

# Ethylene–Propylene–Diene Terpolymer/Silica Compound Modification with Organosilane [Bis(triethoxysilylpropyl)disulfide] and Improved Processability and Mechanical Properties

Kwang-Jea Kim

*Institute of Polymer Engineering, The University of Akron, Ohio 44325-0301*

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**ABSTRACT:** Bifunctional silane [bis(triethoxysilylpropyl)disulfide (TESPD)] was added to a silica-containing ethylene–propylene–diene terpolymer mold compound, and its effects with respect to the vulcanization properties, processability, and physical properties were investigated. The addition of TESPD caused reduced heat generation during mixing, low minimum torque, low drop temperature, and

low extrusion pressure buildup in the extruder. It also caused a high vulcanization torque, high torque rise, high torque maximum, and high elongational modulus. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 237–244, 2010

**Key words:** mechanical properties; polysilanes; processing; reactive processing; silicas

## INTRODUCTION

Organobifunctional silanes, such as bis(triethoxysilylpropyl)tetrasulfide (TESPT) and bis(triethoxysilylpropyl)disulfide (TESPD or S2), chemically bind between a silica surface and a rubber matrix. The use of TESPT, in combination with silica, was patented for practical application in “green” tires by Rauline since 1991.<sup>1,2</sup> To overcome the prescorching problem of TESPT, TESPD was later introduced.<sup>3</sup> The sulfur–sulfur dissociation energy of TESPD is lower than that of TESPT.<sup>4,5</sup> Silanes have been used as dispersing agents<sup>6</sup> to reduce the polarity of silica particles. Organobifunctional silane in silica compounds improves the processability<sup>7–15</sup> and the mechanical properties<sup>14,15</sup> of the compounds. The sulfur level existing in the silane plays an important role during processing.<sup>16</sup>

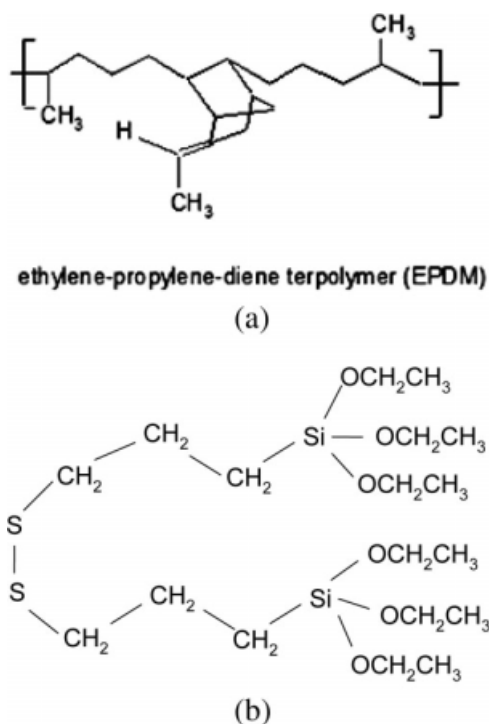
The hydrolysis mechanism is an important factor in alkoxy silane coupling on the silica surface. An alkoxy group in an alkoxy silane first hydrolyzes, then the hydrolyzed hydroxyl group forms a hydrogen bond with a hydroxyl group on a silica surface, and then they form a covalent bond between a silica surface and a silane via a condensation reaction. Finally, the interface between the inorganic silica surface and the organic silane forms a silica–silane bond.<sup>17–20</sup>

The use of bifunctional silanes such as TESPT and TESPD with silica particles in natural rubber (NR) and styrene butadiene rubber (SBR) or SBR/butadiene rubber (BR) has been known to improve several tire properties, such as the gas mileage,<sup>21,22</sup> wet and snow traction because of improved rolling resistance,<sup>2</sup> and degree of crosslinking via improved silica–silane coupling.<sup>12,14,15,23–26</sup> One end of silane chemically bonds on the silica surface via a hydrolysis reaction,<sup>24,26–30</sup> and the other end of silane bonds on the rubber chain via sulfur crosslinking.<sup>15,27,28</sup> The applications of silanes are versatile and include automotive tires (heavy-duty tires, airplane tires, high performance racing tires), engine mounts, door sealing, gas masks, boots, protective gloves, hose, rubber gasket, hose, wire products, automotive and conveyer belts, general rubber goods, building vibration absorption, artificial teeth, recycling of end-of-life polymers, and biodegradable fibers coupling with polymers. However, their applications are mostly focused with an NR, SBR, or BR matrix.

