **Table 10**. The vulcanization curves and behavior of the NR-silica compounds can be divided into three groups according to dump temperature. The first group encompasses the compounds with low dump temperatures (below 150°C), the middle group is represented by the compounds with moderate dump temperatures around 150–155°C, and the third group is the compounds with high dump temperatures (>155°C). At low dump temperature region, both NR-silica and DPNR-silica compounds display pronounced silica flocculation as evidenced by initial torque rise, high maximum torques, and long scorch times. At



**Figure 3.** Vulcanization behavior at 150°C of (a) the NR compounds and (b) the DPNR compounds, mixed till different dump temperatures (DT) in the first mixing stage.

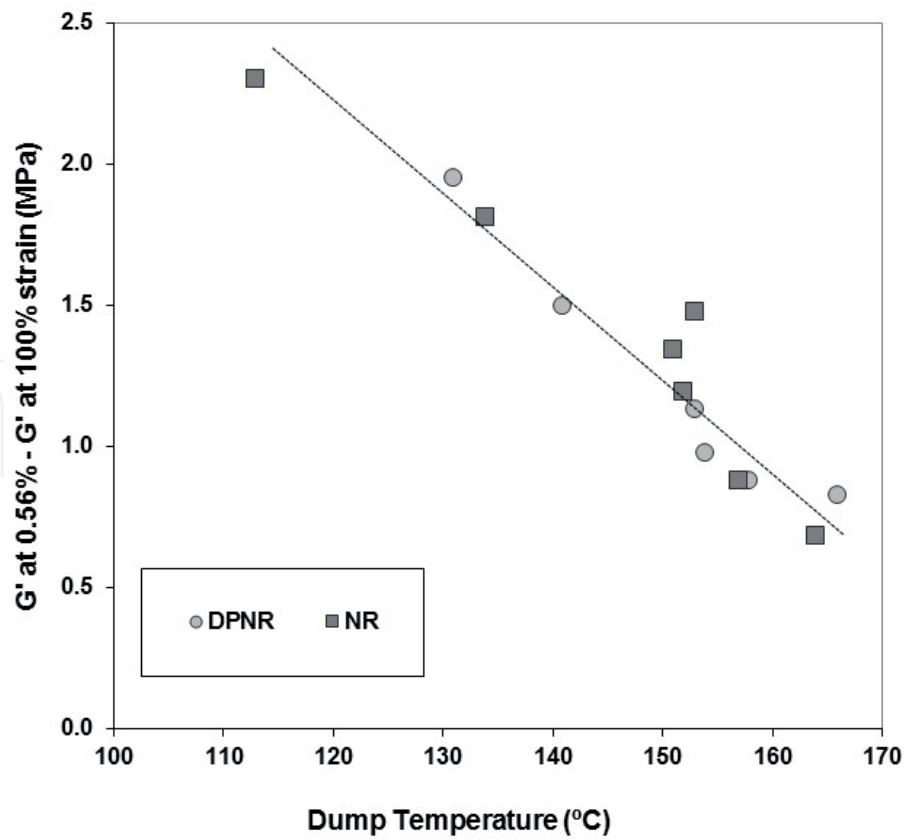
Ingredients	Amount (phr)
Natural rubber (vary as stated in text)	100
Silica Ultrasil 7005	55
Silane TESPT	5
Zinc oxide	2.5
Stearic acid	1
TDAE oil	8
TMQ	2
Sulfur	1.4
CBS	1.7
DPG	2

**Table 10.**  
*Basic compounding formulation used for NR and DPNR.*

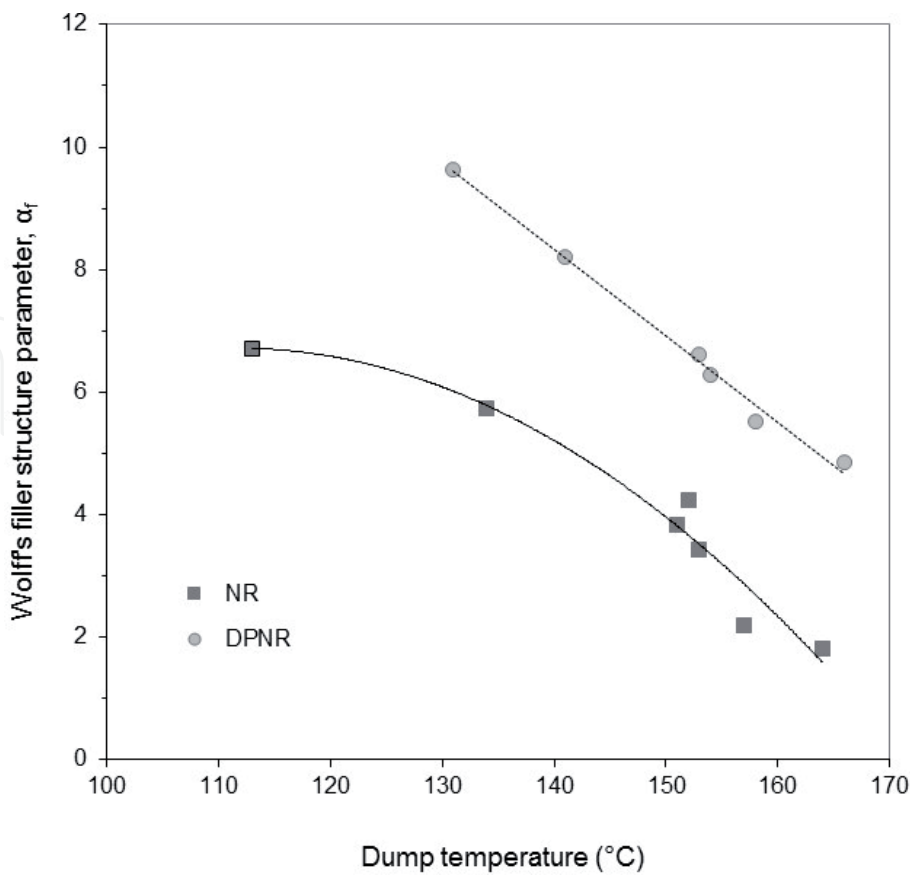
moderate dump temperature region, no appearance of flocculation is observed for NR-silica and DPNR-silica compounds but at lower maximum torques and shorter scorch times compared to those of the compounds with low dump temperature. The maximum torque of the DPNR compound mixed at moderate temperature (around 150°C) is comparable with the NR compound at higher dump temperature region; both NR- and DPNR-silica compounds display a lower maximum torque and no sign of flocculation as the silanization reaction increases and results in a reduction of silica-silica interaction. Nonetheless, the decrease in maximum torque for the DPNR compound at higher dump temperature is much less compared to the NR-silica compound. The low-protein content in DPNR may attribute to better silanization in the compound which gives more filler-to-rubber linkages. Noticeably in the vulcanization curves for these high dump temperatures, there is clear indication of reversion for NR-silica compound. This reversion sign in vulcanization curve has also been reported in NR compound in the presence of TESPT at temperature higher than 150°C where the behavior is totally different as compared to SBR compound [56]. The DPNR-silica compounds show no sign of reversion at high dump temperature as seen in NR compounds. This suggests that a different network structure in the DPNR contributes to the thermal resistance of the cured compound.

