

Bifunctional Silane (TESPD) Effects on Improved Mechanical Properties of Silica Containing Nitrile-Butadiene Rubber/Poly(vinyl chloride) Compound

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ABSTRACT: Organo bifunctional silane (TESPD) is added into silica containing NBR/PVC blend and its effects are investigated with respect to the vulcanization property, the processability, and the physical property. The addition of the TESP into silica filled NBR/PVC compound increases the degree of crosslinking by formation of a strong three-dimensional network structure between silica surface and rubber matrix via coupling

reaction, which results in improved mechanical properties. It also improves the processability of the compound compared to the Control compound. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 2937–2944, 2012

Key words: NBR/PVC; TESP; silica; processability; mechanical property

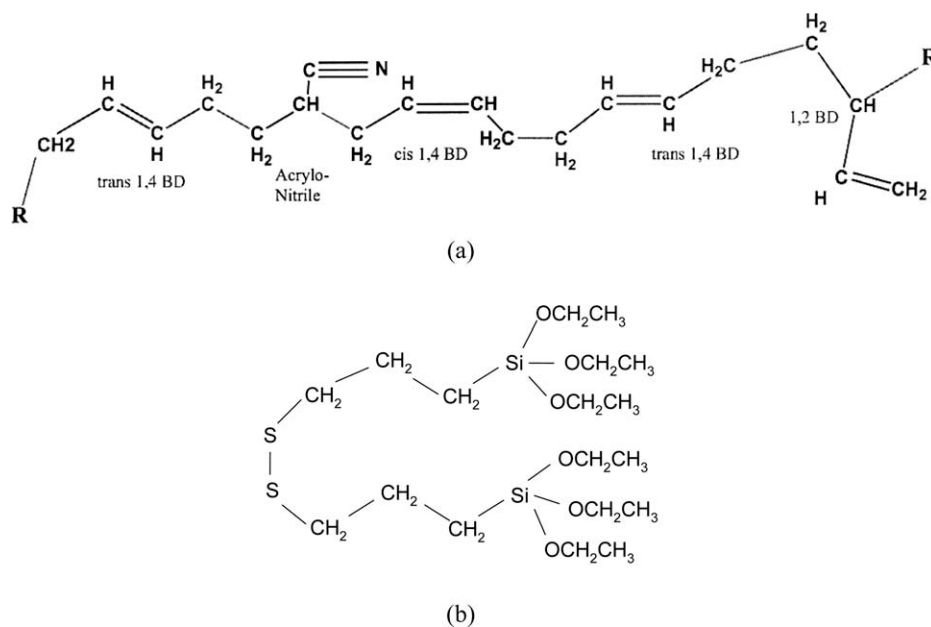
INTRODUCTION

Bifunctional silane, bis(triethoxysilylpropyl)tetrasulfide (TESPT) has been studied since 1970s to improve chemical bonding between silica surface and unsaturated elastomer chain,^{1,2} and it had been first commercially introduced by Michelin in 1990s.^{3,4} Since then the green tire manufacturing industry has been evolutionized significantly for a better gas mileage^{5,6} and performance tire. This is because of bifunctional silane's ability to chemically bonds between silica surface and elastomer chain. The coupling mechanism has been studied by various researchers.^{4–18} One end of silane chemically bonds on silica surface via hydrolysis reaction^{13–16} and the other end of silane bonds on rubber chain via sulfur crosslinking.^{17,18} General silane chemistry has now been widely used in various industries. The silica-elastomer coupling reaction chemistry via bifunctional silanes such as TESPT and TESP has been applied for other applications such as automobiles (e.g., engine mount, door sealing), military vehicles [e.g., air, ground (heavy duty tires, tank innerliner, and underwater), military goods (e.g., gas masks, boots, protective gloves, hose, rubber gasket), aerospace vehicles (e.g., hose, wire products), and

tires (e.g., airplane, heavy-duty, high performance (racing etc.)), belts (e.g., automotives, conveyer), general rubber goods, construction (e.g., building vibration absorption), medical (e.g., artificial teeth), recycling of end-of-life polymers, biodegradable fibers coupling with polymers [cf. bio-resin: poly(lactic acid), poly(trimethylene terephthalate)], etc.^{19,20}

