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Effectively reinforcing roles of the networked silica prepared using 3,3′-bis(triethoxysilylpropyl)tetrasulfide in the physical properties of SBR compounds

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Abstract The networked silica having pre-fabricated networks among silica particles is a new concept for the reinforcement of rubber compounds. The networked silica was designed to improve the fuel efficiency of tires while eliminating the disadvantages such as precure and ethanol production that arise in the conventional reinforcing system using coupling reagents. The networked silica was prepared using bis(triethoxysilylpropyl)tetrasulfide (TESPT) as a connecting chemical at various loading levels. The styrene–butadiene rubber (SBR) compounds reinforced with the networked silica exhibited low filler–filler interaction and high rubber–filler interaction due to the entanglements between the rubber molecules and the connecting chains of the networked silica. The increased physical interaction improved the elastic properties and wear resistance, while lowering the rolling resistance of the rubber compounds, resulting in long tire service life and high automobile fuel efficiency. The enhanced physical properties of the SBR compounds reinforced with the networked silica supported their promising potential as reinforcing fillers for tire manufacture. The networked silica can readily replace the conventional silica-reinforced system, without requiring major modification of the processing conditions.

Introduction

The increased attention directed at reducing carbon dioxide emissions and increasing fuel savings has raised the importance of the evaluation specifications for the fuel efficiency of tires. The replacement of carbon black by silica as a reinforcing filler of rubber compounds lowers the rolling resistance, thereby enhancing the fuel efficiency of tires [1, 2]. However, the high loading of hydrophilic silica to hydrophobic rubber causes poor dispersion and inhibits the reinforcing performance of silica. Coupling reagents possessing both alkoxy groups, to react with the hydroxyl groups of silica, and sulfide groups, to react with the double bonds of rubber molecules, combine silica particles and rubber molecules through chemical bonding. This addition of a coupling reagent affords a higher dispersion of silica, producing a superior reinforcement performance. A typical coupling reagent, bis(triethoxysilylpropyl)tetrasulfide (TESPT), has been widely used in rubber compounds for tire manufacture to maximize the reinforcing performance of silica [3–5].

However, the addition of TESPT as a coupling reagent causes disadvantages: the progress of precuring during the mixing stage and the generation of ethanol during the vulcanization of rubber compounds. Ethanol occluded in rubber compounds induces a degree of heterogeneity among their physical properties, and the expansion of the ethanol during the running of tires may initiate their bursting with severe consequences. Therefore, any ethanol generated during the vulcanization should be removed. In addition, the mixing temperature and time of rubber compounds must be carefully controlled to inhibit the precure.

The treatment of silica particles by silanes or isocyanates with suitable functional groups produces three-dimensional networks. Silica particles connected by the organic chains become entangled with rubber molecules in the networked silica-reinforced rubber compounds, leading to successful reinforcement of the styrene–butadiene rubber (SBR) compounds without the requirement for any

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coupling reagents [6–8]. As silica particles are already connected in the preparation step, there is no further generation of ethanol in either the mixing or vulcanization steps. Since the reinforcing mechanism of the networked silica does not involve chemical bonds formed between silica particles and rubber molecules, the modulus of the rubber compounds reinforced with the networked silica can be widely varied, allowing high tensile strength to be achieved according to the specifications.