A comparison of filler-filler interaction in DPNR-silica-TESPT compounds with NR-silica-TESPT as a function of mixing temperature is shown in **Figure 4**. A common way to measure the filler-filler interaction is calculating the Payne effect from the strain sweep of the dynamic testing or different in the storage modulus of the low or 0.56% and high strain or 100% while maintaining the frequency and temperature at constant value. Both NR- and DPNR-silica-TESPT show the decreasing trend of Payne effect with increasing dump temperature. This trend is due to the increase of silanization reaction with increasing temperature which results in the efficiency of the silane to hydrophobize the surface of the silica. High Payne effect of NR- and DPNR-silica compounds at low dump temperature is in agreement with the sign of flocculation observed in vulcanization curve. The results are also in agreement with other works reported on compound comprising TESPT showed a reduction of flocculation of silica when mixed at higher dump temperature [56, 57].

**Figure 5** illustrates the effect of mixing temperature on Wolff’s filler structure parameter,  $\alpha_f$ . Wolff’s filler structure parameter,  $\alpha_f$ , is determined from the ratio



**Figure 4.**  
*Payne effect of silica compounds with silane TESPT as a function of dump temperature (□) NR and (●) DPNR.*



**Figure 5.**  
*Effect of dump temperature on Wolff's filler structure parameter,  $\alpha_f$  of silica-reinforced compounds: (□) NR and (●) DPNR.*

between the increase in rheometer torque during vulcanization of the filled compounds and that of the unfilled gum [24]:

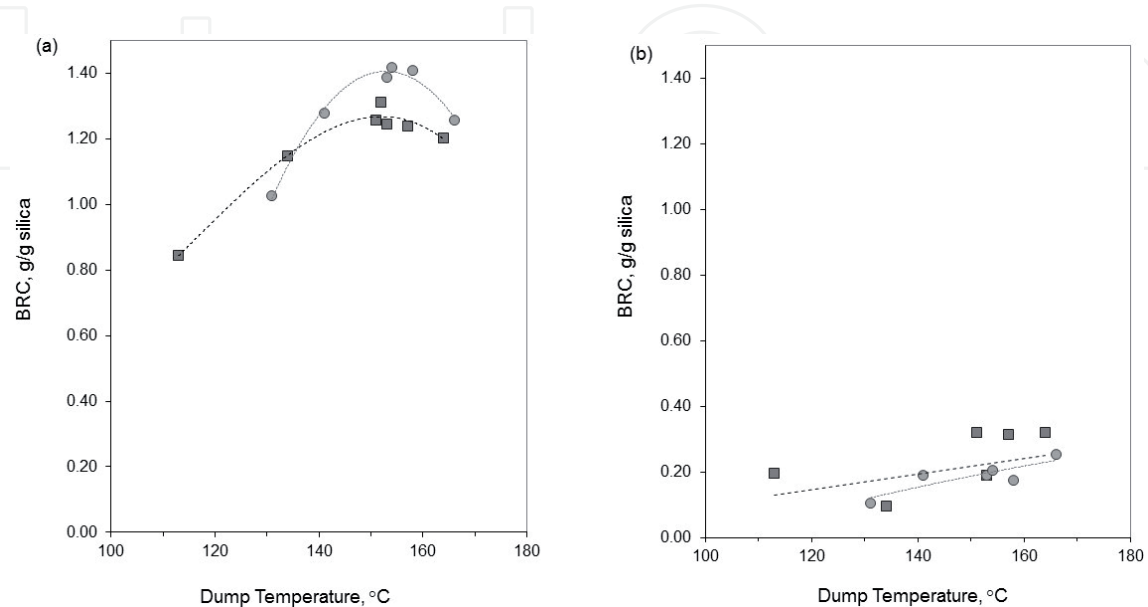
$$\frac{D_{\max} - D_{\min}}{D_{\max}^0 - D_{\min}^0} - 1 = \alpha_f \frac{m_f}{m_p} \tag{1}$$

where  $D_{\max} - D_{\min}$  is the maximum change in torque for the filled rubber,  $D_{\max}^0 - D_{\min}^0$  is torque difference in unfilled rubber, and  $m_f/m_p$  is the ratio of filler to polymer by weight.

As observed earlier with the Payne effect,  $\alpha_f$  is reduced with increasing dump temperature for the DPNR and NR compounds. Better hydrophobation leads to a decrease in silica-silica interaction and consequently results in reduced  $\alpha_f$ . The DPNR compound shows a higher  $\alpha_f$  than the NR compound, indicating a different type of filler and rubber network in the two compounds.