Nitrile-butadiene rubber (NBR), polyisoprene rubber (NR), styrene-butadiene rubber (SBR), and ethylene-propylene-diene terpolymer (EPDM) are the most common elastomers used in rubber industry. Among them, nitrile rubber (butadiene-acrylonitrile copolymer, NBR) is widely used in automotive rubber goods industries. NBR consists of complex of unsaturated copolymers of acrylonitrile (ACN) and butadiene. NBR is used for fuel and oil hose, seals and o-rings, water handling goods, roll covers, hydraulic hoses, cover belting, oil field packers, and seals for all kinds of plumbing and appliances. NBR can withstand the most severe automotive applications with a temperature range from -40°C to $+125^{\circ}\text{C}$. Acrylonitrile (ACN) and butadiene ratios are controlled depending on specific oil and fuel resistance and low temperature applications. Depending on the level of ACN, several basic properties of NBR change due to polarity changes. As the ACN level increases, the resistance against fuel, oil, and abrasion increases, compatibility with polar polymers increases, air/gas impermeability increases, tensile strength increases, cure rate with sulfur cure system increases and glass transition temperature increases. As the ACN level decreases, the collapse resistance

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Scheme 1 Chemical structure of (a) NBR and (b) TESPd [bis(triethoxysilylpropyl)disulfide].

increases, resilience increases, hysteresis increases, low temperature flexibility increases, and cure rate with peroxide cure system increases. Hydrogenated NBR (HNBR) is used to reduce the chemical reactivity of the polymer backbone and to improve heat resistance property. The chemical structure of NBR is shown in Scheme 1.

There were some investigations on acrylonitrile-butadiene rubber (NBR)^{21–25}; however, there were almost no investigations on effects of organo-bifunctional silane on NBR compound, which is one of the most common elastomers used in rubber industry. The use of TESPd in silica filled NR and SBR/BR compound systems have been widely studied; however, there have been no research on application of TESPd in silica containing NBR/PVC (poly(vinyl chloride)) compound for conveyor belt application.

In this research, we investigate TESPd effects on silica filled NBR/PVC blend compound, intended for conveyor belt application, with respect to the curing properties, the processability and the mechanical properties.

EXPERIMENTAL

Materials

The elastomer used was nitrile-butadiene elastomer (NBR), which was an Uniroyal Chemical product by the brand name of Paracril OZO [fluxed blend of Paracril NBR and PVC (70/30)]. Various additives including activator (zinc oxide), processing aid/activator (stearic acid), titanium dioxide, plasticizer [dioctyl phthalate-silica blend (DOP-DLC)], curing agent (sulfur), and accelerators [triethanolamine (TEA), 2,2'-

dithiobisbenzothiazole (MBTS), tetramethylthiuram monofulfide (TMTM)], were used. The silane used in this study was brand name SCA985 [bis (triethoxysilylpropyl)disulfide (TESPD), S2], which was a product of Struktol. The chemical structure of S2 is shown in Scheme 1. The silica used was Hi-Sil 243, which was precipitated silica with BET area 150 (m²/g) and primary particle diameter 19 nm supplied by PPG. The information about the materials used in the study is summarized in Table I.

Mixing

A Banbury internal mixer (BR 1600) was used for masterbatch mixings (MB1 and MB2) of rubbers and additives (batch: the product of one mixing operation). The silane (TESPD) content of the compounds was 3 phr. The masterbatch 1 (MB1) compound was taken out (dropped out) from the mixer after 300 s of mixing. After drop out of the MB1, the real temperature of each compound was measured by probing the compound. At second pass mixing (MB2, curatives addition stage), each compound was further mixed with cure systems for 90 s. The total mixing time of each compound was 6.5 min. The fill factor, ram pressure, and rotor speed were fixed at 70%, 30 psi, and 70 rpm, respectively. The mixing formulations and procedures are included in Table II.

