

## Substitution effect of silica by silane-modified titania on the tensile and dynamic properties of silica-filled SBR compounds

Young Woo Lim, Jong-Ho Kim, and Gon Seo<sup>†</sup>

School of Applied Chemical Engineering and the Research Institute for Catalysis,  
Chonnam National University, Gwangju 500-757, Korea  
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**Abstract**—Titania prepared by the calcination of sludge from waste water coagulated by titanium chloride was used as a substituent of the reinforcing material for silica-filled SBR compounds. The titania, mainly composed of anatase, was loosely aggregated and treated with various alkoxy silanes. The partial substitution of silica by the titania and silane-modified titania usually accelerated the cure rate and enhanced the thermal stability of the silica-filled SBR compounds. The extremely low concentration of hydroxyl groups of titania lowered the silica-silica interaction by introducing titania into the moieties of silica particles, resulting in decreases of the Payne effect and fractional hysteresis. Although the titanias modified with silanes were generally effective in enhancing the tensile and dynamic properties of the silica-filled SBR compounds, the silanes which contained mercapto groups, enabling them to react with rubber molecules, exhibited a high wet traction and low rolling resistance without sacrificing their tensile properties.

Key words: Titania, Silane, Silica, SBR Compounds, Tensile and Dynamic Properties

### INTRODUCTION

The strict regulation on the fuel consumption of vehicles in preparation for the foreseen shortage of crude oil and to reduce the air pollution due to exhaust gas strongly drives the development of tires with high fuel efficiency. Since low fuel consumption by vehicles directly corresponds to low emission of air pollutants, the reduction of fuel consumption is very important for preservation of clean air. The European Union announced a limit for the average carbon dioxide emission of cars of 130 g/km in 2015. This emission regulation is very strict, because the average emission of cars was 158 g/km even in 2007. Although the weight, external shape, and power transmission of cars are major factors in determining their fuel efficiency, the rolling resistance of tires also greatly influences the fuel consumption: a reduction of the rolling resistance by 10% results in an increase of the fuel efficiency of cars by 1-1.25% [1].

Since tires have to support the heavy load of cars and absorb the impact generated during running, the tensile properties of the tread rubber compounds, such as their tensile strength, modulus, and elongation at break, are considered as their fundamental properties. However, the desire for better driving convenience and lower fuel consumption has intensified the dynamic properties of tires: wet traction, hysteresis, heat build-up, and rolling resistance. Although carbon black has been widely used as an effective reinforcing filler of tread rubber compounds to effectively enhance their tensile properties, due to its high dispersion in rubber and strong affinity to rubber molecules [2,3], the tradeoff between the wet traction and rolling resistance of carbon black-filled rubber compounds leads to its replacement by precipitated silica [4,5].

Silica is a well-known reinforcing material for SBR compounds

to improve simultaneously both the wet traction and rolling resistance. The addition of silane coupling reagents, which have alkoxy groups that can combine with silica particles and sulfide groups that can combine with rubber molecules, enhances the dispersion of hydrophilic silica in hydrophobic rubber compounds, resulting in the improvement of both the tensile and dynamic properties [6-8]. However, an excessively high loading of silica of up to 80 phr causes the irreversible formation of a structure among the silica particles during their dynamic deformation, due to the strong interaction between the hydroxyl groups present on their external surface. The formation and destruction of the structure among the silica particles inevitably induce an energy loss during running, resulting in a high rolling resistance and poor fuel efficiency.

Titania, an important white pigment of paint and dye, is a highly stable material against mechanical stress and chemical treatment. Although it is used as a filler for silicone rubber and epoxy resin, it shows poor reinforcing performance in SBR compounds, because of its large particle size [9-11]. Its high price also retards its application in the tread rubber of tires. However, the treatment of titania with nitric acid or oleic acid enhances its performance as a reinforcing material of SBR compounds, especially in terms of its dynamic properties [12,13]. The small number of hydroxyl groups present on titania particles may correspond to the enhancement of the dynamic properties, but the role of surface-modified titania as a filler of SBR compounds has not been systematically examined.

The calcination of the sludge from waste water coagulated by titanium tetrachloride can produce a low-cost titania [14,15]. Since the titanium source has a dual function in the preparation of titania, as a coagulating agent and a raw material, the cost of the titania should be low. Crushing the titania is helpful to reduce its particle size and its surface modification with organic materials is also necessary to enhance its affinity to rubber molecules. Although its poor reinforcing performance and high cost compared to silica make it infea-

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: gseo@chonnam.ac.kr

sible to replace a high portion of silica, the partial substitution of silica by surface-modified titania may considerably improve the dynamic properties of silica-filled SBR compounds by suppressing the formation of the structure among the silica particles during their dynamic deformation.