There have been investigations on ethylene–propylene–diene terpolymer (EPDM),<sup>29–34</sup> however, these studies were not related to organobifunctional silane effects on EPDM, which is one of the most common elastomers used in the rubber industry.

EPDM rubber consists of ethylene and propylene monomers, which combine to form a chemically saturated, stable backbone that provides good heat, oxidation, ozone, and weather aging and a third nonconjugated diene monomer, which can be terpolymerized in a controlled manner to maintain a saturated backbone and place the reactive unsaturation

Correspondence to: K.-J. Kim (kkim@uakron.edu.).



**Scheme 1** Chemical structure of (a) EPDM and (b) TESP.

in a side chain available for vulcanization or polymer modification chemistry.<sup>35,36</sup> The most commonly used diene termonomers are primarily ethylidene norbornene (ENB) followed by dicyclopentadiene (DCPD). DCPD was used in early grades of EPDM and yielded slower curing than other polymers; later, ENB grades, the most widely used diene in commercial EPDMs, offered fast cure rates, as fast as SBR. The concentration of ENB in EPDM ranges from 4 to 5 wt %, and ultrafast curing EPDMs contain about 10 wt % ENB. The EPDM structure shown in Scheme 1 is EPDM that contains ENB. The role of each diene acts as an acceptor of long-chain branching or polymer side chains, which influence the processability and sulfur/peroxide vulcanization rate. As the diene content increases, the degree and rate of cure, collapse (compression set) resistance, and modulus increase; however, as the diene content decreases, the scorch resistance and high-heat stability improve, but the modulus decreases. As the ethylene content increases (i.e., increasing crystallinity), the green strength, flow at high-temperature extrusion, modulus, and degree of filler loading increase; however, as the ethylene content decreases (i.e., decreasing crystallinity), the faster mixing time, milling properties, and low-temperature flexibility improve. As the molecular weight increases, the tensile tear, modulus, degree of filler loading, oil extension, green strength, scorch resistance, and collapse resistance increase; however, as the molecular weight decreases, the mixing time and viscosity

decrease, and the extrusion rate and calendaring properties increase. As the molecular weight distribution increases, the processability, extrusion feed and extrudate smoothness, collapse resistance, and milling property increase; however, as the molecular weight distribution decreases, the die swell decreases, but the extrusion rate, degree of cure, and physical properties improve. ENB provides a fast and highest state of cure, good tensile properties, good compression set resistance, and low-to-moderate long-chain branching, whereas DCPD provides a slow sulfur cure, good compression set resistance, and high long-chain branching. The applications of EPDM rubbers are in automotives, weather stripping, seals, glass-run channels, radiators, garden/appliance hoses, tubing, belts, electrical insulation, roofing membranes, rubber mechanical goods, plastic impact modification, thermoplastic vulcanizates, and motor oil additive applications. EPDM's nonpolar characteristics provide electrical resistance and resistance to polar solvents, such as water, acids, alkalis, phosphate esters, and ketones and alcohols. Amorphous or low-crystalline grades provide good temperature flexibility with glass transition points of about 60°C. When a sulfur donor or peroxide cure systems are used, the collapse resistance is good. EPDM polymers respond well to high filler and plasticizer loading. The chemical structure of EPDM is shown in Scheme 1.

The use of TESP in silica-filled NR and SBR/BR compound systems has mainly focused on tire application; however, there have not seemed to be many investigations into the use of TESP in silica-filled EPDM systems; this is one of the most widely used elastomers in the rubber industry. It was of interest to determine whether the use of TESP in silica-filled EPDM would result in improved mechanical properties as in the case of the NR and SBR matrix systems.

In this research, we investigated the effects of TESP on silica-filled EPDM compounds, which contained various additives with a practical mold compound, with respect to the processability and mechanical properties.