Mooney viscosity measurement

The Mooney viscosity ML (1 + 4) at 100°C was investigated by using a Mooney Viscometer under an apparent shear rate at 2 rpm and according to ASTM D1646. The rotor diameter of the shearing disc

TABLE I
Materials Used in This Study

Usage	Trade name	Supplier	Note
Rubber	Paracril OZO ¹	Uniroyal Chemical	Mixed blend of Paracril NBR and PVC (70/30) ¹
Filler	Hi-Sil 243	PPG	150 (m ² /g)
Activator	ZOCO	Zochem	Zinc Oxide
Activator/processing aid	Stearic acid	Harwick Standard	
Silica surface modifier	TiO ₂	Malvern Minerals	Titanium dioxide
Plasticizer	DPO-DLC ²	Natrochem	Diocetyl phthalate-silicate blend ²
Silane	SCA985	Struktol	S2 (TESPD)
Accelerator	TEA ³	Natrochem	Triethanolamine ³
	MBTS ⁴	Uniroyal Chemical	2-Mercaptobenzothiazole disulfide ⁴
	TMTM ⁵	R. E. Carroll	Tetramethyl thiuram monosulfide ⁵
Vulcanizer	Sulfur	C. P. Hall	

rheometer was 38.1 mm and the thickness of the rotor was 5.5 mm. The machine we used for measuring Mooney viscosity was brand name Mooney Viscometer 2000 (MV 2000) manufactured from Alpha Technology. The shear rate at the outer radius of the shearing disc could be expressed as follows^{26,27}:

$$\dot{\gamma}(R) = \frac{R\Omega}{H} \quad (1)$$

where R is the radius of rotating disc; Ω , the rotor rotation rate; H , the distance between the disc surface and the stationary housing.

Cure rheometer test

An oscillating disc cure rheometer (Model Rheotec) manufactured from Tech Pro was used for measuring vulcanization and reversion resistance properties of the compounds in a pressurized rotational rheometer with a biconical rotor following ASTM D 2084 at 160°C. The oscillation frequency was 100 cycles/min (1.66 Hz) with amplitude of 3°. Minimum torque (M_L), maximum torque (M_H), torque rise ($M_H - M_L$), scorch (premature vulcanization of a rubber com-

pound) time (T_s-2), cure time (T_c-90), and reversion (deterioration of vulcanizate properties that may occur when vulcanization time is extended beyond the optimum) resistance time ($T-2$) were measured.

Viscoelastic property ($\tan\delta$) measurement

Vulcanized specimens were characterized using a Mechanical Energy Resolver (MER-1100B) manufactured by Instrumentors. This instrument measured the oscillatory input of axial compression and tension response of the cylindrical specimen. Oscillatory signal response depending on material was measured and recorded as the elastic and the viscous properties as follows^{24,25}:

$$\tan\delta = G''/G' \quad (2.1)$$

$$G'(\omega) = G^* \cos\delta \quad (2.2)$$

$$G''(\omega) = G^* \sin\delta \quad (2.3)$$

$$\eta'(\omega) = \frac{G''}{\omega} = \frac{G^*}{\omega} \sin\delta \quad (2.4)$$

where ω represents oscillation frequency; G^* , the complex modulus; δ , the phase angle; $G'(\omega)$, the

TABLE II
Formulation and Mixing Procedure for NBR/PVC Conveyer Belt Compound

	NBR/PVC (Control)	NBR/PVC-S2	Mixing condition and procedure
First Stage (MB1) Material			
Paracril OZO	100.0	100.0	70 rpm, 30 psi; Fill Factor 0.7;
Hi-Sil 243	60.0	60.0	Starting Temp. 65°C
Zinc Oxide	5.0	5.0	
Stearic Acid	1.5	1.5	(a) Add rubber. (b) Mix for 30 sec. (c)
TiO ₂	10.0	10.0	Add rest additives. (d) Mix for 1 min
DOP-DLC	30.0	30.0	and sweep. (e) Mix for 2 min and sweep.
TESPD	-	3.0	(f) Mix for 5 min and dump.
Second Stage (MB2) Material			
Sulfur	1.5	1.5	70 rpm; 30 psi
Triethanolamine (TEA)	2.0	2.0	(a) Add 1/2 MB1. (b) Mix for 30 sec. (c)
MBTS	1.5	1.5	Add cures and 1/2 MB1. (d) Drop at 90 sec.
TMTM	0.5	0.5	

