The Effect of Surface Area of Silicas on Their Reinforcing Performance to Styrene-butadiene Rubber Compounds

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Abstract: The effect of the surface area of silicas on their reinforcing performance to styrene-butadiene rubber (SBR) compounds was systematically investigated. The feasibility of the Brunauer-Emmett-Teller surface area ($S_{BET}$) as a parameter representing the characteristics of the silicas was discussed compared to the mesopore volume, $c$ value, oil absorption, and uptake of silane. The increase in $S_{BET}$ of silicas caused a considerable increase in Mooney viscosity, minimum torque, and hysteresis loss of the silica-filled SBR compounds, while significantly enhancing their abrasion property. These changes were explained by the attrition between the hydrophilic silica surface and the hydrophobic rubber chains. As expected, the change in $S_{BET}$ did not induce any remarkable changes in the cure, processing, tensile, and dynamic properties of the silica-filled SBR compounds because the crosslinking density of the rubber chains mainly determined these properties.

Keywords: silica, SBR compound, surface area, reinforcing performance

Introduction

Although the safety, comfort, and service life of passenger car tires have been traditionally considered as major factors in evaluating their performance, in recent years their rolling resistance and wet traction have been included as important criteria in grading them. The reduction of fuel consumption by lowering the rolling resistance is a plausible way to retard the exhaustion of crude oil and to meet the strict regulations on the emissions of carbon dioxide. The improvement of wet traction guarantees the safety and convenience of driving cars. Since the European Union introduced the labelling system to note the levels of fuel efficiency, wet traction, and the noise of tires, it has been widely expanded into many countries to enforce the improvement of tire performance.

Carbon black, a traditionally used reinforcing filler of rubber compounds, cannot improve simultaneously both the rolling resistance and the wet traction of styrene-butadiene rubber (SBR) compounds used in the tread of passenger cars. Precipitated silica gradually replaces carbon black because the silica reinforcing system accompanied by suitable coupling reagents can achieve significant improvements of both rolling resistance and wet traction. The amount of silica added to the SBR compounds has gradually increased to around 100 phr. A typical coupling reagent, bis[3-(triethoxysilyl)propyl] tetrasulfide (TESPT) makes covalent bonds between the hydroxyl groups of silica surface and the double bonds of rubber molecules, and it causes a significant enhancement of the tensile and dynamic properties of the SBR compounds. The notably low rolling resistance and improved wet traction of silica-filled tires enabled them to be called “green tires” or “environmental friendly tires.” The highly dispersive silica with a high surface area, marketed in recent years, makes a further improvement of the resistance to abrasion of the tires without sacrificing their dynamic properties, resulting in a considerable extension of their service life.

Although silica has become one of the most important fillers for the SBR compounds, its physical and chemical specifications relating to various properties of the silica-filled SBR compounds have not been sufficiently prescribed. It is certain that the structure and surface properties of silica significantly influence the properties of the compounds, such as cure, viscosity, mechanical strength, rolling resistance, wet traction, and abrasion; therefore, the effects of the surface area and the structure of the silicas on their reinforcement performance of elastomers has already been studied.

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ious properties of the silica-filled SBR compounds, such as heat buildup, storage modulus, etc., exhibited high correlation coefficients around 0.8 with the external surface area of silicas, but no quantitative interpretation on these results were shown. The effect of the surface area of the silicas on the modulus, rebound, and tangent delta of silica-filled SBR was not fully discussed.\textsuperscript{10} Furthermore, the silica-silica interaction and silica-polymer interaction also caused a large variance in the properties of the silica-filled SBR compounds.\textsuperscript{11} Therefore, a more definite relationship between the surface area of the silicas and the properties of the silica-filled SBR compounds is essentially required to manufacture effective silicas and to design high performance SBR compounds.