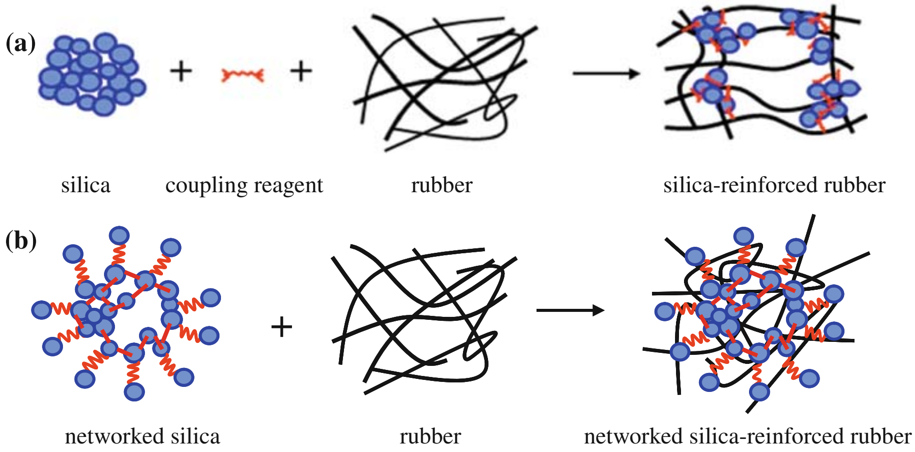
Scheme 1 compares the reinforcing mechanism of the networked silica with the conventional reinforcing system composed of silicas and a coupling reagent. Rubber, silica, and a coupling reagent are added together and mixed in the conventional system. During vulcanization, silica particles are combined with rubber molecules by forming covalent bonds through the coupling reagent [5]. On the contrary, the networked silica, with its previously fabricated networks among silica particles, does not react with rubber molecules, even in the mixing and the vulcanization steps. Rubber molecules intrude into the voids of the networked silica at the mixing stage and become entangled with crosslinked rubber molecules during vulcanization. Since the surfaces of the networked silica are coated with organic moiety, they show a high affinity with rubber molecules, resulting in the high dispersion of silica particles. The entanglements of rubber molecules with the organic connecting chains of the networked silica increases the tensile strength of the rubber compounds, but the absence of any chemical bonds between the silica particles and rubber molecules leads to the retention of the compounds' low modulus.

The performance of the networked silica in reinforcing the SBR compounds strongly depends on the structure and properties of the connecting materials. The networked silica can be prepared by combining silica particles through the chemical reaction of amino and glycidyloxy groups incorporated on the external surface of silica [7]. 3-Aminopropyltriethoxysilane and glycidyloxypropyltriethoxysilane have previously been incorporated on silica particles. The networked silica-reinforced SBR compounds showed high tensile strength, comparable to that of the conventional rubber compounds reinforced with silica and TESPT. However, a low modulus inevitably resulted because of the absence of any chemical bond formation between the silica particles and rubber molecules. The networked silica prepared by methylenediisocyanate, however, showed a considerably improved reinforcing performance when compared to the conventional silica-reinforced system [8]. The SBR compounds reinforced by urethane linkages between the networked silica, to provide a sufficient amount of organic connecting chains, exhibited a comparable tensile strength at a loading amount above 40 phr.

The SBR compounds suitable for tire manufacture should have appropriate tensile and elastic properties, low rolling resistance and high-resistant wear properties. In this study, the networked silicas are prepared using TESPT at various loading levels as a connecting material. The reinforcing performance of the networked silica is confirmed by examining their physical properties. The tetrasulfide linkages of TESPT enable the prepared networked silica to enhance the modulus and tensile strength of the SBR compounds. The feasibility for replacing the conventional reinforcing system composed of silica and TESPT by the networked silica prepared using TESPT as a connecting material is discussed in terms of cure, tensile, elastic, and wear properties.

Experimental

The networked silica was prepared by injecting a TESPT (Degussa, Co.) solution dissolved in ethanol (95%, Deajung) into suspended silica particles (Hi-Sil 255, Oriental



Scheme 1 Comparison of reinforcing mechanisms between (**a**) conventional silica-reinforced rubber compound using coupling reagent and (**b**) networked silica-reinforced rubber compound

Silicas Corporation) following the procedure described in the literature [6]. The amount of TESPT injected was varied as 0.05, 0.10, 0.15, and 0.20 mmol/g of silica. The networked silicas were classified by writing the loaded amount of TESPT in parentheses, such as N-silica(0.10).