The dynamic properties of silica-filled SBR compounds such as wet traction, rolling resistance, hysteresis, heat build-up, and abrasion are examined using various methods. However, the structure and shape of rubber samples largely influenced the measured dynamic properties, and thereby it is generally accepted to deduce the wet traction and rolling resistance from their dynamic mechanical analyzing data: the  $\tan \delta$  values 0 °C and 60-70 °C correspond to wet traction and rolling resistance, respectively [16-18]. Payne effect of the rubber samples indicates the status of silica-silica interaction [19,20]. The fractional hysteresis determined from their hysteresis loops are also helpful to understand their irreversible behavior under dynamic deformation [21,22].

In this study, the titania obtained by the calcination of sludge coagulated by titanium tetrachloride was modified with various alkoxy silanes. The tensile and dynamic properties of the SBR compounds reinforced with silica and silane-modified titania were systematically examined to determine the effect of the partial substitution of silica by titania. The contribution of titania substitution to the wet traction and rolling resistance is deduced from the Payne effect, hysteresis, and  $\tan \delta$  of the SBR compounds reinforced with silica and titania.

## EXPERIMENTAL

### 1. Silane Treatment of Titania

Titania used in this study was obtained from P&E, Korea, and abbreviated as Ti\_P&E. The sludge was coagulated by titanium chloride (20%, P&E), calcined at 600 °C, and crushed with zirconia balls. The titania was mainly composed of anatase with a small amount of co-present rutile, but without any appreciable amount of organic materials.

The Ti\_P&E was treated with 3-mercaptopropyltrimethoxy silane (MPTMS, 95%, Aldrich) which is dissolved in *n*-heptane (98%,

Daejung) at 90 °C for 24 h. The recovered titania obtained by centrifuging was washed with an excess amount of *n*-heptane and dried at 100 °C for 12 h. 3-Glycidoxypropyltrimethoxy silane (GPTMS, 98%, Aldrich), triethoxyvinyl silane (TEVS, 97%, Aldrich), bis(triethoxysilylpropyl)tetrasulfide (TESPT, SCA98, Struktol), and 4-(3,6,9,12,15-penta-oxaocotacosyloxy)-4-ethoxy-5,8,11,14,17,20-hexaoxa-4-silatrtriacontane-1-thiol (PEHTS, VP Si363, Evonik) were used in the silane treatment of the Ti\_P&E. The amount of each silane added was 0.0016 g per g Ti\_P&E.

### 2. Characterization of Titania

The TG curves of the silane-modified titania were recorded on a thermogravimetric analyzer (Mettler-Toledo, TGA/SDTA 851e). The variation of the weight loss with temperature was continuously measured from 30 to 800 °C with a ramping rate of 10 °C/min in an air flow of 50 cm<sup>3</sup>/min.

The adsorption isotherms of nitrogen on the silane-modified titania were obtained by an automatic volumetric adsorption system (Mirae SI, nano POROSITY XG). The samples were evacuated at 250 °C for 3 h prior to their exposure to nitrogen gas, and their surface areas ( $S_{BET}$ ) were calculated from the adsorption isotherms using the Brunauer-Emmett-Teller (BET) equation. The IR spectra were recorded on an IR spectrophotometer (BIORAD, FTS-175C) equipped with an *in-situ* cell (GRASEBY, SPECAC). A titania wafer with a weight of 15 mg was charged on the sample holder and evacuated at 100 °C. The spectra were recorded in 4,000-700 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

### 3. Preparation of SBR Compounds

The SBR compounds reinforced with silica (Oriental Silicas Corporation, Tokusil 255) and titania were prepared through two steps: the fillers and activators were added at the first step and crosslinking reagents and accelerators at the second step. The content of filler, the sum of the contents of silica and titania, was adjusted to 40 phr of SBR (oil-extended, Tufdene 3335, Asahi Co., Ltd.). The first mixing of SBR and filler was carried out in an internal mixer (Namyoung Co., Inc. Korea) at 50 rpm and 120 °C. After adding 3.0 phr of zinc oxide (ZnO, Hanil Co.) and 2.0 phr of stearic acid (S/A, Pyoungwha Co.), mixing was performed for 5 1/2 min. The temperature of the internal mixer was lowered to 70 °C before adding 1.5 phr of

**Table 1. Rubber compositions, and cure properties of SBR compounds reinforced with silica and partially substituted titanias**