## EXPERIMENTAL

### Materials

The elastomer used was EPDM, which was a DSM product by the brand name of Keltan 778 (the Netherlands) and which had a specific gravity of 0.86. The magnesium silicate (talc) used was Polar 9603, which had average particle size of 3–4.5  $\mu\text{m}$  and a specific gravity of 2.7 (Polar Minerals). Various additives, including an activator (zinc oxide), processing aid/activator (stearic acid), plasticizer/softener (Sunpar 2280), curing agent [dipentamethylene thiuram

TABLE I  
Materials Used in This Study

Use	Trade name	Supplier	Notes
Rubber	Keltan 778 <sup>a</sup>	DSM	EPDM
Filler	Hi-Sil 243	PPG	Silica
Filler	Polar 9603	Polar Minerals	Talc
Activator	ZOCO	Zochem	Zinc oxide
Activator/processing aid	Stearic acid	Harwick Standard	Stearic acid
Plasticizer/softener	Sunpar 2280	R. E. Carroll	Paraffinic oil
Silane	SCA985	Struktol	TESPD (S2)
Accelerator	TMTD	Akrochem	
	Tetrone A	DuPont	
	TDEC	Sovereign Chemical Co.	
	MBT	Sovereign Chemical Co.	

<sup>a</sup> EPDM.

hexasulfide (Tetrone A), sulfur substitute], and accelerators [tetramethylthiuram monosulfide (TMTD), tellurium diethyldithiocarbamate (TDEC; activator for thiazole accelerators), and 2-mercaptobenzothiazole (MBT)] were used. Information on the materials used in this study is summarized in Table I. The silane used in this study had the brand name SCA985 (TESPD or S2) and was product of Struktol Co. America (Stow, OH). The chemical structure is shown in Scheme 1(b). The silica used was Hi-Sil 243, which was precipitated silica with a Brunauer–Emmett–Teller (BET) area of 150 m<sup>2</sup>/g and a primary particle diameter of 19 nm (PPG, Pittsburg, PA). Information for the materials used in this study is summarized in Table I.

### Mixing

A Banbury internal mixer (Farrel BR 1600, Ansonia, CT) was used for master-batch mixings (MB1 and MB2) of the rubber and additives (where a *batch* is the product of one mixing operation). The S2 level of the EPDM compound was 4 phr. All of the materials with the same ingredients in each elastomer compound were added in MB1 and discharged (dropped) after 300 s of mixing. Because of the large amount of oil (Sunpar 2280), upside-down mixing was carried out in the EPDM MB1 system. After the drop out of MB1, the real temperature of each compound was measured by probing. In the second-stage mixing (MB2), each compound was further mixed with cure systems for 90 s. The total mixing time of the compound was the same, 6.5 min each. 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

Mooney viscosity was measured as a function of the apparent shear rate at 2 rpm and ML1+4 at 100°C

according to ASTM D 1646. The rotor diameter of the shearing disc rheometer was 38.1 mm, and the thickness of the rotor was 5.5 mm. The machine we used for measuring the Mooney viscosity was a Mooney viscometer 2000 (MV 2000) manufactured by Alpha Technology. The shear rate at the outer radius of the shearing disc [ $\dot{\gamma}(R)$ ] could be expressed as follows:<sup>37,38</sup>

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

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

TABLE II  
Formulation and Mixing Procedure for the EPDM (Mold) Compound

	EPDM (control)	EPDM-S2
First-stage material		
Keltan 778	100.0	100.0
Hi-Sil 243	40.0	40.0
Mistron vapor	80.0	80.0
Zinc oxide	5.0	5.0
Stearic acid	1.0	1.0
Sunpar 2280	50.0	50.0
SCA985	—	4.0
Second-stage material		
TMTD	0.8	0.8
Tetrone A	0.8	0.8
TDEC	0.8	0.8
MBT	1.5	1.5

The mixing procedure conditions were as follows: 70 rpm, 30 psi, fill factor = 0.7, and starting temperature = 65°C (150°F). The mixing procedure was as follows:

In the first stage (MB1), (1) rubber was added and (2) mixed for 30 s. (3) The rest of the additives were added, (4) mixed for 1 min and swept, (5) mixed for 2 min and swept, and (6) mixed for 5 min and dumped. In the second stage (MB2, 70 rpm, 30 psi), (1) one half of MB1 was added and (2) mixed for 30 s. (3) The cures and one-half of MB1 were added and (4) dropped at 90 s.