The filler-to-rubber interaction of silica-filled DPNR can be assessed from bound rubber content (BRC). Bound rubber is the layer of rubber polymer that covers the filler surface and unextracted by the solvent during swelling process. The bound rubber content is a combination of tightly bound rubber skin and loosely bound rubber shell [58]. These combination or referred to as total BRC can be measured using the bound rubber measurement in normal atmosphere. The tightly bound rubber skin can be measured from bound rubber measurement in an ammonia atmosphere which is referred to as the chemically BRC [59, 60].

The chemically and physically bound rubber content of silica-filled DPNR as compared to silica-filled NR is illustrated in **Figure 6**. The chemically bound rubber of both silica-filled NR and DPNR increases with increasing dump temperature up to 150°C. The increase of chemically bound rubber as a function of dump temperature for NR-silica-TESPT system has been reported [56, 25]. This can be explained by the higher rate of silanization with increasing mixing temperature. However, at 150°C, there is saturation in the amount of TESPT which has reacted and the surface of silica covered. Precipitated silica has about four to five silanol groups per nm<sup>2</sup>. Hence, there is no increase in chemically bound rubber for compounds mixed till above 150°C dump temperature. Above 150°C, the chemically bound rubber slowly decreases for DPNR and NR. In comparison, DPNR has more chemically

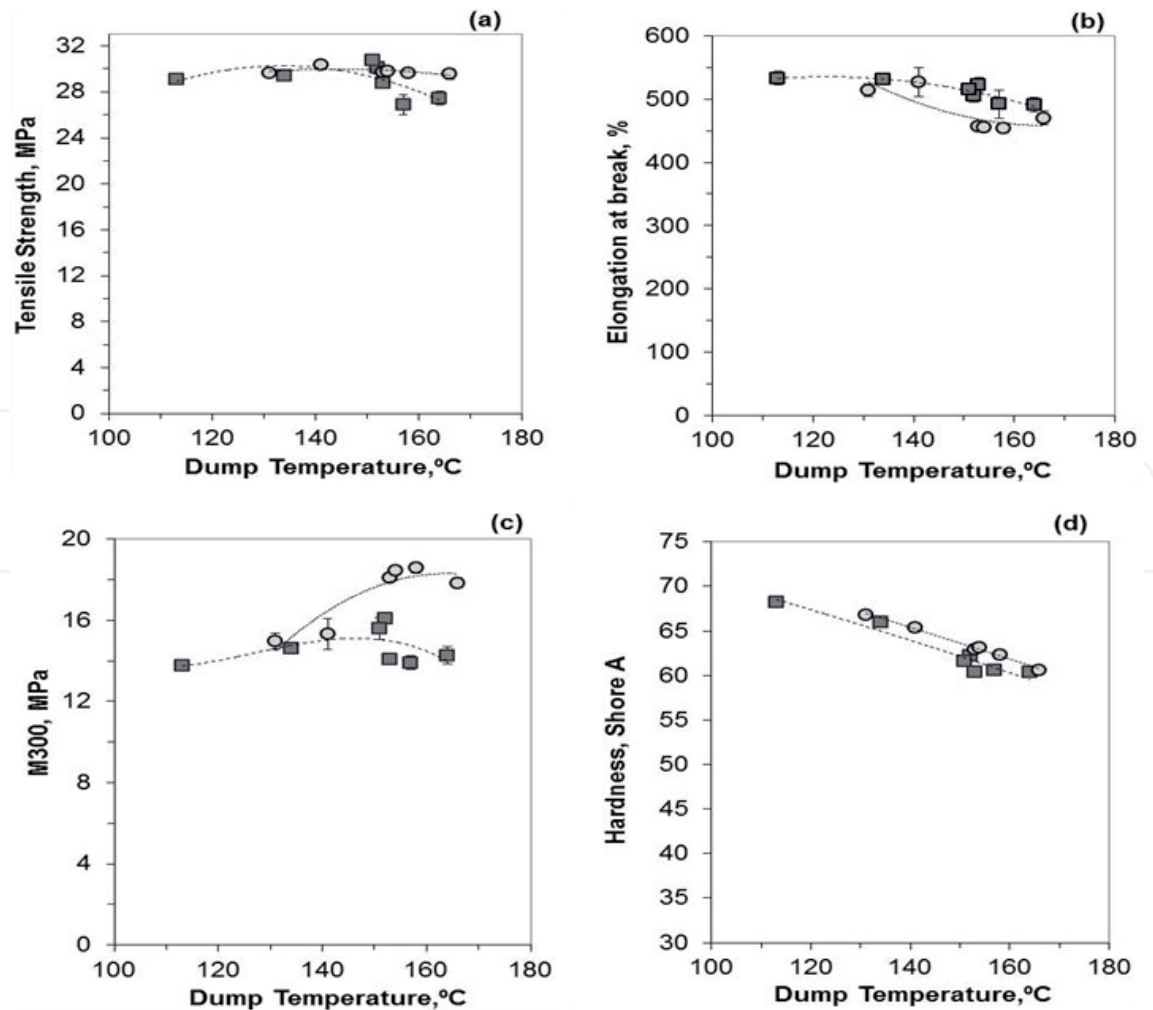


**Figure 6.** Comparison of (a) chemically and (b) physically bound rubber content of silica compound containing TESPT at varying dump temperature: (□) NR and (●) DPNR.

bound rubber than NR, particularly at high dump temperature. In **Figure 6(b)**, the small increase in the physically bound rubber of the DPNR-silica and NR-silica compounds containing TESPT at higher dump temperature can be explained by the saturation of silica-TESPT coupling. Additional interactions above 150°C between the non-hydrophobized silica surfaces and rubber are physical of nature.