Rubber compound	Titania				Filler amount (phr*)			$t_{c90}$ (min)
	Name	Incorporated amount of silane (mg/g titania)	$S_{BET}$ (m <sup>2</sup> /g)	Titania	Silica <sup>2)</sup>	Total		
R-1	-	-	54	-	40	40	16.4	
R-2	Ti_P&E	-	59	1	39	"	15.2	
R-3	"	-	"	2	38	"	14.8	
R-4	"	-	"	4	36	"	14.4	
R-5	"	-	"	7	33	"	12.9	
R-6	Ti_PEHTS	1.4	56	2	38	"	15.8	
R-7	"	"	"	4	36	"	15.0	
R-8	Ti_MPTMS	1.2	57	"	36	"	15.3	
R-9	Ti_TESPT	1.1	54	"	36	"	15.5	
R-10	Ti_TEVS	1.1	34	"	36	"	15.9	
R-11	Ti_GPTMS	1.1	35	"	36	"	15.3	

※ Commonly added materials: SBR: 137.5 phr, TESPT: 3.2 phr, sulfur: 1.5 phr, CBS: 1.5 phr, DPG: 1.0 phr, ZnO: 3.0 phr, and S/A: 2.0 phr

\* Part per hundred parts of rubber

sulfur (Miwon Co.), 1.5 phr of *n*-cyclohexyl-2-benzothiazylsulfenamide (CBS, Miwon Co.), and 1.0 phr of diphenylguanidine (DPG, Kumho Monsanto Co.) and the second mixing step was carried out for 3.0 min. A two-roll mill (C. W. Brabender Instruments Inc., PM-300, model #138-B) was used to produce a plate-type rubber compound by extruding it.

Table 1 lists the species and amount of titania substituted in the 11 kinds of SBR compounds prepared. The content of Ti\_P&E varied from 1 to 7 phr and that of Ti\_PEHTS was set to 2 or 4 phr. However, that of the other silane-modified titanias was fixed at 4 phr.

The cure curves of the SBR compounds were recorded on an oscillating disk rheometer (Benz Co., model #674) at 160 °C following ASTM D2084. To achieve sufficient crosslinking, all of the SBR compounds were cured under a pressure of 25 MPa at 100 °C for 30 min in a cure press (Dake, model #44-751), regardless of the species and substituted amount of titania. The cured SBR compounds were put in an oven at 100 °C for 24 h for thermal degradation.

A Mooney viscometer (Monsanto 1500) was employed to measure the viscosity. The sample was plugged into a die preheated at 100 °C and its torque was measured after 4 min.

The tensile properties of the cured SBR compounds were determined from their stress-strain curves recorded by a universal tensile tester (Shimadzu Autograph AGS-500). A dumbbell-type sample was strained with a speed of 100 mm/min following ASTM D 412. A dynamic mechanical analyzer (TA Instruments DMA 2980) measured their storage modulus and  $\tan \delta$  using a 6×30 mm sample. The Payne effect was examined from the variance of the storage modulus with the elongation in the range of extension of 0.01–20% under 1 Hz oscillation. The  $\tan \delta$  was determined from the variation of the storage modulus with temperature in the range of –30–250 °C with a ramping rate of 5 °C/min. The amplitude was set at 10  $\mu\text{m}$ . The hysteresis was determined from the hysteresis loops obtained by the tensile tester. The samples were repeatedly stretched to 100% elongation and then retracted. The fractional hysteresis (FH), which is defined as the ratio of the energy dissipated to the energy supplied on stretching, was determined from the areas of work done during extension ( $A_{\text{ext}}$ ) and work done during retraction ( $A_{\text{ret}}$ ), using the following expression:

$$\text{FH} = \frac{A_{\text{ext}} - A_{\text{ret}}}{A_{\text{ext}}} \quad (1)$$

## RESULTS AND DISCUSSION

### 1. Physical Properties of Silane-modified Titania

Fig. 1 exhibits the SEM image of Ti\_P&E. The apparent particle sizes of Ti\_P&E were in the range of 1–5  $\mu\text{m}$ , but they were comprised of the primary particles with about 100 nm. The size of the primary particles were slightly large compared with the particle size of precipitated silica (20–40 nm) conventionally used as a reinforcing filler for SBR compounds.

