Effect of Nano Zinc Oxide on the Cure Characteristics and Mechanical Properties of the Silica-Filled Natural Rubber/Butadiene Rubber Compounds

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ABSTRACT: With the increasing interest in environmental and health issues, legal restrictions, such as European Union (EU) End of Life Vehicle Directives, were strengthened. This led us to incorporate nano zinc oxide (nano-ZnO), with particle sizes of 30–40 nm and specific surface areas of 25.0–50.0 m^2/g, instead of conventional ZnO into natural rubber (NR)/butadiene rubber (BR) compounds to decrease the content of zinc in the formulation. In the unfilled system, only a 20 wt % nano-ZnO content, compared to conventional zinc oxide content, showed the cure characteristics and mechanical properties of the same level. This was because the increase in the specific surface area of the nano-ZnO led to an increase in the degree of crosslinking. The effect of nano-ZnO on the cure characteristics and mechanical properties was more pronounced in the silica-filled system than in the unfilled system. This was mainly because of the dispersing agent used in the silica-filled system, which also improved the dispersion of nano-ZnO. The silica-filled NR/BR compounds containing 0.3–3.0 phr of nano-ZnO showed improved curing characteristics and mechanical properties, such as optimum cure time, 100 and 300% modulus, tensile strength, and tear strength compared to the compound with 5 phr of conventional ZnO. The optimum amounts of nano-ZnO and stearic acid were only 1.0 and 0.1 phr, respectively. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 1535–1543, 2010

Key words: nanotechnology; rubber; viscoelastic properties; vulcanization

INTRODUCTION

It can be said that nanotechnology begins with nanomaterials and is connected with the systems of nanoprocessing, nanoparts, and nanoproducts by the ripple effect. In particular, nanopowder materials constitute the most active research field among various nanomaterials. Currently, active research is being conducted into nanoclays and carbon nanotubes, as well as nano zinc oxide (nano-ZnO) in the rubber industry.[1]

When Goodyear first achieved the vulcanization of rubber, 8 parts of sulfur were used per 100 parts of rubber, and the vulcanization process needed 5 h at 140°C. After that, the addition of zinc oxide (ZnO) allowed the vulcanization time to be reduced to 3 h. Subsequently, the vulcanization time was significantly reduced to 1–3 min by the use of only 0.5 phr of an accelerator.[2]

ZnO is an important inorganic pigment for the rubber industry, and over the past 100 years, the rubber industry has used an increasing number of the physical and chemical properties of ZnO.[3] According to Beniska and Dogadkin,[4] ZnO promotes the initial response by activating the vulcanization accelerator but does not have any direct influence on the vulcanization process between sulfur and the rubber chains. Moore et al.[5] showed that ZnO plays the role of a catalyst, and Barton et al.[6] argued that ZnO has an influence on the degree of crosslinking of natural rubber (NR) and improves the heat resistance of the vulcanizate. In this way, ZnO has become indispensable for the crosslinking of rubber with sulfur. In general, the optimum content of ZnO is known to be 5 phr in NR and butadiene rubber (BR).[2] The particle size of ZnO ranges from 0.1 to 0.4 μm, and the corresponding specific surface area is in the range 10–20 m^2/g.[7] According to some studies, a substantial reduction in the mechanical properties of the vulcanized rubber is observed when the content of ZnO is less than 2 phr.[8,9]

However, with the increasing interest in the environmental and health issues and the consequent

strengthening of legal restrictions, such as European Union (EU) End of Life Vehicle Directives, various zinc compounds, including ZnO, have been singled out for attention. Around 2% of ZnO is included in tire rubber, and this is the main source of zinc pollution from road transportation.[10] Accordingly, rubber products are now required to use minimum amounts of ZnO.[11] To reduce the amount of ZnO, several methods have been suggested, such as the premelt mixing of ZnO, stearic acid, and an accelerator to improve their interaction with each other,[12] the manufacturing of zinc-loaded clay with clay as a carrier[11] and the use of nano-ZnO to increase the available surface area.[11,13]

Particularly, most of the studies on nano-ZnO have been carried out on carbon-black-filled compounds. In the study of Wang and Chen,[13] the carbon-black-filled compounds included 1–5 phr nano-ZnO. In this case, a nano-ZnO master batch was used to improve the dispersion. As a result, the optimum cure time [t_{90}; i.e., the time at which 90% of the maximum torque was achieved] and the elongation at break were increased. In addition, this study reported that increasing the content of nano-ZnO reduced the wear resistance of the vulcanizates. On the other hand, in the study of Heideman et al.,[11] with carbon black as a filler, t_{90} decreased when 0.05–3.0 phr nano-ZnO was used, and the greater the amount of nano-ZnO was, the greater the wear resistance was.[11] In this case, zinc was loaded on the clay to reduce the amount of ZnO required in the rubber compounds.