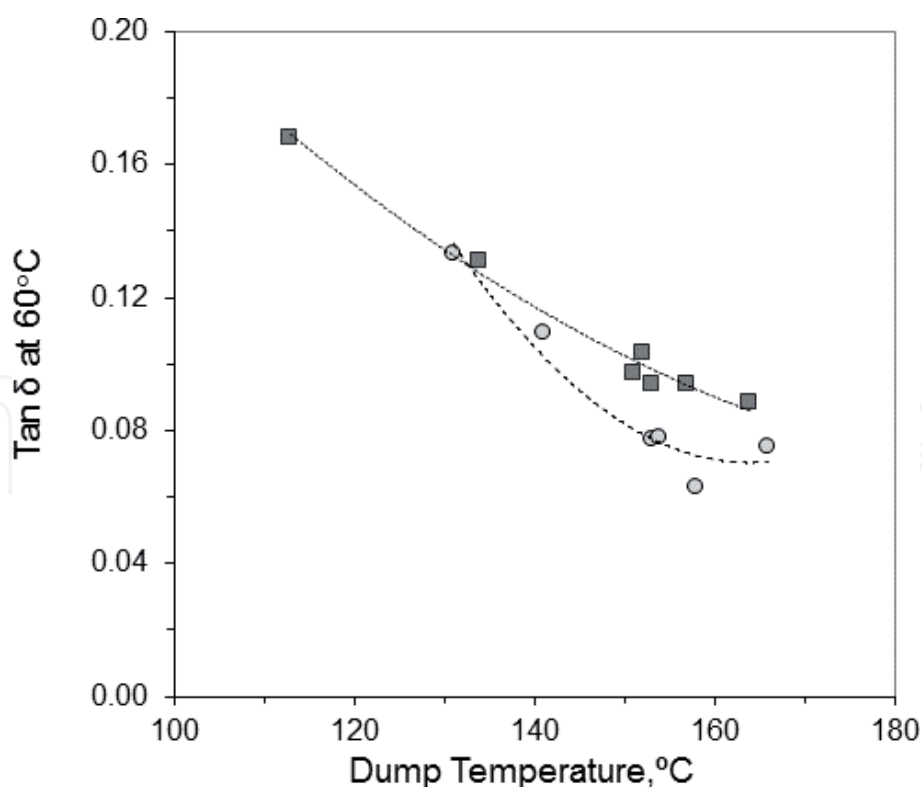
The effect of dump temperature on the physical properties of silica vulcanizates is depicted in **Figure 7**. At dump temperatures above 150°C, NR vulcanizate shows a clear reduction in tensile strength and is in good agreement with the occurrence of reversion and decrease in the maximum torque observed in the vulcanization curve. This shows that mixing temperature is of importance for the NR-silica compounds. This observation is also seen in the case of synthetic equivalent of NR, IR [61]. However, this reduction in tensile strength at high dump temperature is not seen for the low-protein DPNR-silica vulcanizates. The elongation at break for the NR and DPNR vulcanizates reduces slightly with increasing dump temperature.

A decrease in both moduli at 300% elongation (M300) and 100% elongation (M100) at higher dump temperatures is seen for the NR vulcanizates. In contrast, DPNR vulcanizates exhibit higher moduli with the increasing mixing dump temperature. The reduction in the tensile properties of NR at high mixing temperature is in good agreement with the occurrence of reversion and decrease in the maximum torque observed in their vulcanization curves. In addition, it has been reported that the reinforcement index (M300/M100) and tear resistance of NR-silica-TESPT vulcanizate is improved with increasing dump temperature to an optimum point



**Figure 7.** Physical properties of silica vulcanizates: (□) NR and (●) DPNR; (a) tensile strength, (b) elongation at break, (c) modulus at 100% elongation (M100), (d) modulus at 300% elongation (M300).





**Figure 8.**  
The effect of dump temperature on tan delta at 60°C of silica compound: (□) NR and (●) DPNR.

of 135–150°C [56]. In contrast, reversion is not seen in the vulcanization curve of DPNR, and the effect of dump temperature on torque difference is also smaller. Another possible reason for the better properties achieved for DPNR is the difference in the naturally occurring networking as compared to NR. The network structure of purified DPNR has been proposed is associated with phospholipids linking both terminal end groups of the rubber chain via hydrogen bonding and ionic linkages, while the protein bonds are released because of deproteinization [43].

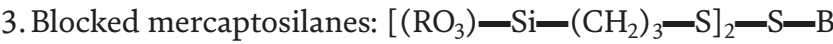
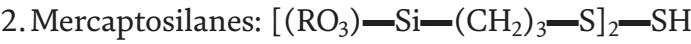
Commonly, the loss  $\tan \delta$  at 60°C of a cured compound is employed as indication for the rolling resistance of tires made thereof. The lower the  $\tan \delta$  at 60°C, the lower the rolling resistance expected in real tire performance. **Figure 8** illustrates indications of rolling resistance of the silica-filled vulcanizates. Both NR and DPNR vulcanizates show a strong decrease in  $\tan \delta$  at 60°C with increasing dump temperature. This must obviously be the result of more coupling of silica to the rubber with greater silanization efficiency at high temperatures. The DPNR vulcanizates exhibit the lowest  $\tan \delta$  at 60°C at high dump temperature. This actually relates well with the higher chemically bound rubber content of DPNR compared to the NR compound.

In general, DPNR shows better mechanical and dynamic properties as compared to NR. The decrease in the mechanical properties of NR vulcanizates mixed at high dump temperature correlates well with the reversion sign in vulcanization curve and decrease in the maximum torque. Interestingly, the DPNR-silica compounds show no sign of reversion at high dump temperature as seen in NR compounds and better retention of the properties.