### Cure rheometer testing

An oscillating disc cure rheometer (Rheotec model) modified from Tech Pro, Inc. (Cuyahoga Falls, OH), was used to measure the 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 ( $\omega$ ) was 100 cycles/min (1.66 Hz) with amplitude of 3°. The minimum torque ( $M_L$ ), maximum torque ( $M_H$ ), torque rise ( $M_H - M_L$ ), scorch (premature vulcanization of a rubber compound) time, cure time, and reversion (deterioration of the vulcanizate properties that may occur when the vulcanization time is extended beyond the optimum) resistance time were recorded.

### Viscoelastic property ( $\tan \delta$ ) measurement

The vulcanized specimens were characterized with a mechanical energy resolver (MER-1100B) manufactured by Instrumentors, Inc. (Strongsville, OH). This instrument measured the oscillatory input of axial compression and tension response of a cylindrical specimen. The oscillatory signal response depending on the material was measured and recorded as the elastic and the viscous properties as follows:<sup>37,38</sup>

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

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

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

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

where  $G^*$  is the complex modulus,  $\delta$  is the phase angle,  $G'(\omega)$  is the storage modulus,  $G''(\omega)$  is the loss modulus, and  $\eta'(\omega)$  is the dynamic viscosity. Depending on each sample group condition (23 or 100°C), the static servo position (signal acceptor position) was adjusted.

### Screw extrusion

The MB1 compound was extruded through an extruder. A single-screw lab extruder manufactured by C. W. Brabender Instruments, Inc. (CWB, South Hackensack, NJ) attached to a roll feeder (model 1513) was used, and data were obtained from a PC attached to the CWB extruder at the time of extrusion of the compounds. The drive type of the extruder for single-screw extrusion was a Plasticorder PL2100 manufactured by CWB. The length/diameter ratio of the barrel was 15 : 1 (barrel diameter = 19 mm) with a compression ratio of 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 pressure buildup (in pounds per square inch) of each compound at the exit of the die was measured.

### Tensile testing

An Instron tensile tester (model 4201, Grove City, PA) with a data acquisition system was used to obtain the tensile test data of the dumbbell specimens. The average of three specimens was obtained with the ASTM D 412-87 method. This instrument met ASTM E 4 and measured the mechanical properties of the materials; it was a table-mounted units consisting of loading frame and a control console as separate assemblies. The modulus (Pascals) of each compound was measured at 300% elongation (stress at 300% strain). The average thickness and width of the specimens were 2.2 and 6.3 mm, respectively.