The compositions of the SBR compounds, prepared with 40 phr of silica and mixed according to the procedures described in our previous papers [7, 8], are listed in Table 1. Two other SBR compounds, one reinforced only with silica and one with silica and TESPT (3.6 phr), were also prepared for comparison. The prepared SBR compounds were denoted by adding 'R-' to the abbreviated silica reinforcing systems, such as R-unfilled, R-silica, R-silica-TESPT, and R-N-silica(0.10).

An oscillating disk rheometer (ODR, model 674, Edwon H. Benz Com.) was used to obtain torque–time curves (or rheocurves) at 160 °C, according to ASTM D2084. The optimum cure time of the compounds was determined as 30 min to achieve a sufficient crosslinking of the rubber samples.

The dynamic storage modulus of the vulcanized samples was characterized from low (0.01%) to intermediate (30%) strain at a frequency of 1 Hz and at room temperature using a dynamic mechanical analyzer (DMA, TA instruments), to investigate the filler–filler interaction. Temperature scans were also run from −70 to 100 °C at a heating rate of 5 °C/min with a frequency of 1 Hz and an imposed strain of 0.05% to obtain the loss tangent (tan δ) of the compounds.

A universal tensile tester (AGS-500D, Shimadzu Autograph) was used for the tensile measurements of the compounds. All tests were performed at room temperature with a crosshead speed of 100 mm/min according to ASTM D412. The samples were also stretched up to 100% elongation at a crosshead speed of 100 mm/min and retracted to unstressed state for measuring the hysteresis losses. The fractional hysteresis (FH), defined as the energy dissipated relative to the energy supplied on stretching, was determined from the areas of A_{ext} (work done during extension) and A_{ret} (work done during retraction), using the following expression:

$$\mathrm{FH} = \frac{A_{\mathrm{ext}} - A_{\mathrm{ret}}}{A_{\mathrm{ext}}}. \tag{1}$$

Table 1 Formulations of SBR compounds

Composition (phr[a])	Unfilled	Silica only	Silica + TESPT	Networked silica
SBR[b]	137.5	137.5	137.5	137.5
Sulfur	1.5	1.5	1.5	1.5
CBS[c]	1.5	1.5	1.5	1.5
DPG[d]	1.0	1.0	1.0	1.0
Zinc oxide	3.0	3.0	3.0	3.0
Stearic acid	2.0	2.0	2.0	2.0
Silica[e]	–	40.0	40.0	–
TESPT[f]	–	–	3.2	–
N-silica	–	–	–	40.0

[a] Parts per hundred parts of rubber

[b] Tufdene3335 (Ashai Co., Ltd.)

[c] *N*-Cyclohexyl-2-benzothiazolesulfenamide

[d] Diphenylguanidine

[e] Hi-Sil 255 (Oriental Silicas Corporation)

[f] bis(Triethoxysilylpropyl)tetrasulfide (Degussa Co.)

A blade abrader at a rotating speed of 10 rpm was used to measure the abrasion properties of the compounds [9, 10]. A wear rate (W_R) of the SBR compounds was measured over a wide range of frictional work input (W_F) at room temperature. The W_R values were determined by the average loss in weight per revolution of the sample and examined as a function of the amount of work expended in frictional sliding per unit area of surface and per revolution.

Results and discussion

The rheocurves of rubber compounds vary considerably according to the silica-reinforcing system. Figure 1 shows the rheocurves of the SBR compounds with various silica-reinforcing systems. Since the rheocurves of R-N-silica(0.05) and R-N-silica(0.15) were very similar to that of R-N-silica(0.10), they were omitted for brevity. R-unfilled, without silica, exhibited a very low torque and the vulcanization was completed in a short time of around 7.5 min. The addition of silica significantly increased the torque of the SBR compound, as shown in the rheocurve of R-silica.