As mentioned above, the effect of the structure and the surface area of the silicas on their reinforcing performance is very significant.\textsuperscript{12} Several parameters representing their performance were suggested; that is, surface area, particle size, surface energy, oil absorption, pore volume, and the amount of hydroxyl groups exposed. Among these parameters, the surface areas of the silicas calculated from the adsorption isotherms of nitrogen using the Brunauer-Emmett-Teller equation ($S_{\text{BET}}$) have been conventionally used to denote their particle size and aggregated structure, while there are various methods for the determination of the surface area.\textsuperscript{13} Occasionally, the surface area determined from the uptake of cetlytrimethylammonium bromide (CTAB) is considered to be more appropriate to reveal the actual surface area available for the access of large rubber chains.\textsuperscript{14} Otherwise, the volumes of micropores and mesopores reflect the aggregated state of the silicas in terms of the accessibility and diffusion of the rubber molecules. The $c$ value determined from the Brunauer-Emmett-Teller plots reflects the interaction between the adsorbate and the surface.\textsuperscript{15} A high $c$ value indicates the strong adsorption of the adsorbate on the surface. The oil absorption is traditionally used to represent the surface property of carbon black.\textsuperscript{16} The amount of oil absorbed indicates the surface affinity to organic substances and the amount of the surface area to be covered by them. Since the hydroxyl groups of silicas rapidly react with chlorotrimethylsilane (CTMS), its incorporated amount to silicas illustrates the amount of surface hydroxyl groups to be reacted with the silane. If the concentration of hydroxyl groups is even on the surface, the incorporated amount of CTMS directly reflects the surface exposed.\textsuperscript{17}

In this study, we use four silicas with different surface areas to investigate the effect of the surface area on the viscoelastic, cure, tensile, dynamic, and abrasion properties of the silica-reinforced SBR compounds. In order to minimize the deviation attributed to the preparation method, the silicas manufactured by the same company were chosen. The surface area, pore volume, oil absorption, $c$ value, and the number of reactive hydroxyl groups of the silicas were also measured to discuss their feasibility as a parameter reflecting their reinforcing performance. Although the addition of the silicas to the SBR compounds considerably improved their tensile and abrasion properties, the variance of the properties with the surface area differed significantly according to the properties themselves. The tensile properties of the SBR compounds, such as modulus and tensile strength, did not exhibit any definite relationship with the surface area of the silicas, but their viscosity and abrasion properties were definitely dependent on the surface area of the silicas that were added.

**Experimental**

1. **Silicas and their characterization**

Four precipitated Newsil silicas with different nominal surface areas ($S115$, $S155$, $S175$, and $S200$) manufactured by WuXi Company (China) were used. The number after “S” denotes their nominal surface areas.

The morphology of the silica samples was investigated using a scanning electron microscope (SEM, JEOL, JSM-7500) and the actual aggregated state of the silicas was examined by a transmission electron microscope (TEM) (JEOL, KEM 2000 FX II). Adsorption isotherms of nitrogen on the silica samples were obtained using an automatic volumetric adsorption system (Mirea SI, Nanoporosity-XQ). The silica samples were evacuated at 200 °C for 3 h prior to exposure to nitrogen gas at the liquid nitrogen temperature to obtain nitrogen adsorption isotherms. $S_{\text{BET}}$ and $c$ values were calculated from the isotherms using the BET equation.\textsuperscript{15} The pore volumes ($V_{\text{meso}}$) of the silica samples were calculated using the Barrett-Joyner-Halenda (BJH) method. The surface areas determined from the uptake of CTAB ($S_{\text{CTAB}}$) were provided by the manufacturer.

The oil absorption of the silicas was measured using linseed oil. A silica sample of 10–15 g was thinly dispersed on a glass plate and mixed with linseed oil (Aldrich). The amount of oil absorption was determined at the point where the mixture of silica and linseed oil made a stable lump that
could not be broken under forced rolling. The mean of three measured oil absorptions was taken as the oil absorption of the silica.

The amount of hydroxyl groups on the silica surface was estimated from the incorporated amount of CTMS on the silica. A silica sample of 1 g was added into a 100 g of n-hexane (95%, Duksan) containing CTMS (≥ 99%, Aldrich) of 0.5 g and was refluxed for 2 h. The recovered CTMS-treated silicas were dried at 100 °C and their thermogravimetric (TG) curves were recorded on a thermal analysis system (TG/DTA 200, SEIKO). The weight loss with the temperature was measured in an air flow (Sinil Gas) of 100 mL·min⁻¹ from an ambient temperature to 800 °C at 10 °C·min⁻¹. The amount of CTMS incorporated was ascertained from the weight loss determined in the range of 200–500 °C due to the burning of the organic species.