The amount of silane incorporated in the silane-modified titania can be determined from their TG curves, as shown in Fig. 2. The weight loss on Ti\_P&E below 200 °C might be due to the removal of water from its surface. However, the silane-modified titania exhibited other weight losses at 200–400 °C caused by the removal of organic species contained in the silanes themselves. The added amounts

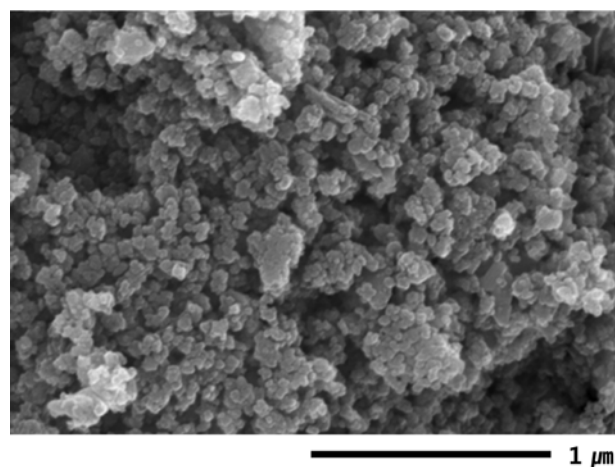


Fig. 1. SEM photo of Ti\_P&E.

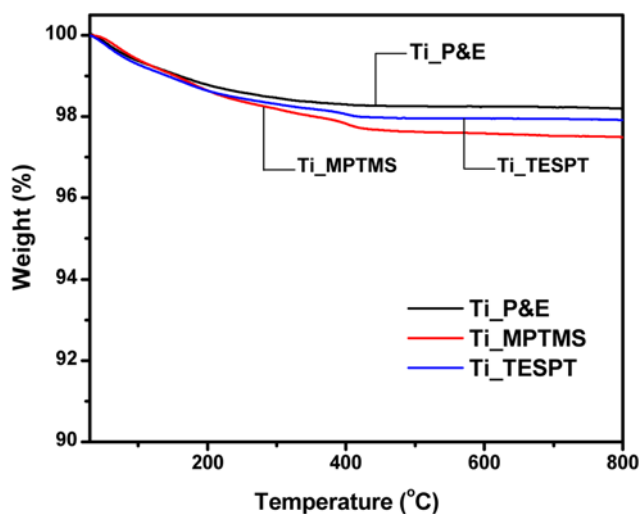


Fig. 2. TG curves of the silane-modified titanias.

of the silanes were the same, 1.6 mg/g Ti\_P&E, but the incorporated amounts of the silanes varied according to their species. The amount of silane incorporated in Ti\_PEHTS was the largest, 0.14 wt%, and that on Ti\_MPTES was 0.12 wt%. Those on the other silane-modified titanias were the same, 0.11 wt%. The large molecular weight (988 g/mol) of PEHTS may be responsible for its having the largest incorporated amount.

The BET surface areas of the silane-modified titanias are also listed in Table 1. The surface area of Ti\_P&E was 59 m<sup>2</sup>/g and the incorporating the silanes very slightly reduced the surface areas of Ti\_PEHTS, Ti\_MPTMS, and Ti\_TESPT. However, Ti\_TEVS and Ti\_GPTMS exhibited considerably smaller surface areas of around 35 m<sup>2</sup>/g compared with Ti\_P&E, but the exact reason for this reduction is not clear yet.

The surface concentration of hydroxyl groups on titania is much lower than that on silica. Fig. 3 shows the IR spectra of the silane-modified titania to compare the amount of hydroxyl groups with that of silica. The absorption band observed at 3,700–3,000 cm<sup>–1</sup> is assigned to the OH bond [23]. The band for silica was very large, while that for Ti\_P&E was very small, indicating the very low concentrations of hydroxyl groups on it. The further decrease of the

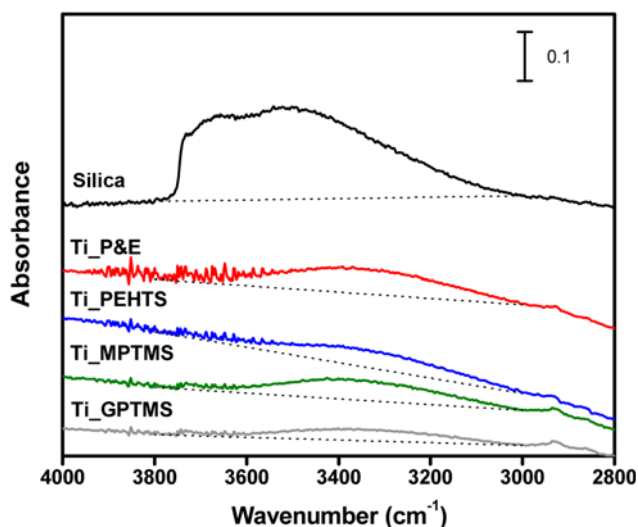


Fig. 3. IR spectra of the silane-modified titanias after evacuation at 100 °C for 1 h.