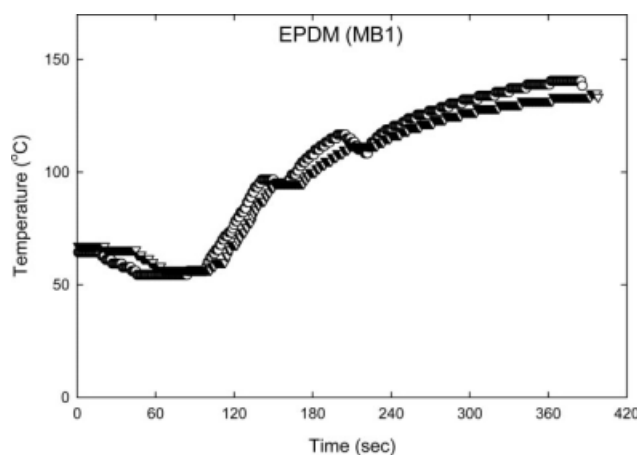
## RESULTS

### MB1 mixing temperature changes

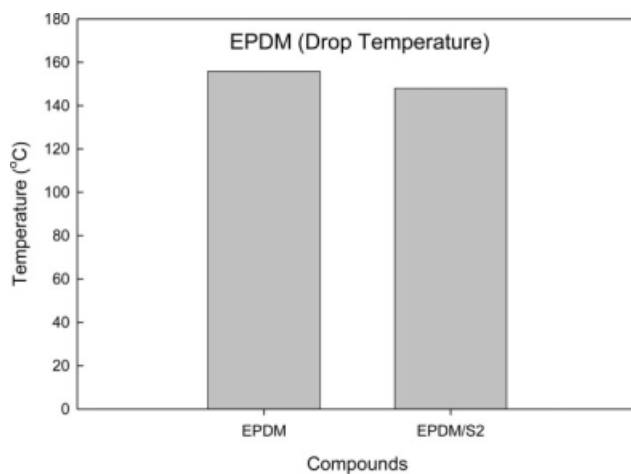
Figure 1 shows the mixing temperature changes (MB1) of the EPDM compound in the Banbury internal mixer. The addition of S2 lowered the rate of temperature rise in the control compound; this implies that it reduced the generation of the viscous heat in the compound.

### Drop temperature

Figure 2 represents the drop/probe temperatures of each compound measured from MB1. The silane-added compound (EPDM/S2) showed a lower drop temperature than the control (EPDM).



**Figure 1** Mixing temperature change (MB1) of the EPDM compounds in a Banbury internal mixer.



**Figure 2** Drop/probe temperature of each compound measured from MB1.

### Vulcanization curve

Figure 3 shows the vulcanization curve changes of the EPDM compound for 30 min at 160°C. The EPDM/S2 compound showed a higher  $M_H$ , lower  $M_L$ , higher  $M_H - M_L$ , and decreased scorch time compared to the control.

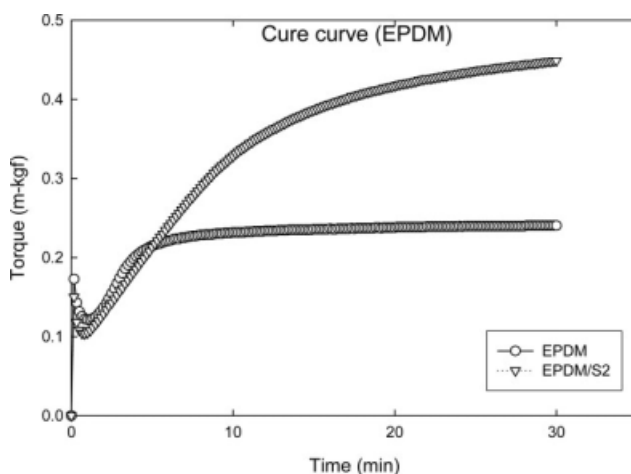
Figure 4 clearly shows  $M_H - M_L$  of the EPDM/S2 compound. The silane-added compound (EPDM/S2) showed a higher  $M_H - M_L$  than the control.

Figure 5 shows  $M_H$  and  $M_L$  of each compound. The silane-added compound (EPDM/S2) showed a higher  $M_H$  and lower  $M_L$  than the control.

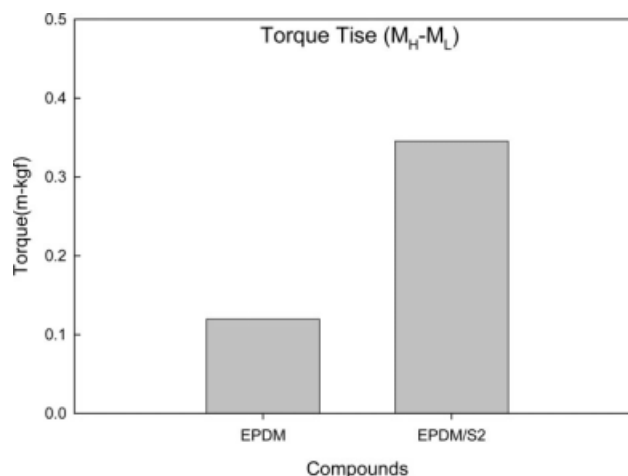
Figures 3–5 clearly show that the addition of silane (TESPD) improved the processability (lower  $M_L$ ) and the degree of crosslinking (higher  $M_H$ ) of the EPDM compound.