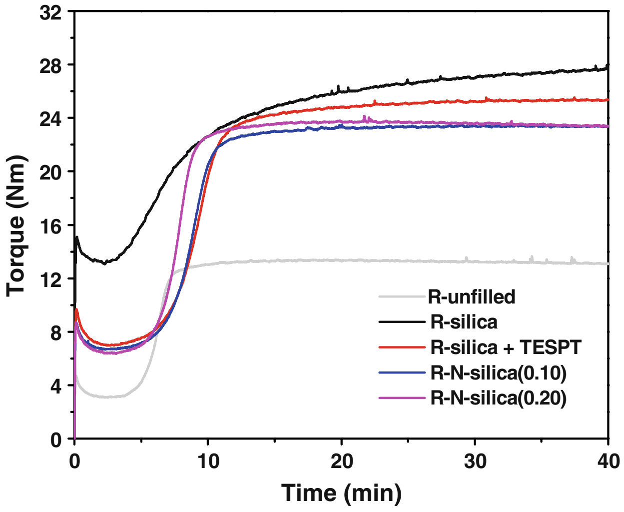


Fig. 1 Rheocurves recorded at 160 °C for SBR compounds reinforced with the networked silica

The slow increase in the torque, however, required a long cure time for sufficient crosslinking. On the contrary, the addition of both silica and TESPT to the SBR compound produced the ideal rheocurve of R-silica + TESPT with a low initial torque, sufficient scotch time, and rapid cure rate. The small molecular size of TESPT induces a low viscosity capable of a highly efficient mixing. The similar rheocurves of the networked silica-reinforced rubber compounds, R-N-silica(0.10), and R-N-silica(0.20), to that of R-silica + TESPT indicated that the silica and TESPT reinforcing system for the SBR compounds could be simply replaced by the networked silica without inducing any differences in the cure process conditions.

The variation of the storage modulus with strain reveals the extent of filler–filler interactions of rubber compounds. Figure 2 shows a decrease in the storage modulus of the silica-reinforced SBR compounds with increasing strain amplitude according to the Payne effect [11]. The decrease in the storage modulus of the compounds at high strain is caused by the breakdown of the silica–silica interaction [12]. The SBR compound reinforced with only silica exhibited a high storage modulus at a low strain, but it decreased rapidly with increasing strain amplitude. A poor dispersion and large agglomeration of the silica particles resulted in a high silica–silica interaction and a high storage modulus at a low strain, while the increase in the strain caused severe destruction of the silica–silica interaction, resulting in the rapid decrease of the storage modulus. The addition of TESPT with silica into the SBR compounds coupled the silica particles with the rubber molecules through the TESPT molecules, thus decreasing the possibility for direct interaction among the silica particles and thereby lowering the storage modulus. The lowest storage modulus exhibited by R-N-silica(0.20) indicated an existence of organic moieties between the silica particles, which prevented the direct silica–silica interaction and improved the rubber–silica interaction. The rubber molecules can intrude into the openings formed among the silica particles in the networked silica-reinforced compounds, which considerably reduced the silica–silica interaction. The breakdown of the silica–silica interaction upon increasing strain was negligible over R-N-silica(0.20), compared to R-silica and R-silica + TESPT, suggesting that the high dispersion of silica particles enhanced the interaction between the rubber molecules and silica particles.

The primary objective of silica reinforcement for rubber compounds is to attain a tensile property of sufficient quality to guarantee the safety of tires in terms of the structural maintenance and the sorption of impulse. Figure 3 shows the stress–strain curves of SBR compounds reinforced with networked silica and Table 2 gives the tensile properties. The SBR compound without silica filler (R-unfilled) exhibited a very low tensile strength and a short elongation. The addition of silica (R-silica) considerably increased both the tensile strength and the elongation at break, but its modulus was relatively low. The rubber compound reinforced by silica and TESPT (R-silica + TESPT) showed a tensile strength and modulus sufficiently high for tire manufacture, while its elongation decreased. When the networked silicas were added to the SBR compounds (R-N-silica), they effectively reinforced the compounds and achieved high tensile strength and modulus. Increased TESPT loading in the preparing networked silica increased the tensile strength and modulus of the SBR compounds but slightly decreased their elongation. This increased TESPT content caused a definite increase in the organic connecting chains among the silica particles which could become entangled with rubber molecules, resulting in a high tensile strength. The