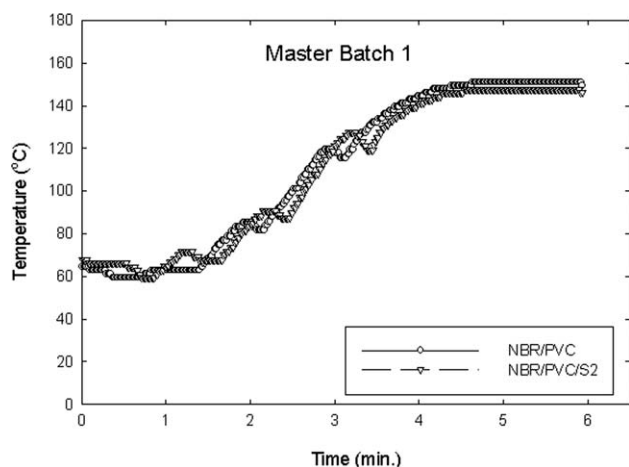


Figure 1 The mixing temperature change (MB1) of the NBR/PVC compounds in a Banbury internal mixer.

storage modulus; $G''(\omega)$, the loss modulus; and $\eta'(\omega)$, the dynamic viscosity.

Screw extrusion

A Single Screw Laboratory Extruder (SSE) manufactured by C. W. Brabender Instruments (CWB) attached with roll feeder (Model 1513) was used and the data were obtained from a PC attached to CWB at the time of extrusion of the compounds. The drive type of the extruder for SSE was a Plasti-Corder PL2100 manufactured by CWB. The length/diameter (L/D) ratio of the barrel was 15 : 1 (barrel diameter 19 mm) with compression ratio of three-to-one (3 : 1). The processing temperature and screw speed were set to 100°C and 30 rpm, respectively. A Garvey type ASTM Extrusion Die (see ASTM D 2230-88) was attached at the exit of the screw. The screw torque (Nm) of the extruder and the pressure buildup (MPa) at the exit of the die of each compound were measured.

Tensile test

An Instron tensile tester (Model 4201) with data acquisition system was used to obtain tensile test data of dumbbell specimen. The average of three specimens was obtained following the ASTM D 412-87 method. This instrument meets the ASTM E4 and measures mechanical properties of the materials, which was a table mounted unit consisting of loading frame and control console as separate assemblies. The crosshead speed and distances were 500 mm/min and 10 mm, respectively. The modulus (Pa) of each compound was measured at 300% elongation. The average thickness and width of the specimens were 2.2 and 6.3 mm, respectively.

For the measurements of viscosity, cure property, viscoelasticity, and mechanical property, the average value measured from three specimens was taken.

RESULTS

MB1 mixing temperature changes

Figure 1 represents the mixing temperature changes (MB1) of the NBR/PVC compound in a Banbury internal mixer. Comparing the NBR/PVC and the NBR/PVC/S2 compounds, the NBR/PVC/S2 showed slightly lower temperature rise at the same mixing time than the NBR/PVC, that is, the addition of S2 into the NBR/PVC generated less viscous heat; however, the difference was not significant. This matches with the probe temperature results in next section.

Probe temperature

Figure 2 shows the probe temperature of each compound measured from MB1. The NBR/PVC/S2 compound showed a lower drop temperature than the NBR/PVC. This matches with MB1 temperature change results as shown in Figure 1 because the TESPd added compound generated less viscous heat during mixing thus the inside temperature of the compound was lower than that of the Control (without TESPd). Hydrolysis is endothermic reaction, which absorbs heat from environment thus reduces temperature rise of the compound. After the hydrolysis of the TESPd, condensation reaction occurs between hydrolyzed TESPd and hydroxyl group on silica surface,¹⁰ water is produced as a byproduct, which acts as a coolant of the compound due to its latent heat during high shear mixing. The extent of probe temperature deviation between compounds was within 3%.

Vulcanization curve

Figure 3 shows the vulcanization curve changes of the NBR/PVC compound for 30 min at 160°C. The S2 added compound showed a higher torque rise ($M_H - M_L$), and higher M_H , lower M_L than the

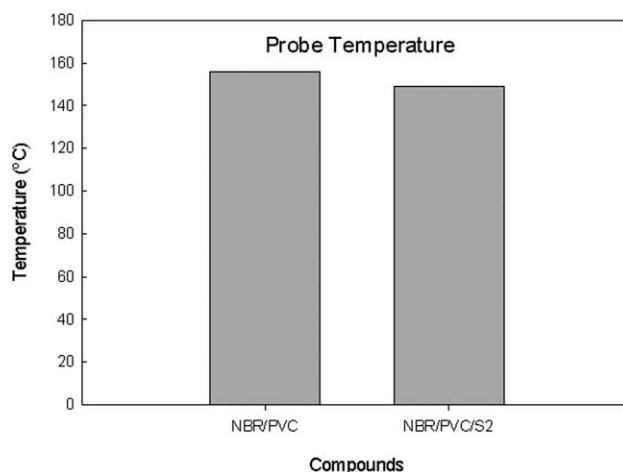


Figure 2 The probe temperature of the NBR/PVC compounds from MB1.