#### 4.2 Influence of silane coupling agents

Organofunctional silanes used for sulfur-cured rubber compounds can be categorized into the following groups [25]:

1. Di- and polysulfidic silanes:  $[(RO_3)-Si-(CH_2)_3-S]_2-S_x$



where R = CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub> or other groups, B = CN or C<sub>7</sub>H<sub>15</sub>C=O, and x = 0–8.

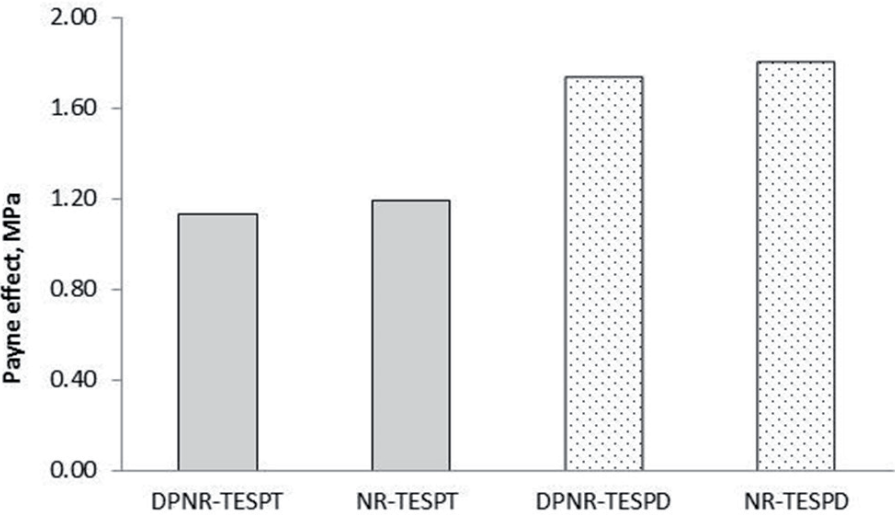
The comparison of reinforcing effect of different types of silane in DPNR-silica compound is given in **Table 11**. Silane Si-69 is an organosilane TESPT from Evonik. X50s is a blend of silane Si69 and N330 black in the ratio 1:1 by weight, and it is in solid form. All types of silanes give high reinforcement of silica in DPNR especially TESPT with excellent tensile properties and better abrasion resistance.

The commonly and effectively used silane coupling agent in rubber system is TESPT. The polysulfidic silanes like TESPT contribute additional sulfur to the compound unlike the other type of silanes. The influence of sulfur ranks in polysulfidic silane is compared between silica-DPNR and silica-NR. Bis-triethoxysilylpropyl-disulfide (TESPD) has an average sulfur rank of 2.2, while TESPT has an average sulfur rank of 3.83. The compound is prepared based on the earlier formulation (**Table 10**), and 4.4 phr of TESPD is used as the equivalent moles to 5 phr TESPT in

Properties	Polysulfidic silane		Mercaptosilane	Block mercaptosilane
Silane	Si-69	X50S	Si 363	NXT
phr	5	10	6.2	5
Tensile strength, MPa	31	31	28	30
Elongation at break, %	560	550	540	600
M100, MPa	2.8	2.9	2.9	2.3
M300, MPa	13.3	14.2	13.1	10.2
Hardness, IRHD	67	69	65	65
Resilience, %	67	68	74	64
Abrasion resistance index (ARI), %	120	123	121	108

*\*Rubber formulation: rubber 100, Zeosil 1165 55, ZnO 3, StA 2, TMQ 2, TDAE 8, DPG 1.1, CBS 1.5, S 1.5, cured at 150°C for 10 min.*

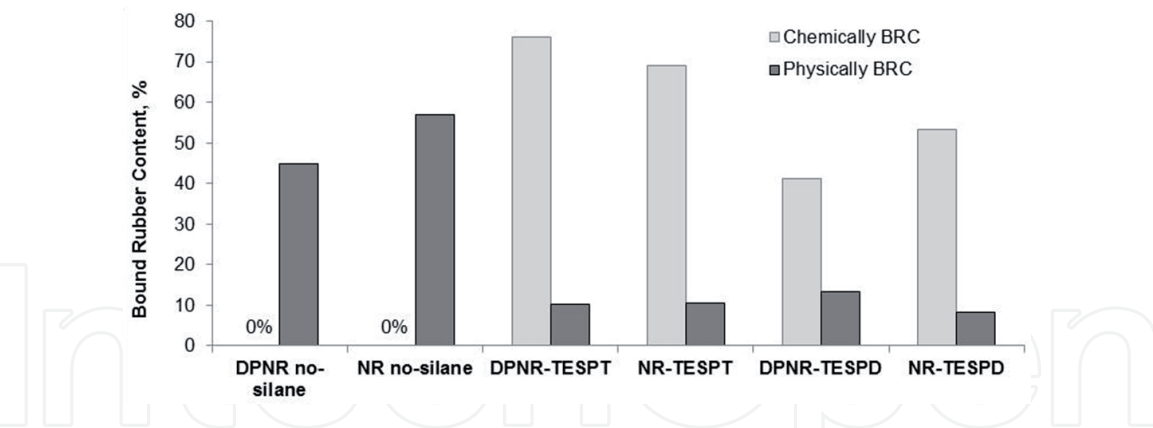
**Table 11.**  
Physical properties of DPNR-silica with different type of silanes used.



**Figure 9.**  
Comparison of Payne effect between TESPT and TESPD compound.

ethoxy functionality. The TESP<sub>D</sub> and TESPT were compared on an equimolar basis with correction for the missing sulfur in the final mill mixing stage. The optimal loading of TESPT is at approximately 9.0% wt relative to the amount of silica [62]. In **Figure 9**, the Payne effect between NR and DPNR compounds is compared. DPNR compounds show slightly lower Payne effect compared to NR either with TESPT or TESP<sub>D</sub>. For both NR and DPNR compounds, the Payne effect of compound with TESP<sub>D</sub> is higher than those with TESPT. In this case, the reactivity of TESPT toward silica is higher in hydrophobizing silica surface than TESP<sub>D</sub> in both rubbers. The silanization silica with TESP<sub>D</sub> occurs at lower rate than TESPT. Similar observation has been reported where the TESPT-based NR compound shows lower filler-filler interaction and better silica dispersion than those of the TESP<sub>D</sub> compounds [63].