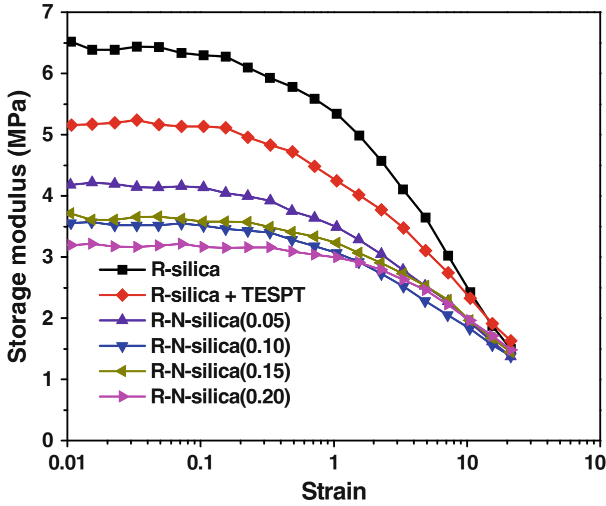


Fig. 2 Variation of storage modulus with strain for the SBR compounds reinforced with the networked silica

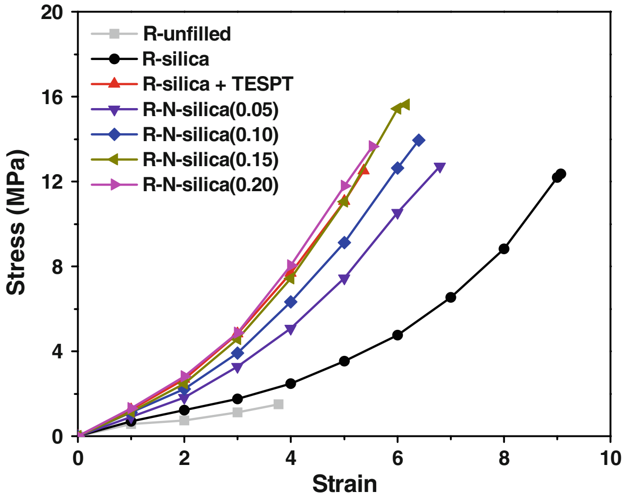


Fig. 3 Tensile properties of SBR compounds reinforced with the networked silica

Table 2 Tensile properties of SBR compounds reinforced with the networked silica

Rubber compound	Modulus (MPa)		Tensile strength (MPa)	Elongation (%)
	100%	300%		
R-unfilled	0.6	1.1	1.50	377
R-silica	0.7	1.8	12.4	907
R-silica + TESPT	1.3	4.8	12.5	537
R-N-silica(0.05)	0.9	3.3	12.7	680
R-N-silica(0.10)	1.1	3.9	14.0	640
R-N-silica(0.15)	1.1	4.6	15.6	617
R-N-silica(0.20)	1.3	4.9	13.7	553

tetrasulfide groups of TESPT in the networked silica also reacted with the double bonds of rubber molecules and enhanced both the tensile strength and the modulus. Since R-N-silica(0.15) reinforced with the networked silica exhibited very high tensile properties, the SBR compound reinforced with silica and TESPT could be replaced by the compound reinforced with the networked silica prepared by TESPT without any significant loss of performance. However, the R-N-silica(0.20) reinforced by the networked silica with an excessive TESPT content exhibited decreased tensile strength and elongation. This reflected the formation of covalent bonds due to the coupling reaction between TESPT and the double bonds of the rubber molecules, which increased the modulus of the SBR compounds and lowered both the tensile strength and the elongation in the R-N-silica(0.20). A suitable TESPT content produced the networked silica with high reinforcing performance, but an excessive amount degraded the networked silica.