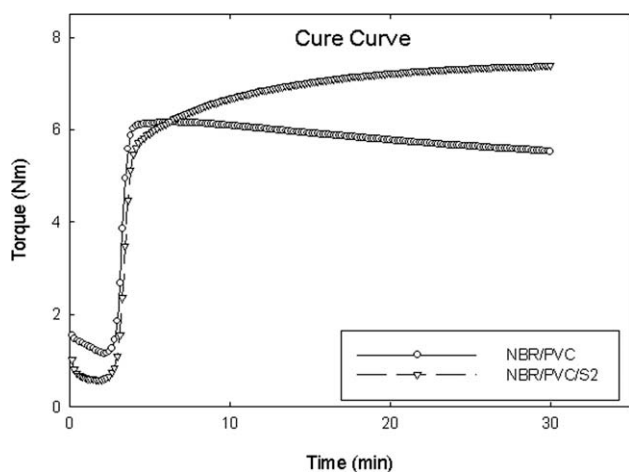


Figure 3 The vulcanization curve change of the NBR/PVC compounds for 30 min at 160°C.

NBR/PVC compound as shown in Figures 4 and 5, respectively. The NBR/PVC/S2 compound did not show significant changes in scorch time delay (Ts-2) compared to the NBR/PVC.

Figure 4 shows the torque rise ($M_H - M_L$) of each compound. Silane added compound (NBR/PVC/S2) showed a higher torque rise than the NBR/PVC.

Figure 5 shows the maximum torque (M_H) and the minimum torque (M_L) of each compound. Silane added compound (NBR/PVC/S2) showed a higher torque maximum (M_H) and lower minimum torque (M_L) than the NBR/PVC. Vulcanization curve data showed that the addition of TESP (S2) improved the processability and the degree of crosslinking of the NBR/PVC compound. This implies that the S2 acts as a lubricant during mixing and crosslinking agent during vulcanization.

Viscoelastic property ($\tan\delta$)

Figure 6 shows the loss $\tan\delta$ value [Eq. (2.1)] of each compound. At room temperature, the $\tan\delta$ value of

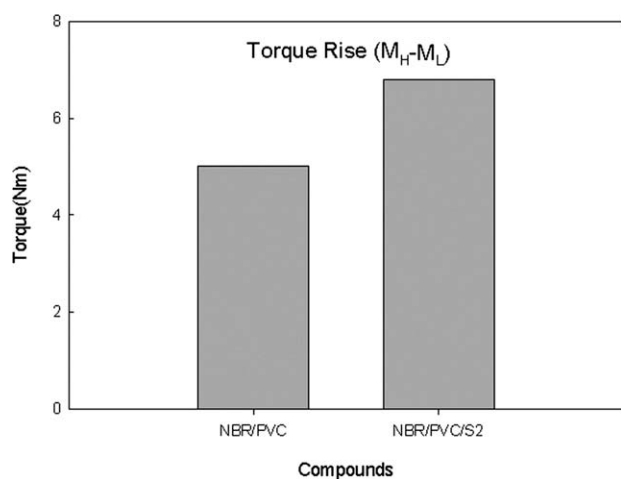


Figure 4 The torque rise ($M_H - M_L$) of the NBR/PVC compounds.

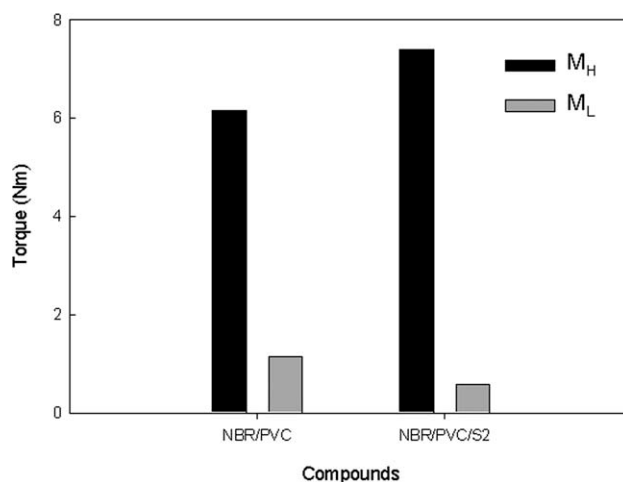


Figure 5 The maximum torque (M_H) and the minimum torque (M_L) of the NBR/PVC compounds.