2. Preparation of rubber compounds

The SBR compounds used in this study were based on a mixture of 70 phr of SBR and 30 phr of butadiene rubber (BR) and their composition is listed in Table 1. The silica content in all the SBR compounds was set at 80 phr. The SBR compounds were mixed according to the procedure (ISO 5794-3-2011) described in our previous paper.¹⁸,¹⁹ Mixing was carried out using an internal mixer (Namyang Co.) with a capacity of 300 cm³. At first, SBR and BR were masticated for 1.5 min, then the silica and TESPT were added. The master batches of the SBR compounds were obtained by mixing the rubber mixture containing the additives listed in Table 1 at 120–140 °C for 6.5 min. After mixing the master batches additionally for 1 minute, insoluble sulfur and accelerators, such as CBS, DPG, and TBzTD, were added. The preparation of the compounds was finished with further mixing at 80 °C for 2.5 min. The prepared SBR compounds were finally pressed to obtain rubber sheets using a two-roll mill (PM-300, model #138-B, C.W. Brabender Inc.) at 50 °C with rotating 8 rpm. The silica-filled SBR compounds were named by writing the nominal surface area of silica added to “R”, like R175.

Mooney viscosities of the compounds were determined by a Mooney Viscometer 1500 (Monsanto 1500) as the values of ML (1 + 4) 100 °C following the procedure described in ASTM D1646. An oscillating disk rheometer (Daekyung Co. Model No. DRM-100) was used to obtain the rheocurves at 160 °C, according to ASTM D2084. The compounds were cured at 160 °C for 1 minute more than $t_{90}$ times (required for 90% cure) in a cure press (Daekyung Co. Model No. DHP-300) operated under the pressure of 0.25 MPa.

Rubber moieties of the silica-filled SBR compound sheets (3 × 3 mm) were removed using a plasma etching system (Mirae SI Model No. MPE-100). The plasma generated under 200 W in an argon atmosphere was irradiated to a sheet for 60 min. The plasma etched surface of the sheet was examined using an SEM, as mentioned above. Samples for the swelling tests were square-type sheets 2 cm in length and 2 mm in thickness.²⁰ The samples were immersed into toluene (99.5%, Duksan) at room temperature and the increase

| Table 1. The Composition of SBR Compounds |
|-----------------------------------------|
| Step | Material | Content (phr) |
|------|----------|---------------|
| Master batch | SBR (VSL-5025, Lanxess Co.) | 70.0 |
| | BR01 (KBR-01, Kumho Petrochemical Co.) | 30.0 |
| | Expansion oil for SBR | 26.25 |
| | Silica | 80.0 |
| | Carbon black (N330, Orion Engineered Carbons Co.) | 6.4 |
| | Zinc oxide (ZnO, Daewoon Co.) | 3.0 |
| | Stearic acid (Duksan Industrial Co.) | 2.0 |
| | bis[(3-Triethoxysilyl)propyl]tetrasulfide; TESPT, Dow Corning Co. | 6.4 |
| | N,N'-[1,3-Dimethylbutyl]-N'-phenyl-p-phenylenediamine; 6PPD Flexsys Co. | 1.5 |
| | Wax (Daewoon Co.) | 1.0 |
| | TDAE oil (Kukdong Oil & Chem Co.) | 11.25 |
| Final mixing | Insoluble sulfur (Miwon Chemical Co.) | 2.1 |
| | N-Cyclohexyl-2-benzothiazoyl sulfenamide (CBS, Miwon Chemical Co.) | 1.5 |
| | N,N'-Diphenylguanidine (DPG, Kumho Petrochemical Co.) | 2.0 |
| | Tetrabenzylthiuram disulfide (TBzTD, Flexsys Co.) | 0.2 |
was measured in mass at given time intervals. The swelling ratio \( (Q) \) was calculated by \( Q = (W_r/\rho_r + W_s/\rho_s)/(W_r/\rho_r) \), where \( W_r \) and \( W_s \) were the weights of rubber before and after the swelling treatment, respectively, and \( \rho_r \) and \( \rho_s \) were the densities of the rubber and the solvent, respectively. The cross-linking density of the SBR compounds was calculated using the procedure described in the literature.\(^{21}\)