The comparison of BRC between NR- and DPNR-silica compounds both with and without silanes is shown in **Figure 10**. The use of silanes TESPT and TESP<sub>D</sub> in NR- and DPNR-silica compounds results in almost totally chemically BRC formation. The silanization of silica with TESP<sub>D</sub> or TESPT has successfully hydrophobize silica surface through silica-TESPT and silica-TESP<sub>D</sub> couplings. The silica-silane coupling is translated into reduction of the specific component of the surface energy of silica,  $\gamma_{sp}^s$ , and gives rise in the interaction of rubber and filler. DPNR-TESPT shows slightly higher chemically BRC than NR-TESPT-silica compound. In comparison, both DPNR and NR compounds with TESPT have higher BRC than compound with TESP<sub>D</sub>. This corresponds well with the lower Payne effect of the DPNR-silica compounds with TESPT as compared to with TESP<sub>D</sub>. For both DPNR- and NR-silica compounds without silane, only physically BRC, are formed as no chemically BRC is obtained after ammonia treatment. It is interesting to see that NR-silica without silane has higher physically BRC compared to DPNR-silica without silane. This relates back to the interaction of proteins with silica that provide filler-rubber



**Figure 10.**  
Comparison of bound rubber content between TESPT and TESP<sub>D</sub> compounds.

Compounds	TS (MPa)	EB (%)	M100 (MPa)	M300 (MPa)	Hardness (shore A)	tan δ at 60°C
DPNR-silica-TESPT	29.7	460	3.5	18.1	63	0.077
NR-silica-TESPT	28.8	520	2.4	14.1	61	0.094
DPNR-silica-TESP <sub>D</sub>	29.4	520	3.8	14.9	70	0.139
NR-silica-TESP <sub>D</sub>	29.5	550	2.6	13.3	64	0.145

*\*Rubber formulation: rubber 100, Ultrasil7005 55, silane 5, ZnO 2.5, StA 1, TMQ 2, TDAE 8, DPG 2, CBS 1.7, S 1.4, cured at 150°C for 7 min.*

**Table 12.**  
Comparison of physical properties between DPNR-TESPT and DPNR-TESP<sub>D</sub> vulcanizates\*.

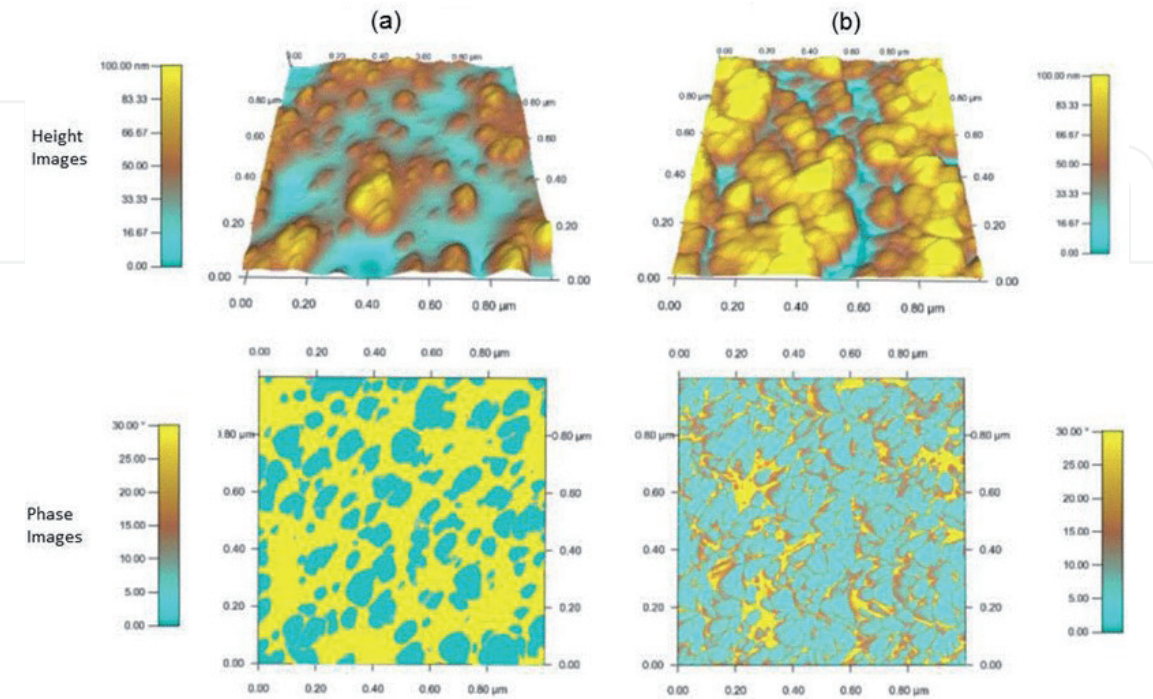
network in the NR-silica [64]. With reduced protein present in the DPNR, less network are formed in comparison to NR and this is reflected with lower BRC.

The comparison of physical properties between DPNR-silica-TESPT and DPNR-silica-TESPD vulcanizates is shown in **Table 12**. The tensile strength for all vulcanizates is not affected by the type of silane. The tensile properties of DPNR vulcanizate are comparable to NR vulcanizates. The indication of rolling resistance of the tread compounds can be observed from  $\tan \delta$  at 60°C from temperature sweep using dynamic mechanical testing. It is obvious that the use of TESPT gives lower  $\tan \delta$  at 60°C for DPNR-silica and NR-silica compounds as when compared to those using TESP. A study on the role of different functionalities in silane on silica-filled NR has shown that the TESPT gives superior efficiency than TESP due to the effect of sulfur donation by TESPT [65]. In addition, the DPNR vulcanizates generally give lower  $\tan \delta$  at 60°C than the NR vulcanizates which indicate an improvement in rolling resistance of tread compound made from DPNR.