the NBR/PVC/S2 compound was lower than that of the NBR/PVC. At 100°C, the $\tan\delta$ of the NBR/PVC/S2 compound was lower than that of the NBR/PVC. Lower $\tan\delta$ value comes from high storage modulus (G') or low loss modulus (G'') of the compound as shown in eqs. (2.2) and (2.3), respectively; however, we eliminated the possibility from low loss modulus contribution because the torque rise value contributed to an improvement of crosslinking of the compound, which was directly related to high G' . Thus, the contribution was from the high storage modulus (G') of the compound. The extent of viscoelasticity deviation between compounds was within 2%. This implicates the addition of TESP into NBR/PVC increased elastic property of the compound.

Mooney viscosity

Figure 7 shows the Mooney viscosity of the NBR/PVC compounds. The silane treated compound

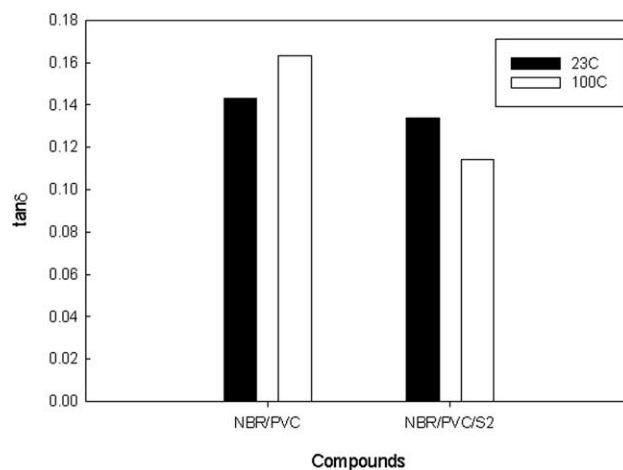


Figure 6 The $\tan\delta$ value of the NBR/PVC compounds.

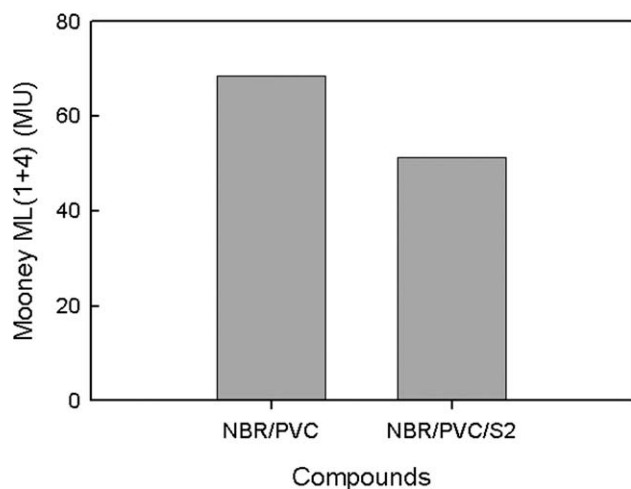


Figure 7 The Mooney viscosity ML (1 + 4) measured at 100°C of the NBR/PVC compounds.

(NBR/PVC/S2) showed a lower Mooney viscosity than the Control (NBR/PVC). This result matched with the trend of cure curve data, which showed the lower minimum torque (M_L) of the TESPd added compound. The extent of Mooney viscosity deviation between compounds was within 3%.

Extrusion torque

Figure 8 shows the (a) extrusion torque and (b) pressure build up of each compound in an extruder. Silane added compound (NBR/PVC/S2) showed a slightly lower torque and lower extrusion pressure build up compared to without silane (NBR/PVC) one. This trend matched with the cure curve data and the Mooney viscosity measurements, which showed the lower minimum torque (M_L) and the lower Mooney viscosity of the TESPd added compound, respectively.

Tensile test

Figure 9 shows the tensile modulus of each compound at 300% elongation. Silane added compound (NBR/PVC/S2) showed a higher elongation modulus at 300% elongation than the NBR/PVC. This trend matched with the cure curve data the TESPd added compound (NBR/PVC/S2), which showed a higher torque rise compared to the NBR/PVC. The extent of elongation measurement deviation between compounds was within 3%.