Tensile measurement of the silica-reinforced SBR compounds was carried out using a universal tensile tester (Daekyung Model No. DUT-500C) at room temperature with a crosshead speed of 100 mm·min\(^{-1}\) according to ASTM D412. Moduli were determined from the slopes of the strain–stress curves and the tensile strength and elongation at break were obtained at the stress and strain at the break point, respectively. In the measurement of hysteresis losses, the samples were stretched up to 100% elongation and retracted at a crosshead speed of 100 mm·min\(^{-1}\). Hysteresis loss was defined by the energy dissipated relative to the energy supplied on stretching, and calculated the areas of \( A_{\text{ext}} \) (work done during extension) and \( A_{\text{ret}} \) (work done during retraction) that were determined from the stress-strain curves.

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). The Payne effect was defined as the difference in the storage modulus between 0.01% and 30% strains. Temperature scans were also run from −80 °C to 100 °C at a heating rate of 5 °C·min\(^{-1}\) with a frequency of 1 Hz and a strain of 0.05% to obtain the loss tangent (\( \tan \delta \)) of the compounds. The glass transition temperature \( (T_g) \) was also determined from the temperature scan results of the DMA experiments. The hardness of the silica-filled SBR compounds was measured using a Shore A durometer, according to ISO 7619-1.\(^{22}\)

A blade abrader at a rotating speed of 10 rpm was used to measure the abrasion properties of the compounds.\(^{23}\) The abrasion was determined by the average loss in weight per revolution of the sample.

**Results and Discussion**

1. **Structure and properties of silicas**

In order to achieve the high performance of silica as a reinforcing filler for the SBR compounds, the silica should be comprised of extremely small, nano-sized particles with a large external surface area, which enables them to sufficiently interact with rubber chains. Figure 1 shows SEM images of the silicas. The size of the primary silica particles were commonly ranged at 20–50 nm, regardless of their surface area. In the TEM images shown in Figure 2, the primary particles made loosely-bound agglomerates of 1–2 μm.

The adsorption of nitrogen on solid materials reflects their porous characteristics. Figure 3 shows the adsorption isotherms of nitrogen on the silicas. The overall shapes of the isotherms were very similar to the type II classified by IUPAC, exhibiting a predominant adsorption occurring on the external surface. The gradual increase in the amount of
nitrogen adsorbed with $P/P_0$ also indicated the accumulation of nitrogen molecules on the external surface, not in micropores. The shift of the isotherms upward with the increase in the nominal surface area of the silicas confirmed that the differences in their surface areas were caused by the increase in the volume of the mesopores. Figure 4 illustrates $t$-plots of the nitrogen adsorption isotherms on the silicas to verify the contribution of micropores to the surface area. The convergence of $t$-plots to zero at around zero thickness ($P/P_0\rightarrow0$) indicated negligible amounts of micropores. The calculated volumes of the micropores from these $t$-plots were actually around $0.01\text{ cm}^3\cdot\text{g}^{-1}$, which was considerably smaller than those of the mesopores determined from the BJH method range of $0.24$–$0.66\text{ cm}^3\cdot\text{g}^{-1}$. The high linearity of the BET plots (not shown) obtained from the adsorption isotherms of nitrogen on the silicas implied that their adsorption of nitrogen satisfied the assumption for the BET equation; therefore, the calculated values of $S_{\text{BET}}$ and $c$ were sufficiently rational.\textsuperscript{15}

The reactive chlorine atoms of CTMS reacted with the exposed hydroxyl groups of silica, incorporating on it with the release of hydrogen chloride.\textsuperscript{17} The amount of CTMS incorporated was determined from the TG curves of CTMS-incorporated silicas (not shown): the weight loss below 100 °C was attributed to the desorption of water adsorbed physically on the hydroxyl groups, while the weight loss above 200 °C was attributed to the combustion of the methyl groups of CTMS incorporated into the silicas. The amount of CTMS incorporated to S115 was small, while that of CTMS incorporated into S200 was relatively large, indicating that the silica with a high surface area had more hydroxyl groups compared to a silica with a small surface area.