4.3 Morphology of silica-reinforced DPNR

The dispersion morphology of silica-DPNR vulcanizates as compared to silica-NR vulcanizates by AFM morphology in the absence of silane coupling agent is illustrated in **Figure 11** [58]. The size of the silica aggregates in DPNR without silane is bigger than in the NR vulcanizate as seen from the height image at  $1 \times 1 \mu\text{m}$ . The phase image of DPNR-silica without silane shows smaller silica aggregates of 100nm size as dispersed in the matrix. The size of the silica aggregates in the DPNR vulcanizate is almost comparable to that in NR, although they seem to be closer together.

An improved micro-dispersion of silica in DPNR and NR vulcanizates with the use of TESPT is shown in AFM height images in **Figure 12** as compared to morphology without coupling agent. Primary particles of silica in the size of 50 nm are clearly visible in both DPNR and NR in addition to silica aggregates of approximately 100nm. The difference between DPNR and NR can be observed from the phase image. The distances between the silica aggregates of size 50–100 nm are



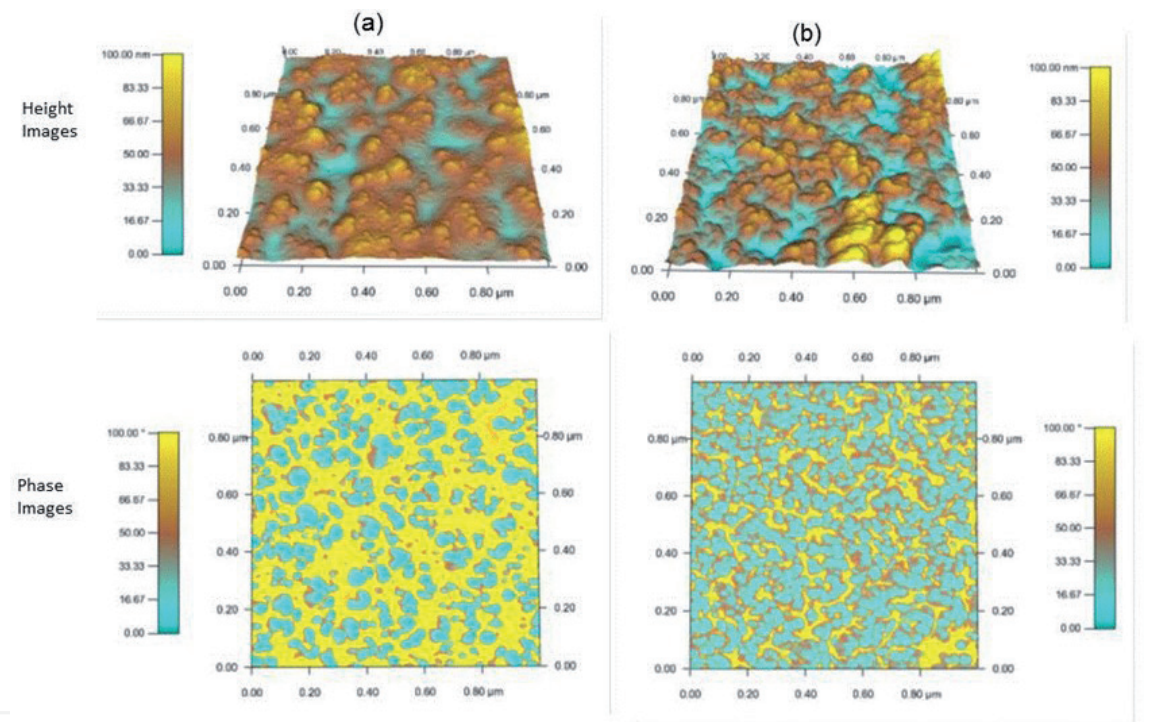
**Figure 11.** Micro-dispersion of silica in NR and DPNR vulcanizates in the absence of silane coupling agent (a) NR-silica (b) DPNR-silica.



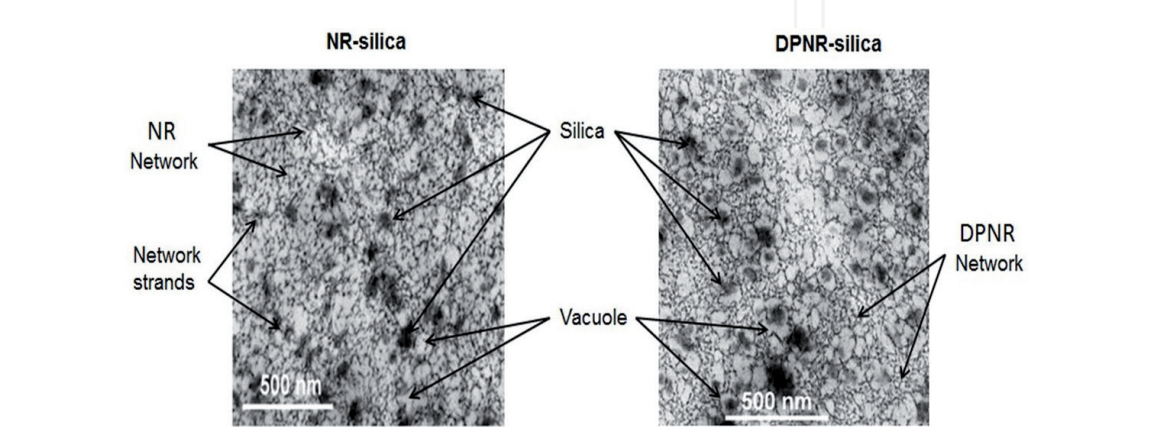
clearly visible in the NR-silica-TESPT vulcanizate. However, in DPNR-silica-TESPT, the distance between the aggregates looks a little smaller, indicating a somewhat better micro-dispersion. Besides, there is an intermediate region between the silica and rubber phases, suggesting the bound rubber layer [65–67].