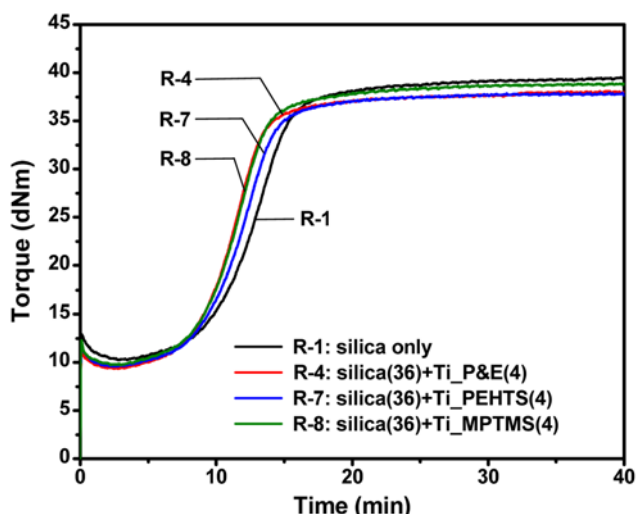


Fig. 4. Cure curves of the SBR compounds reinforced with silica and partially substituted titanias.

absorption band after the silane modification suggested the consumption of hydroxyl groups in the reaction with the alkoxy groups of the silanes. The small absorption bands in the spectra of the silane-modified titania at 3,000-2,800  $\text{cm}^{-1}$ , which were attributed to C-H bonds, confirmed the incorporation of silanes.

## 2. Effect of the Partial Substitution on the Cure Properties

The silane species used in the modification of titania and their substitution amounts affect the cure properties of the silica-filled SBR compounds. Fig. 4 exhibits the cure curves of the SBR compounds reinforced with silica and titania. The substitution of silica by 4 phr of titania was generally responsible for the small reductions of minimum and maximum torques and the small increases in the cure rate, while the changes in torque with the substitution were not considerable, regardless of the silane used in the titania modification. The low concentration of hydroxyl groups of titania compared with silica reduced the adsorbed amount of accelerators and activators, and thus, their amounts deactivated by the adsorp-

tion on titania were small. Therefore, the partial substitution of silica by titania increased the cure rate of the silica-filled SBR compounds, resulting in a significant shortening of the  $t_{c90}$  time of compound R-5 with 7 phr of Ti\_P&E to 12.9 min from 16.4 min for compound R-1 reinforced with silica only (Table 1). Otherwise, the differences between  $\tau_{max} - \tau_{min}$  corresponding to the degree of crosslinking were similar, being 28-29 dNm for the SBR compounds reinforced with silica and titania. Their Mooney viscosities were 63-65 as ML(1+4) and were similar to or slightly less than that of compound R-1 reinforced with silica only.

## 3. Effect of the Partial Substitution on the Tensile Properties

The partial substitution of silica by Ti\_P&E lowered the tensile strength of the silica-filled SBR compounds, as shown in Fig. 5. However, the partial substitution by the silane-modified titania did not induce any meaningful decrease in their tensile properties in terms of the modulus, tensile strength, and elongation at break. Table 2 lists the tensile properties of the SBR compounds reinforced with silica and titania. There were no meaningful differences in the 100% and 300% moduli, regardless of the substitution amount and the

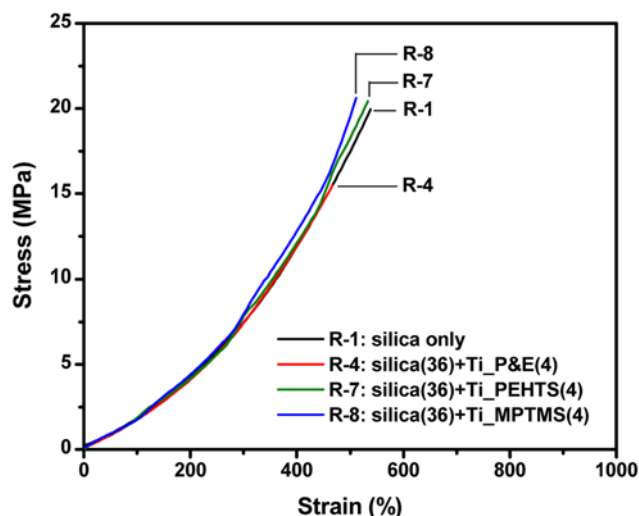


Fig. 5. Strain-stress curves of the SBR compounds reinforced with silica and partially substituted titanias.