Table 2 summarizes $S_{\text{BET}}$, $S_{\text{CTAB}}$, $c$ value, mesopore volume, oil absorption, and the amount of CTMS incorporated into the silicas. Although the $S_{\text{BET}}$ values of the silicas measured in this study were slightly different from their nominal values, they gradually increased with their nominal values. Since the $S_{\text{CTAB}}$ of the silicas, provided by their manufacturer, increased with the increasing $S_{\text{BET}}$ with a good linear relationship, $S_{\text{CTAB}}$ was no longer meaningful as an independent parameter in discussing the effect of the surface area on their reinforcing performance. The gradual increase in mesopore volume of the silicas with $S_{\text{BET}}$ indicated that the variance in their $S_{\text{BET}}$ was responsible for the voids formed among the silica particles. This means that the $S_{\text{BET}}$ of the silicas was

| Silica | $S_{\text{BET}}$\textsuperscript{(a)} (m\textsuperscript{2}·g\textsuperscript{-1}) | $S_{\text{CTAB}}$\textsuperscript{(b)} (m\textsuperscript{2}·g\textsuperscript{-1}) | $V_{\text{meso}}$\textsuperscript{(a)} (cm\textsuperscript{3}·g\textsuperscript{-1}) | $c$\textsuperscript{(a)} | Oil absorption (g·100 g\textsuperscript{-1}) | Amount of CTMS Incorporated (mmol·g\textsuperscript{-1}) |
|--------|----------------------------------|----------------------------------|-------------------------------|---------|-------------------|-----------------------------|
| S115   | 116                              | 105                              | 0.240                         | 156     | 218               | 0.41                        |
| S155   | 136                              | 145                              | 0.373                         | 152     | 216               | 0.49                        |
| S175   | 161                              | 165                              | 0.400                         | 145     | 222               | 0.64                        |
| S200   | 185                              | 185                              | 0.660                         | 162     | 237               | 0.75                        |

\textsuperscript{(a)} determined from nitrogen adsorption isotherms

\textsuperscript{(b)} provided by the manufacturer
predominantly dependent on their aggregation pattern of primary particles of the silicas, not on the size of the primary particles. The \( c \) values obtained from the nitrogen adsorption isotherms of the silicas were closely dispersed in a narrow range of 145–160. The similar \( c \) values of all the silicas, regardless of their surface areas, reflected their similar surface energies, which consisted of the same constituents and arrangements. Although the amount of oil absorption on the silicas increased with the increasing \( S_{\text{BET}} \), the differences among them were very small. Since the formation of the oil layer was checked by the naked eye, the perceived thick oil layer lowered the sensitivity of the surface structure. All these parameters mentioned above varied according to the silicas, but the \( S_{\text{BET}} \) measured from the adsorption isotherms of nitrogen was found to be the best parameter representing the surface effect of the silicas in terms of their variance width and sensitivity.

2. Viscoelastic, cure, tensile, and dynamic properties of SBR compounds

Since the reinforcing property of silica is primarily dependent on the dispersion of silica in rubber compounds, the dispersed state of the silica particles in rubber was examined after plasma sputtering. The incident plasma beam selectively removed the soft rubber, while the hard silica particles remained even after plasma sputtering. The high dispersion of the silica particles in the rubber compounds indicated their even distribution, and the cohesion of the silica particles caused deep and wide valleys among the silica particles. Figure 5 exhibits SEM images of the SBR compounds sputtered by the plasma for 60 min. The high loading of silica, 80 phr, caused a highly packed state of the silica particles after plasma sputtering. The lack of large silica lumps indicated that the silica particles were evenly dispersed. The similar dispersion of the silicas, regardless of their surface area, excluded the adverse contribution of their dispersion to the reinforcing performance.