DISCUSSION

It has been known that the treatment of TESPd on silica surface improves the processability of the compound as well as its mechanical properties.^{8,9,28–38} The improved processability of the com-

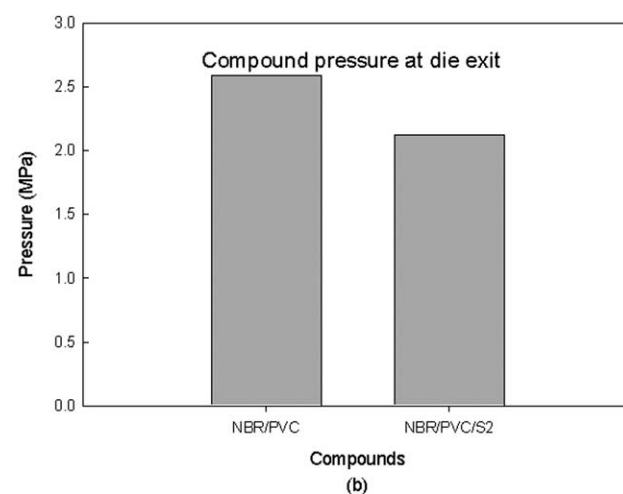
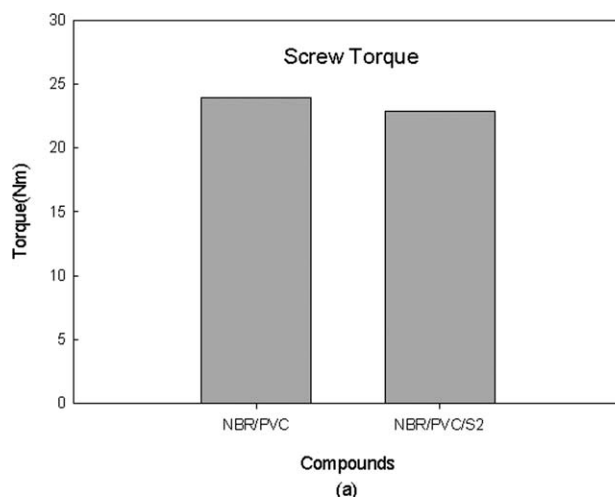


Figure 8 Processability of the NBR/PVC compounds in an extruder (a) screw torque (Nm) of the extruder at extrusion and (b) pressure buildup (MPa) at the exit of the die.

ound is due to silane coupling on silica surface during mixing, alkoxy groups in silane couples with hydroxyl groups on silica surface via

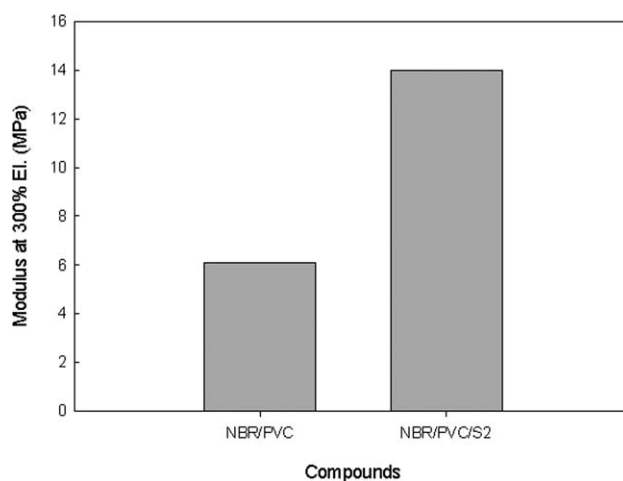


Figure 9 The tensile modulus of the NBR/PVC compounds at 300% elongation.