### Viscoelastic properties ( $\tan \delta$ )

Figure 6 shows the  $\tan \delta$  value of each compound. At room temperature and at 100°C, the  $\tan \delta$  values



**Figure 3** Vulcanization curve change of the EPDM compounds for 30 min at 160°C.



**Figure 4**  $M_H - M_L$  of the EPDM compounds.

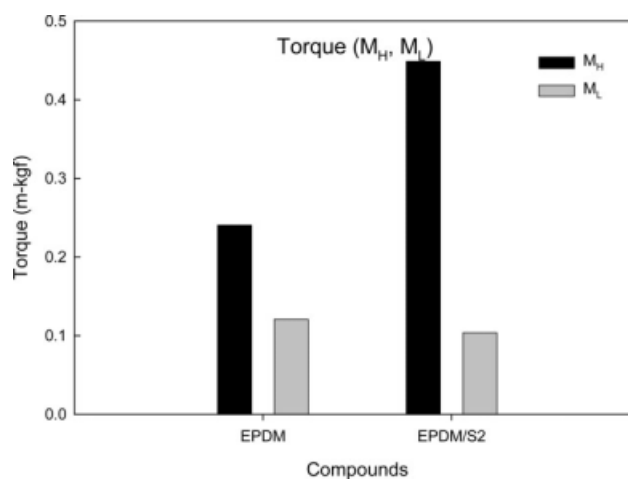
of the EPDM/S2 compound were lower than those of the control. The  $\tan \delta$  values of the EPDM/S2 and the control at 100°C were higher than those at room temperature.

### Mooney viscosity

Figure 7 shows the Mooney viscosity of each compound. The EPDM/S2 compound showed a lower Mooney viscosity than the control. This was related to the fact that the TESPd acted as a lubrication agent in the EPDM compound during processing.

### Extrusion pressure buildup

Figure 8 shows the extrusion pressure buildup of each compound processed through an extruder. The EPDM/S2 compound showed a lower pressure buildup than EPDM. This implies that the addition of TESPd improved the processability of the EPDM compound.



**Figure 5**  $M_H$  and  $M_L$  of the EPDM compounds.

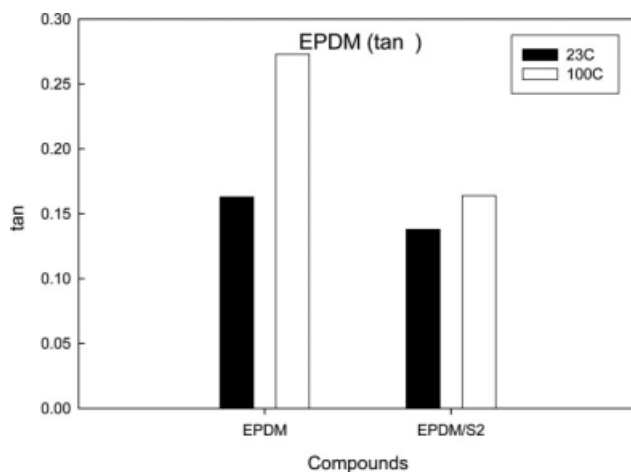


Figure 6 Tan  $\delta$  value of the EPDM compounds.

### Tensile testing

Figure 9 shows the tensile modulus of each compound at 300% elongation. The silane-added compound (EPDM/S2) showed a higher elongational modulus than the control. The improvement of the mechanical properties by the addition of the TESP showed that the bifunctional silane (TESPD) acted as a coupling agent; this promoted crosslinking between the silica surface and double bonds in EPDM and resulted in a strong three-dimensional network structure by the formation of an EPDM–silane–silica–silane–EPDM structure.