Silica added into the SBR compounds inevitably influences their viscous and cure properties because the cure additives are generally adsorbed on it and become inactive. Figure 6 shows the rheocurves of the SBR compounds reinforced by the silicas with different surface areas. The overall shapes of the rheocurves were similar, while both the minimum and maximum torques of the compounds increased with the increase in the surface area of the added silica. The higher variance of the minimum torque with the surface area rather than the maximum torque revealed its significant influence on the minimum torque. Table 3 lists the viscosity, scorch time, \( T_{40} \) time, and torques of the silica-filled SBR compounds determined from their Mooney viscosity curves and rheocurves. \( T_{40} \) time is defined by the time required for a 40% cure and is used as a parameter corresponding to the cure rate. Mooney viscosity of the compounds increased as the surface area of the silicas increased, resulting in a very high viscosity on R200. In contrast, scorch times \( t_s \) and \( t_{35} \) did not show any definite trend with the surface area of the silicas. The change in \( T_{40} \) time with the surface area of the silicas was not considerable. However, \( t_{\text{min}} \) increased with the surface area of the silicas, while \( t_{\text{max}} \) was invariant. Delta torque decreased with the increase the surface area, but the
width of its variance was relatively small. The small variances in the cure rate and the scorch time revealed that these properties are mainly dependent on the cure process of rubber, not on the interface between silica particles and rubber chains.

In order to clearly illustrate the dependence of the cure and the viscous characteristics of the compounds on the surface area, Figure 7 shows their correlation diagrams with the surface area of the silicas. ML (1 + 4) and $\tau_{\text{min}}$ proportionally increased with the surface area, while the delta torque decreased. The variations of the scorch time ($t_{35}$) with the surface area were very small. Mooney viscosity represents the attrition between the rubber chains and the silica particles determined at a relatively low temperature of 100 °C, and $\tau_{\text{min}}$ reflects the attrition at the initial stage of cure at a cure temperature of 160 °C. The fact that the addition of the silicas with a high surface area resulted in a high Mooney viscosity and $\tau_{\text{min}}$, suggests that these properties are mainly dependent on the attrition that occurred at the interface between the silica particles and the rubber chains. The strong interaction between the SBR and the silicas restricts the motion of the rubber chains at the interface. In contrast, $\tau_{\text{max}}$, $T_{40}$ time, and the scorch times did not vary remarkably with the surface area of the silicas because these properties were mainly dependent on the cure process of the compounds. The decrease in delta torque with the increase in the surface area was due to the inactivation of the cure additives through their adsorption.

Tensile properties of the silica-filled SBR compounds are very important in applying them as a tread compound of passenger car tires because tires should maintain their shape and endure under huge loads. Table 4 lists the hardness, crosslinking density, modulus, tensile strength, and elongation at break of the SBR compounds reinforced by the silicas with different surface areas. The hardness and 50% modulus slightly increased with the increase in the surface area, reflecting the solidification effect related to the increase in the interface. However, 200% and 300% moduli, tensile strength, and elongation at break of R200 were less than those of R175, indicating the adverse effect of the high surface area of silica on these properties. Generally, the addition of the silicas caused significant improvement in the tensile properties of the SBR compounds compared to those of non-filled ones, but the variances of the tensile properties with the surface area of the silicas were not considerable. It is rational that the tensile properties of the silica-filled SBR compounds are mainly dependent on the crosslinking state of the rubber. The cova-

| Table 4. Tensile Properties of SBR Compounds |
|------------------------------------------|
| **Rubber compound** | **Hardness** | **Crosslinking density ($10^{19}$)** | **Modulus (MPa)** |
|              |            |                                   | **M-50** | **M-100** | **M-200** | **M-300** | **T.S. (MPa)** | **E.B. (%)** |
| R115                   | 67         | 8.2                                | 2.2     | 4.4      | 10.2     | -         | 15.2 | 276        |
| R155                   | 68         | 8.3                                | 2.2     | 4.4      | 10.1     | -         | 16.3 | 298        |
| R175                   | 69         | 8.3                                | 2.3     | 4.4      | 10.2     | 17.0      | 17.8 | 312        |
| R200                   | 71         | 9.5                                | 2.4     | 4.4      | 9.6      | 15.8      | 16.5 | 311        |

Figure 7. Correlation diagrams between the cure property of the SBR compounds and the surface area of the silicas.
The Effect of Surface Area of Silicas on Their Reinforcing Performance to Styrene-butadiene Rubber Compounds

lent bonds formed between the silica particles and the rubber molecules through coupling reagents significantly enhance the tensile properties of the compounds, but the surface area does not work as a predominant factor governing the bond formation.