The ideal elastic behavior of rubber compounds causes reversible extension and retraction under a cyclic strain, without any loss of energy. On the contrary, most rubber compounds exhibit hysteresis upon cyclic extension: the stress during the retraction is much less than that during the extension. The decreases in the interaction between the rubber molecules and the filler or the physical disentanglements by stress are considered persuasive causes to explain the stress softening of rubber compounds, i.e., the Mullins effect [13, 14]. The stress-induced breakage of chemical bonds in rubber compounds induces a permanent stress softening, while some physical disentanglement is restored when the stress is removed. The strength of the rubber–filler interaction is an important factor in determining the stress softening represented by hysteresis. Figure 4a compares the hysteresis observed on the SBR compounds reinforced with only silica, with silica and TESPT, and with the networked silica prepared using TESPT. After an extension to 100%, the restoring paths of the SBR compounds were recorded. The stress at 100% elongation increased in the order of R-silica < R-N-silica(0.10) < R-silica + TESPT, but the extent of stress softening, i.e., the Mullins effect, decreased in the order of R-silica > R-silica + TESPT > R-N-silica(0.10). The SBR compound reinforced with the networked silica, N-silica(0.10), showed the lowest hysteresis loss in the extension–retraction cycling paths.

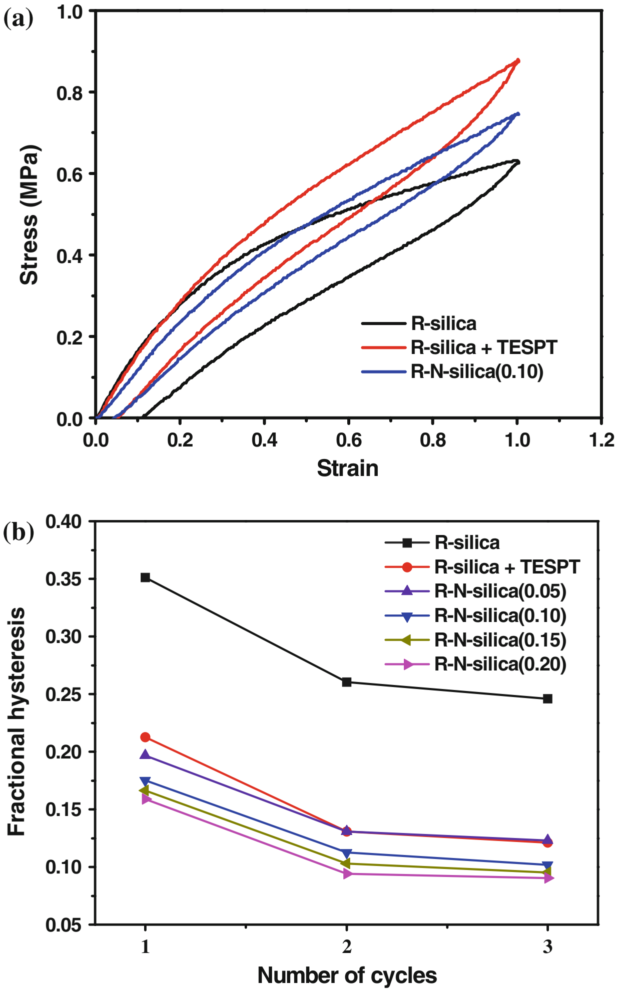


Fig. 4 Hysteresis (**a**) and fractional hysteresis (FH) (**b**) of SBR compounds reinforced with the networked silica

Fractional hysteresis, defined by the restored fraction of energy to the amount of energy supplied at extension, denotes the extent of hysteresis results with comparable numbers. Figure 4b shows the FH of the SBR compounds reinforced with silicas measured over three cyclic paths. Large energy dissipation occurred in the first extension, but further extension caused low FH, indicating the severe deterioration of the interaction between the rubber molecules and silica particles during the first extension. The addition of TESPT considerably lowered the FH by enhancing the rubber–filler interaction strength, thereby suppressing the deterioration of the interaction. The SBR compounds reinforced with the networked silica exhibited a lower FH, indicating their better elastic properties and rubber–filler interactions. The physical entanglements between rubber molecules and organic connecting chains of the networked silica reduced the breakage of the interaction at the extension, leading to almost complete restoration to the original state of the SBR compounds at the retraction.