Attempting to analyze the morphology of filler-to-rubber interactions in silica compounds at high loading, which in this study is 55 phr of silica, is difficult as the silica aggregates are very close together. In order to gain insight into the filler-to-rubber interaction, TEM network visualization was carried out where the vulcanizate was swollen in styrene, styrene polymerized, staining the rubber network and visualization using TEM [68].

TEM network visualizations of silica-filled NR and silica-filled DPNR vulcanizates without silane coupling agent are depicted in **Figure 13**. Silica aggregates of around 50–100 nm size can be seen as dark particles throughout the DPNR and NR vulcanizates. The rubber network can be visualized after the staining process, and the region is identified with mesh structure. Likewise, the region of

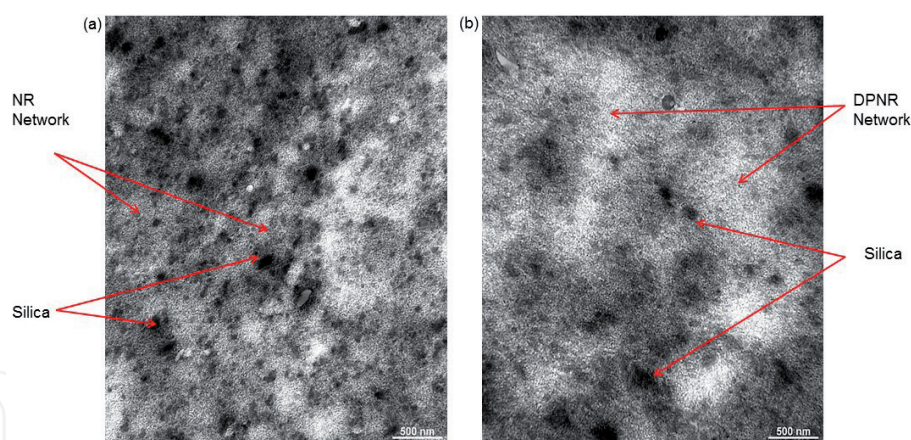


**Figure 12.** Micro-dispersion of silica in NR and DPNR vulcanizates in the presence of silane coupling agent (a) NR-silica (b) DPNR-silica.



**Figure 13.** Comparison of TEM network visualization micrographs of silica-filled NR and DPNR vulcanizates without coupling agent.





**Figure 14.** Comparison of TEM network visualization micrographs of silica-filled (a) NR and (b) DPNR vulcanizates with silane coupling agent, TESPT.

polystyrene is the unstained part. Some silica aggregates in silica-filled NR are surrounded by voids or vacuoles, and some have connecting network strands to the NR network. This indicates there exist some bondings of silica to the rubber networks. This observation is totally different with the network visualization of the silica-filled DPNR. The silica aggregates in the DPNR system without silane have clear vacuoles surrounding them [62]. The vacuoles are formed through polymerization of styrene in the gap between the silica aggregates and the rubber chain. The formation of such vacuoles is due to a weak interface between silica particles and rubber chains [66]. The weak filler and rubber interaction in the system without silane is derived from the silica characteristic of surface energy with low dispersive component,  $\gamma_{sd}$ , which results in less adsorption of rubber chains to the surface of the silica. There are less vacuoles present in the NR vulcanizate as compared to the DPNR vulcanizate without silane, which suggests higher filler-to-rubber interactions in the former.

A comparison of the TEM network visualization between NR and DPNR vulcanizates with TESPT coupling agent included is shown in **Figure 14**. The presence of TESPT results in strong attachment of rubber chain to the surface of silica aggregates. No sign of vacuoles present in the system after network visualization. This is due to the establishment of chemical bonding between silica-TESPT-rubber in the compound during silanization and vulcanization. In addition, the size of silica aggregates in both NR and DPNR with TESPT is smaller than those without TESPT. This relates to the results of low Payne effect and high chemically BRC for NR and DPNR reinforced with silica and silane system. In addition, the vulcanizates with silanes exhibit denser rubber network compared to those without silane. This is in agreement with the results of cross-link density where the silica-filled NR and DPNR with TESPT have higher cross-link density compared to those without silane due to sulfur released from TESPT [62].

## 5. Conclusions

Deproteinized natural rubber is a purified form of natural rubber, which is characterized by its very low nitrogen, ash, and volatile matter contents compared to the commercial natural rubber. Similar to natural rubber, DPNR can be reinforced with carbon black as well as silica according to the intended applications.

DPNR reinforced with carbon black filler has low creep and stress relaxation, low water absorption, low compression set, and a more consistent modulus. Carbon

black-filled DPNR exhibits excellent dynamic properties which are suitable for engineering applications.

Reinforcement of DPNR by silica filler is different from carbon black as silane coupling agent is required. Mixing temperature has a dominant effect in mixing DPNR and silica as well as NR and silica in the presence of a coupling agent. NR suffers some loss of dynamic and mechanical properties due to thermo-mechanical degradation when mixed at above optimum mixing temperature of approximately 155°C. On the other hand, DPNR shows a smaller influence of dump temperature and more constant mechanical properties. Higher silica-silane-rubber coupling in DPNR-silica-TESPT compounds is shown with improvement in the dynamic properties especially the lower  $\tan \delta$  at 60°C which indicates the lower rolling resistance of tire. The dispersion morphology of silica and rubber-to-filler interaction in DPNR is elucidated by atomic force microscopy and TEM network visualization.


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