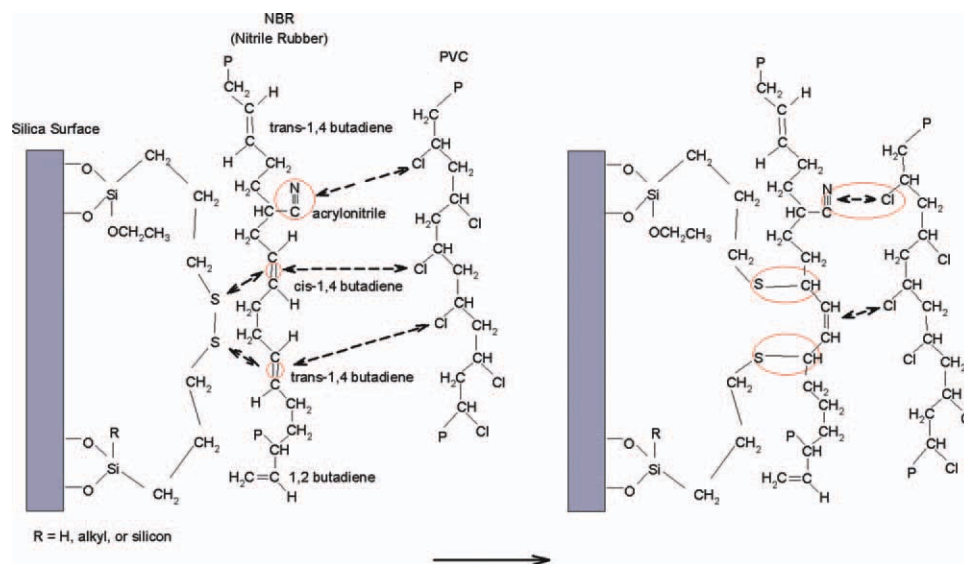


Figure 10 Schematic illustration of TESPd coupling with silica surface and NBR and the interfacial adhesion of PVC on NBR chain. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrolysis mechanism.¹⁹ This induces interfacial slip between silica and silica, silica and rubber as described by Kim and Vanderkooi.⁹ The addition of TESPd into silica filled double bond containing elastomer leads to formation of a strong three-dimensional network structure interface between silica surface and elastomer chain.¹⁹

Results showed that the addition of bifunctional silane (TESPD) into the silica/NBR/PVC compound (silica/NBR/PVC/S2) resulted in an improved processability (i.e., reduced heat generation during mixing, low M_L , low drop temperature, and low extrusion torque and low pressure build up inside the extruder) and improved mechanical properties (high vulcanization torque, high torque rise ($M_H - M_L$), high torque maximum (M_H), and high elongational modulus) compared to without TESPd (silica/NBR/PVC) one.

The processability improvement by the addition of TESPd into the silica/NBR/PVC compound seemed due to induced slip interface between silica and silica, silica and NBR/PVC, which was similar to the lubrication mechanism as described above.⁹ The mechanical property improvement resulted from the mechanism that one end of TESPd chemically bonded on silica surface via hydrolysis reaction and the other end of TESPd bonded on double bond in NBR chain via sulfur crosslinking, which was a similar mechanism of bifunctional silane coupling on silica surface and double bond containing polymer chain as generally accepted.^{13–18} There have been researches on compatibility of blends of PVC and NBR.^{37–39} Sen and Mukherjee showed that these two polymers were thermodynamically compatible with increasing acrylonitrile content in NBR.³⁷ Wang

et al. reported that the interfacial interaction between PVC and NBR was increased with decreasing NBR particle size due to larger interface between the two polymers.³⁹ Alkoxy silane coupling on silica surface via hydrolysis mechanism is well described by researchers.^{10,40}

Based on their research, we present the sulfur, in silica/TESPd, crosslinking with double bonds in NBR chain and formation of a compatible structure between silica/TESPd/NBR and PVC as shown in Figure 10. The sulfur group in silica/TESPd couples with double bonds in NBR chain via vulcanization. The polar groups in NBR (double bonds in butadiene and triple bonds in acrylonitrile) and in PVC (chlorine atom, which has three lone pairs) attract each other due to polar-polar attraction thus we presume they entangle well as illustrated in Figure 10.

It is clear that the treatment of TESPd on silica filled NBR/PVC compound increases processability and forms a three-dimensional silica-TESPd-NBR crosslinked network structure and NBR/PVC compatible blend.

CONCLUSIONS

The addition of bifunctional silane (TESPD) into silica filled NBR/PVC compound improved processability during mixing and formed a strong three-dimensional network structure between silica and NBR via coupling reaction and increased mechanical property of the NBR compound. The interfacial adhesion between NBR and PVC seemed to have no detrimental effects on mechanical property of the

NBR/PVC compound due to compatibility between the two polymers.

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