In addition to the tensile and elastic properties of rubber compounds, the wet traction and rolling resistances are also important in determining their feasibility for tire manufacture. Although these properties can be determined by various methods, the tan δ value measured with increasing temperature provides a rough, but practical comparison of these properties. Figure 5 shows the variation of tan δ, the ratio of viscous to elastic properties, according to temperature in the range from −30 to 100 °C, on the SBR compounds reinforced with the networked silica. The highest tan δ value of R-N-silica(0.20) indicated the most mobile environment of rubber molecules in the networked silica-reinforced SBR compounds. The rubber molecules were mainly entangled with the organic connecting chains of the networked silica, which allowed them to move more freely than those in a chemically bonded reinforcing system. The tan δ values of the SBR compounds at 0 and 60 °C are shown in Table 3. In tire manufacturing, the tan δ value of a given rubber compound at 0 °C generally corresponds to the wet traction of the tire using the given rubber compound [15]. The rolling resistance of tires was roughly deduced from the tan δ value of the rubber compound at 60 °C [16]. A high tan δ value at 0 °C is therefore required to enhance the wet traction of tires and a low tan δ value at 60 °C to enhance the fuel efficiency by lowering the rolling resistance of the tires. The R-N-silica(0.10) showed a relatively high tan δ value at 0 °C and the R-N-silica(0.15) showed the lowest tan δ value at 60 °C, indicating that the reinforcement of the SBR compound with the networked silica simultaneously enhanced both the wet traction and the fuel efficiency of the tires. The addition of TESPT to the silica-reinforced SBR compound increased the tan δ value at 0 °C while also decreasing the tan δ value at 60 °C. However, the networked silicas such as N-silica(0.10) and N-silica(0.15) have a much greater potential to further enhance the wet traction and the fuel efficiency than the conventional silica-reinforced system does.

Table 3 Tan δ values of SBR compounds reinforced with the networked silica at 0 and 60 °C

Type of silica	Tan δ	
	0 °C	60 °C
Silica only	0.45	0.108
Silica + TESPT	0.60	0.066
N-silica(0.05)	0.59	0.076
N-silica(0.10)	0.66	0.066
N-silica(0.15)	0.61	0.054
N-silica(0.20)	0.70	0.055

Silica reinforcements of the SBR compound improve its resistances against wear. Figure 6 shows the wear properties of the SBR compounds reinforced with networked