In contrast to the tensile properties, the dynamic properties of the silica-filled SBR compounds are substantially dependent on the surface area of the silicas. Table 5 shows the Payne effect, glass-transition temperatures, hysteresis loss, tan δ, and abrasion of the SBR compounds. The high values of the Payne effect exhibited the presence of strong silica-silica interaction because of the high silica loading, 80 phr, but the difference among the values—according to the surface area of the silicas—was not remarkable. The considerably high Payne effect of R200 suggested that the high surface area promoted the aggregation of silica particles. The slightly high Payne effect of R175 and R200, which had relatively high surface areas, might be responsible for the non-interactive area between the silica particles and the rubber chains. Hysteresis loss gradually increased with the increase in the surface area of the added silicas, regardless of the cycle, and thus they reflected the hysteresis that originated at the interface. The tan δ values at 0 °C and 70 °C of the SBR compounds corresponded to the wet traction and rolling resistance, respectively. The wet traction was invariant with the surface area of the silicas, while the rolling resistance that corresponded to tan δ at 70 °C slightly increased with the increase in the surface area. Since the wet traction mainly depends on the modulus of a rubber compound, the effect of the surface area on it may be negligible. On the other hand, the dependence of rolling resistance on the surface area indicated the loss of energy at the interface by hysteresis. Also, the abrasion of the compounds greatly reduced with the increase in the surface area. The low abrasion of R200 by 25% compared to that of R115 reliably exhibited the importance of the surface area to the abrasion property.

Figure 8 shows the correlations between the dynamic properties of the silica-filled compounds and the surface area of the silicas.

Table 5. Dynamic Properties of SBR Compounds

| Rubber compound | Payne effect | $T_g$ (°C) | Hysteresis loss (J) | tan δ at | Abrasion (g) |
|-----------------|--------------|------------|---------------------|----------|--------------|
|                 |              |            | 1 cycle  | 2 cycle  | 3 cycle                  | 0 °C  | 70 °C   |             |
| R115            | 10.3         | −22        | 0.99     | 0.29     | 0.26                     | 0.238 | 0.078  | 0.075      |
| R155            | 10.2         | −22        | 1.02     | 0.32     | 0.27                     | 0.230 | 0.075  | 0.071      |
| R175            | 10.1         | −25        | 1.17     | 0.36     | 0.30                     | 0.227 | 0.084  | 0.063      |
| R200            | 12.4         | −28        | 1.47     | 0.42     | 0.34                     | 0.230 | 0.088  | 0.052      |

Figure 8. Correlation diagrams between the dynamic property of the SBR compounds and the surface area of the silicas.

Conclusions

The size of the primary particles of the silicas used in this study commonly ranged from 20 nm to 50 nm and they aggregated to form loosely-bound agglomerates of 1–2 μm. Since the silicas have a negligibly small amount of micropores,
their surface areas are mainly dependent on the aggregation state. Although the volume of the mesopores, $c$ value, oil absorption, and the amount of incorporated CTMS varied with the surface area, the extent of their variances were so small that they were inappropriate to use as a parameter representing the reinforcing performance of silicas to the SBR compounds.

The Mooney viscosity and $\tau_{\text{max}}$ of the silica-filled SBR compounds increased with the surface area, while the variances of their scorch time and $\tau_{\text{max}}$ with the surface area were very small. The high viscosity of the compound reinforced by the silicas with a high surface area indicated that the restriction of the rubber chains at the interface between the silica particles and the rubber was responsible for the viscosity. In contrast, tensile properties, such as modulus, tensile strength, and elongation at break of the compounds, did not vary with the surface area of the silica because they were mainly dependent upon the cured state of the compounds. The hysteresis loss of the compounds gradually increased with the surface area, but the abrasion considerably decreased with the surface area of the reinforced silicas. The effect of the surface area on the Payne effect and the wet traction was small. Silicas with a high surface area are beneficial in improving the abrasion of the compounds, but are unfavorable for viscosity and rolling resistance.

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