## DISCUSSION

In our silica/EPDM compound system, the addition of bifunctional silane (TESPD) caused reduced heat generation during mixing, low  $M_L$ , low drop temperature, and low extrusion pressure buildup inside the extruder. These were all correlated with the fact that the TESP acted as a lubricant during mixing,

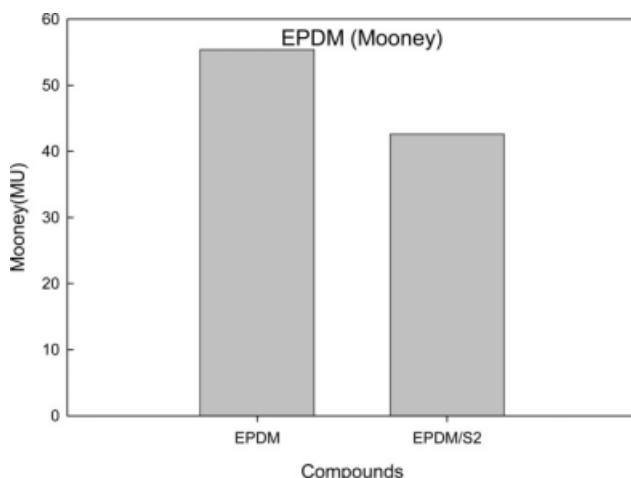


Figure 7 Mooney viscosity of the EPDM compounds.

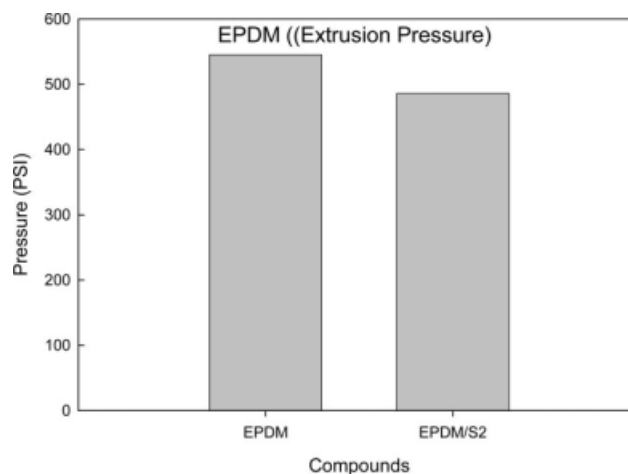


Figure 8 Extrusion pressure build-up of the EPDM compounds processed through an extruder.

which led to improved processability. The silane lubricates interfaced between the polymer–polymer, polymer–silica, and silica–silica during mixing. It also caused a high vulcanization torque,  $M_H - M_L$ ,  $M_H$ , and high elongation modulus; this implies improved mechanical properties. After vulcanization, a strong three-dimensional network structure interface was formed between the silica surface and EPDM matrix via coupling reaction, which was a similar to that described in another article<sup>14</sup> (see Fig. 10).

Similar results were found in other rubber systems. The addition of bifunctional organosilane (TESPT or TESP) improved the processability and mechanical properties of silica-filled NR and SBR compounds.<sup>7–14,36</sup> This was because the ethoxy group attached on silane chemically reacted with the silanol group on the silica surface at the mixing stage via a hydrolysis mechanism; this led to a slip