Table 2. Tensile properties of SBR compounds reinforced with silica and partially substituted titanias

Rubber compound	Modulus (MPa)		Tensile strength (MPa)	Elongation (%)
	100%	300%		
R-1	1.8±0.1	7.5±0.4	19.1±3.5	523±63
R-2	1.8±0.0	7.6±0.2	17.8±2.3	502±43
R-3	1.8±0.1	7.7±0.2	16.9±2.5	482±43
R-4	1.7±0.1	7.4±0.2	14.9±3.2	446±62
R-5	1.6±0.1	7.4±0.2	15.5±1.6	461±24
R-6	1.8±0.1	7.8±0.1	18.3±2.9	496±42
R-7	1.8±0.1	7.7±0.2	20.4±1.1	516±14
R-8	1.9±0.1	7.8±0.1	20.9±1.5	534±27
R-9	1.7±0.1	7.2±0.2	17.7±3.5	497±63
R-10	1.9±0.1	7.6±0.2	16.0±2.6	462±48
R-11	1.8±0.1	7.6±0.3	15.8±3.3	455±57

silane species used in the modification of Ti\_P&E. However, the tensile strengths of the SBR compounds varied considerably with the substitution of titania: increasing the substituted amount of Ti\_P&E gradually decreased the tensile strength and elongation, while compounds R-7 and R-8 reinforced with silica and Ti\_PEHTS and Ti\_MPTMS, respectively, exhibited a slightly higher tensile strength than compound R-1 reinforced with silica only. Their elongations were not decreased by the substitution either. On the other hand, compounds R-9, R-10, and R-11 reinforced with silica and Ti\_TESPT, Ti\_TEVS, and Ti\_GPTMS, respectively, exhibited lower tensile strengths than compound R-1. The partial substitution of silica by Ti\_P&E without modifying it with any silane caused a considerable reduction of the tensile strength, but those by the titania modified with PEHTS and MPTMS even improved the tensile strength. These silanes commonly have mercapto groups, which allow the titania particles to combine with the rubber molecules through covalent

bonds, and they are effective as a modification material of titania to improve the tensile strength of SBR compounds.

Fig. 6 shows a comparison of the tensile properties of the SBR compounds reinforced with silica and titania before and after thermal degradation. The thermal treatment of the SBR compounds initiates the cleavage of the chemical bonds and their structural conversion, and these changes generally induce the deterioration of the tensile properties: the modulus increases, but the tensile strength and elongation at break are considerably lowered [24]. The 300% modulus of all of the SBR compounds was increased by the thermal degradation, as expected. The tensile strength of the SBR compound reinforced with silica only slightly decreased, while that of the SBR compounds reinforced with silica and titania was increased, except for the one reinforced with Ti\_MPTMS. The elongation was also reduced for the SBR compounds reinforced with silica and titania (not shown). Therefore, the improvement of the thermal stability of the SBR compounds by their reinforcement with silica and partially substituted titania was confirmed, even though their substitution amounts are as small as 4 phr. The reducible titania captures the radicals formed in the thermal degradation, resulting in better thermal stability [25].

#### 4. Effect of the Partial Substitution on the Dynamic Properties

The surface properties of the silane-modified titania induce a change in the dynamic properties of the silica-filled SBR compounds when they are partially substituted with silica. Fig. 7 exhibits the Payne effect curves of the SBR compounds reinforced with 36 phr of silica and 4 phr of the various silane-modified titania. The substitution of silica by the silane-modified titania effectively lowered the Payne effect, indicating that the substituted titania lowered the filler-filler interaction. Since the silane-modified titanias have very low content of hydroxyl groups, the substitution of silica by the titanias reduces the possibility for the formation of the structure among the silica particles. Especially, the substitution by Ti\_PEHTS, Ti\_TESPT, and Ti\_MPTMS lowered the storage modulus of the SBR compounds