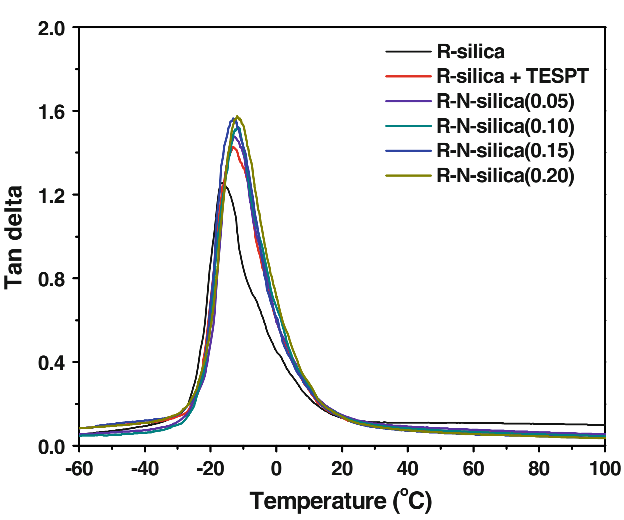


Fig. 5 Tan δ values of SBR compounds reinforced with the networked silica

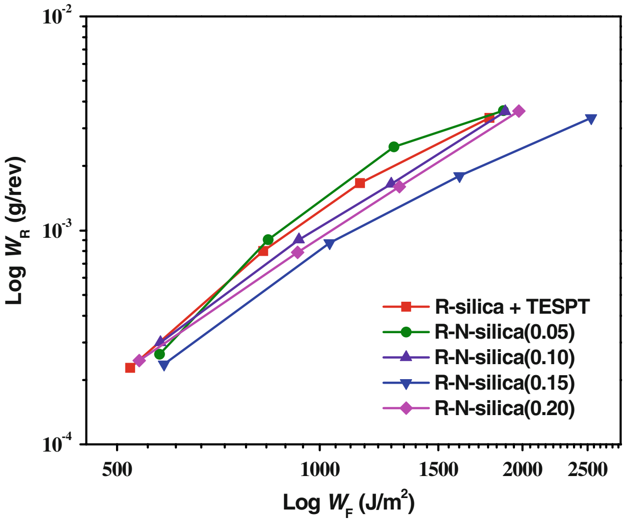


Fig. 6 Abrasion properties of SBR compounds reinforced with the networked silica

silica. The variation of W_R of the SBR compounds according to the W_F was measured using a blade abrader. The W_R increased with increasing W_F on all the SBR compounds, but the rate of increase differed considerably according to the silica-reinforcing system. The wear results of R-unfilled and R-silica are not shown here because of their extremely poor wear resistance. The wear resistance was considerably improved by adding the networked silica. The reinforcement with N-silica(0.15) exhibited the lowest W_R among the prepared SBR compounds, indicating its highest resistance against wear. The improved wear properties of the SBR compounds reinforced with the networked silica was responsible for their high tensile strength and modulus, and low FH. The physical entanglements of the rubber molecules with the organic connecting chains was also effective in suppressing the extraordinary increase in modulus which made the rubber compounds too stiff and degraded their wear properties.

The networked silica, which has previously been used to build networks among silica particles, is a new concept when compared to the conventional silica-reinforced system in which coupling reagents combine silica particles with rubber molecules. TESPT, a widely used coupling reagent, shows high performance in enhancing the tensile, elastic, and wear properties of rubber compounds. However, the mechanism of the silica-reinforcing system with TESPT is based on the covalent bond formation, which inevitably leads to ethanol generation, precure due to sulfide groups, and high modulus levels. The networked silica prepared using TESPT as a connecting material can replace the conventional silica-reinforced system with TESPT, without requiring any heavy and complex modification of the composition and cure conditions of SBR compounds. Furthermore, the improved physical entanglements between the rubber molecules and organic connecting chains results in better wet traction, lower rolling resistance, and stronger wear resistance. The increase in the physical interactions between the rubber molecules and silica particles also enhances the elastic properties of rubber compounds, resulting in high fuel efficiency and long service life of tires. The optimization of the networked silica preparation in terms of loading amount and type of connecting materials will ensure that suitable rubber compounds are prepared for tire manufacturing with enhanced tensile, elastic, and wear properties.

Conclusion

The networked silica prepared using TESPT as a connecting material was used as a replacement for the conventional silica-reinforced system. No major modification of the SBR compounds was required in terms of mixing or curing because the SBR compounds reinforced with the networked silica showed similar physical properties to those reinforced with the conventional system. The SBR compounds reinforced with the networked silica generally exhibited low silica–silica interaction and high rubber–silica interaction due to the networks formed among the silica particles and the entanglements of the rubber molecules with their organic connecting chains. Since the tensile and elastic properties of the SBR compounds were improved by the physical entanglements, their FH and W_R values were decreased. The high tan δ value at 0 °C and the low tan δ value at 60 °C of the SBR compounds reinforced with the networked silica supported their potential as reinforcing fillers for tire manufacture with the advantages of enhanced wet traction and lowered rolling resistance.

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