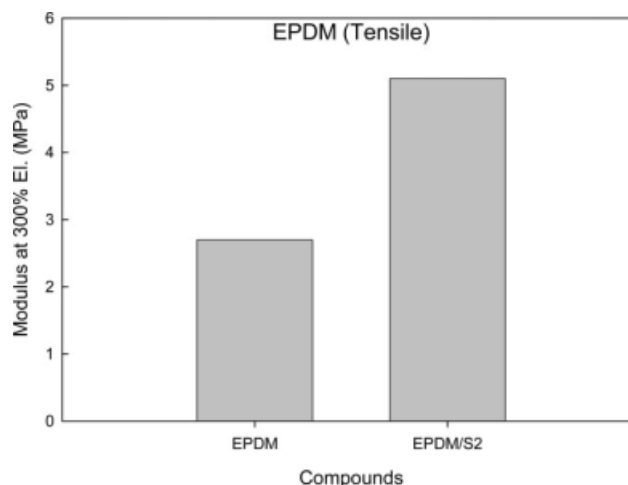
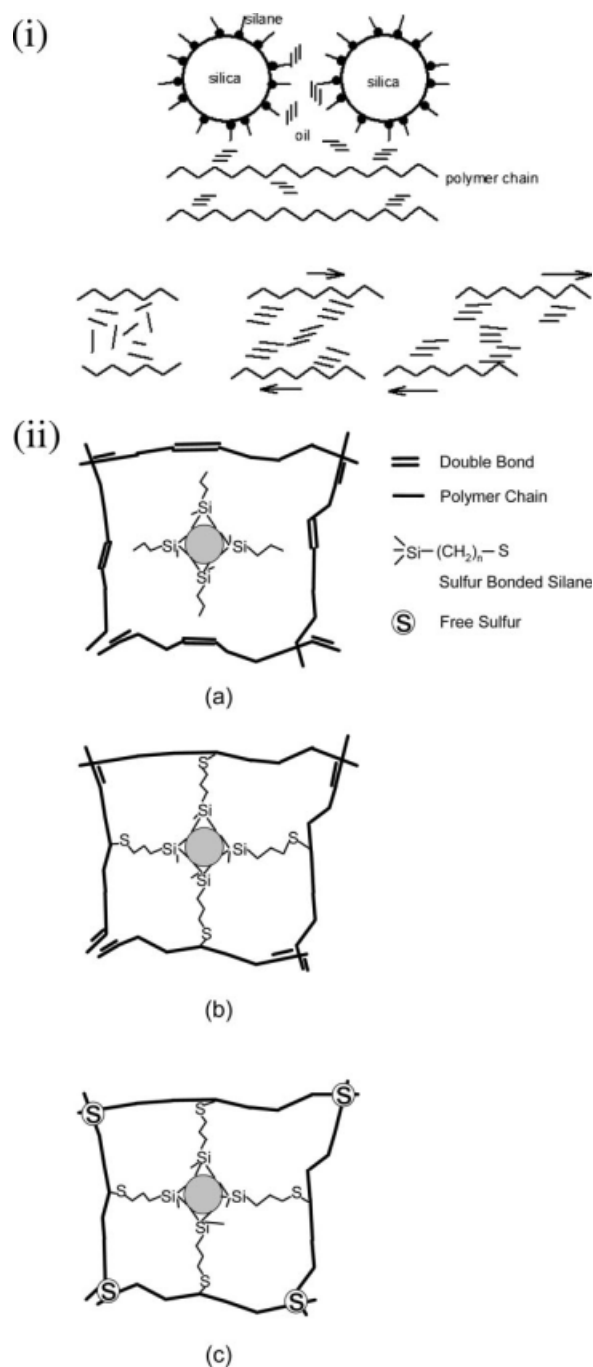


Figure 9 Tensile modulus of the EPDM compounds at 300% elongation.



**Figure 10** Bifunctional silane effects on the (i) interfacial slip between silica–silica, silica–silane, and silane–silane and (ii) vulcanized silane-treated silica: (a) TESP (no sulfur), (b) TESPd, and (c) TESPT.<sup>14</sup>

between interfaces between the polymer–polymer, polymer–silica, and silica–silica, and sulfur groups located on the other side of the silane, which reacted with double bonds on rubber chains at the vulcanization stage, which led to a formation of a stable silica–silane–rubber network.<sup>36</sup>

The location of double bonds (ENB) was on the side of the EPDM as a pendant group, whereas that of the NR and SBR was in the backbone chain. This

seemed to make the coupling reaction of TESPd with ENB in EPDM more difficult than in NR and SBR. The double bonds in ENB had better mobility compared to the ones in NR or SBR because of its structure. This matched with, as is generally known, the slow cure and degree of crosslinking of EPDM as compared with NR and SBR under the same conditions stated in the Introduction.

## CONCLUSIONS

The addition of TESPd into the silica-filled EPDM compound increased  $M_H - M_L$ ,  $M_H$ , and elongation modulus and decreased the MB1 temperature, viscous heat generation,  $\tan \delta$ ,  $M_L$ , Mooney viscosity, and pressure buildup in the extruder.

The addition of TESPd into the silica-filled EPDM compound significantly increased the mechanical properties and processability.

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