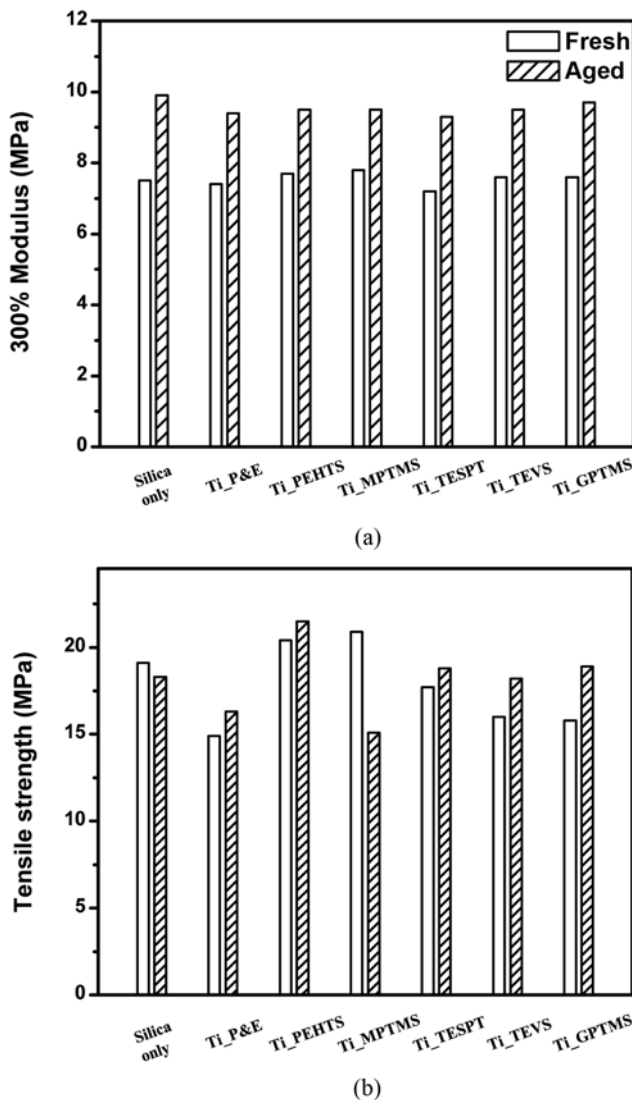


Fig. 6. (a) 300% modulus, and (b) tensile strength of the fresh and thermally aged SBR compounds reinforced with silica and partially substituted titanias: The amount of titania substitution is 4 phr and the horizontal axis denotes the substituted titanias.

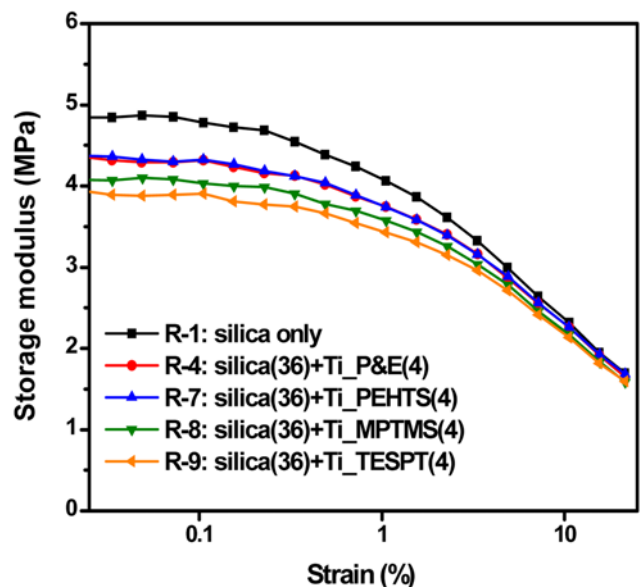


Fig. 7. Variation of storage modulus with strain for the SBR compounds reinforced with silica and partially substituted titanias.

**Table 3. Dynamic properties of SBR compounds reinforced with silica and partially substituted titanias**

Rubber compound	Payne effect	FH			Tan $\delta$		
		1 Cycle	2 Cycle	3 Cycle	$D_{max}$	$D_{0^\circ C}$	$D_{70^\circ C}$
R-1	2.37	0.266	0.153	0.139	1.27	0.636	0.068
R-2	2.13	0.274	0.153	0.144	1.30	0.715	0.066
R-3	2.22	0.243	0.132	0.121	1.27	0.693	0.059
R-4	2.09	0.233	0.120	0.112	1.30	0.739	0.060
R-5	1.72	0.209	0.104	0.096	1.41	0.623	0.048
R-6	2.14	0.244	0.131	0.121	1.30	0.598	0.058
R-7	2.06	0.234	0.120	0.112	1.29	0.615	0.055
R-8	2.16	0.230	0.115	0.106	1.35	0.659	0.059
R-9	1.99	0.208	0.112	0.106	1.34	0.745	0.059
R-10	2.16	0.220	0.117	0.112	1.37	0.733	0.059
R-11	2.22	0.228	0.114	0.106	1.37	0.669	0.063

at low strain. This means that the presence of mercapto and sulfide groups leads to the formation of covalent bonds between the titania particles and rubber molecules and good dispersion of the titania particles among the silica particles [26-28].

Table 3 lists the Payne effect, FH, and tan  $\delta$  values of the SBR compounds reinforced with silica and the silane-modified titania. Their Payne effects, corresponding to the filler-filler interaction in the rubber compounds, decreased with increasing substituted amount of Ti\_P&E. The Payne effect of compound R-5 reinforced with 7 phr of Ti\_P&E and 33 phr of silica was 1.72, which is considerably smaller than that of R-1, viz. 2.37. The SBR compounds reinforced with both silica and titania commonly exhibited lower Payne effects, confirming that the substitution of silica by titania, regardless of the silane modification, was effective in lowering the filler-filler interaction. The insertion of titania particles into the silica-filled rubber compounds suppressed the formation of the structure among the silica particles because of their scarce hydroxyl groups.

The FH corresponds to the energy loss in the repeating extension-retraction cycles of rubber compounds due to their irreversible behavior. A low FH represents more reversible performance during their cyclic deformation which requires a small energy loss. Compound R-2 exhibited a slightly higher FH at cycles 1, 2, and 3 compared to that of compound R-1, indicating a very small adverse effect. However, the partial substitution of silica by titania, regardless of the silane modification, lowered the FH of the SBR compounds. The 20-40% reduction of FH afforded by the substitution of silica by 4 phr of titania indicated that the substitution was very effective in suppressing the irreversible behavior of the silica-filled SBR compounds. The weakening of the interaction between the rubber molecules and filler particles and the loosening of the entanglement of the rubber molecules usually cause stress softening, due to the so-called Mullins effect [28]. The substitution of hydrophilic silica by hydrophobic titania enhances the interaction between the filler particles and rubber molecules. The exceptionally low FH values of compounds R-5 and R-9 may be related to the large enhancement of the filler-rubber interaction: the former was reinforced with the largest amount of titania, 7 phr of Ti\_P&E, and the latter with Ti\_TESPT which can form covalent bonds between the titania particles and rubber molecules.

The tan  $\delta$  of rubber compounds at 0 °C ( $D_{0^\circ C}$ ) corresponds to the wet traction of the SBR compounds, while that at 70 °C ( $D_{70^\circ C}$ ) to their rolling resistance [16-18]. A high  $D_{0^\circ C}$  indicates a high wet traction and a low  $D_{70^\circ C}$  a low rolling resistance. The maximum tan  $\delta$  ( $D_{max}$ ) is related to the mobility of the rubber molecules. Therefore, the high or similar values of  $D_{max}$  of the SBR compounds reinforced with silica and partially substituted silane-modified titania indicated the free mobile state of the rubber molecules within them compared to compound R-1 reinforced with silica only. Compounds R-2, R-3, and R-4 reinforced with silica and substituted with 1, 2, and 4 phr of Ti\_P&E, respectively, exhibited higher  $D_{0^\circ C}$  values than R-1. Moreover, the  $D_{70^\circ C}$  values of the former were smaller than that of the latter. The increases in  $D_{0^\circ C}$  and decreases in  $D_{70^\circ C}$  with increasing substituted amount of Ti\_P&E indicated that both the increase of the wet traction and lowering of the rolling resistance can be simultaneously facilitated by the substitution of silica with titania. The silane-modified titanias also exhibited a similar improvement in both their wet traction and rolling resistance when they were substituted with 4 phr of silica.

The enhancement of the wet traction due to the substitution of silica by titania can be explained by the relatively free motion of the rubber molecules in the SBR compounds when they are reinforced with silica and titania. Since the substitution of hydrophobic titania reduces the formation of the structure among the silica particles, the large deformation of the rubber compounds that occurs under strong impacts improves their wet traction. On the other hand, the lowering of the rolling resistance by the substitution of silica by titania was caused by the suppression of the irreversible behavior of the SBR rubber compounds, as mentioned before in the discussion of the Payne effect and FH. The insertion of titania with an extremely small number of hydroxyl groups among the silica particles reduces the formation and collapse of the structures among the silica particles during dynamic deformation. The organic materials of the silanes incorporated into the titania particles may enhance the entanglement of the rubber molecules around them, resulting in the reversible performance of the rubber molecules.

## CONCLUSIONS

The substitution of silica by the silane-modified titania in the SBR compounds, even at 4 phr, improved their thermal stability and dynamic properties without sacrificing their tensile properties. The extremely low concentration of hydroxyl groups on titania induced its better dispersion into the organic rubber molecules. The insertion of titania particles among the silica particles reduced the silica-silica interaction and suppressed the formation of the structure among the silica particles during dynamic deformation, resulting in a high wet traction and low rolling resistance. Especially, the titanias modified by PEHTS and MPTMS containing mercapto groups acted as very effective substituted reinforcing materials of silica in enhancing both the tensile and dynamic properties of the SBR compounds.

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