In this study, we used nano-ZnO with particle sizes of 30–40 nm and specific surface areas of 25–50 m^2/g. The existing studies, with carbon black as a filler, presented contradictory opinions, especially for the wear resistance of the compounds. Accordingly, at first, we evaluated the effect of nano-ZnO on the cure characteristics, mechanical properties, wear resistance, and morphology of nano-ZnO in the unfilled NR/BR compounds and, after that, also in the silica-filled NR/BR compounds. We also evaluated the reduced amounts of ZnO in the silica-filled NR/BR compounds by using nano-ZnO.

EXPERIMENTAL

Materials

In this experiment, 20 phr NR (SMR-3L), 70 phr BR (KBR-01, Kumho Petrochemical Co., Ulsan, Korea), and 10 phr high-styrene resin (HSR; KHS-68, Kumho Petrochemical) were used as a base rubber blend. After they were blended with each other, we used Zeosil 155 (Rhodia-Korea, Inchun, Korea) as a filler, KS-1 (Kilchun Chemical Co., Ulsan, Korea; specific gravity = 5.47–5.64, particle size = 300–600 nm, and

specific surface area = 3.0–7.0 m^2/g) as the conventional ZnO, and SUNZNO-NAS (Sunjin Chemical Co., Ansan, Korea; specific gravity = 5.67, particle size = 30–40 nm, specific surface area = 25–50 m^2/g, and surface-treated with alkyl silane) as the nano-ZnO. We used stearic acid, process oil, sulfur, 2,2′-dithiobenzothiazole (MBTS), and tetramethyl thiuram monosulfide (TMTM) as vulcanization accelerators and Si-69 [bis(3-triethoxysilylpropyl)tetrasulfane] as a coupling agent.

Preparation of the silica-filled NR/BR compounds

In this experiment, 20 phr NR, 70 phr BR, and 10 phr HSR were blended for 5 min at 40°C with a two-roll mill with a roll speed ratio of 1 : 1.4. First, the premixed NR/BR/HSR blend was added to ZnO or nano-ZnO as an activator, with stearic acid as a lubricant and 4,4-bis(α,α-dimethylbenzyl)diphenylamine as an antioxidant (Naugard 445); after that, it was compounded in a Banbury-type mixer (Shokai, Tokyo, Japan) for 5 min at 85°C. Second, silica (Zeosil-155), a dispersing agent [poly(ethylene glycol) (PEG-4000)], and a silane coupling agent (Si-69) were added to the mixed compound, and they were compounded again in a Banbury-type mixer for 7 min at 85°C. Finally, the master batch was manufactured by the addition of process oil (W-1900), and the batch was mixed for 5 min. Then, the master batch was added to sulfur as a curing agent and MBTS/TMTM was added as an accelerator; after that, we maximized the mixing efficiency by using the two-roll mill. To prevent scorching caused by the dissipation of heat from the compound, the mixing of sulfur and the accelerator was completed within 3 min after their addition to the master batch. For the unfilled system, the same manufacturing process was used, except for the addition of silica, the silane coupling agent, and the dispersing agent.

We determined t_{90} by measuring the increase of the torque values of the nonvulcanized rubber compounds at 160°C using a curemeter [model 2000 oscillating-disk rheometer (ODR), Myung-Ji Tech, Seoul, Korea]. To manufacture the vulcanizates, the compound was pressurized for t_{90} in a hydraulic press at 160°C.

Characterization

Cure characteristics (ODR)

The cure characteristics of the nonvulcanized rubber compounds were measured with a curemeter (MYUNG-JI Tech, model ODR 2000, Seoul, Korea) under the following conditions: oscillation angle = ±1°, temperature = 160°C, and running time = 30 min.

TABLE I
Experimental Formulations of the NR/BR Compounds for the Unfilled System (phr)

	UF-1	UF-2	UF-3	UF-4	UF-5	UF-6	UF-7	UF-8
NR (SMR-3L)					20			
HSR (KHS-68)					10			
BR (KBR-01)					70			
Silica (Zeosil-155)					0			
Coupling agent (Si-69)					0			
PEG-4000					0			
ZnO	5.0	0.5	0	—	—	—	—	—
Nano-ZnO	—	—	—	3.0	1.5	1.0	0.5	0.3
Stearic acid	1.0	1.0	1.0	0.1	0.1	0.1	0.1	0.1
Naugard 445					1			
W-1500					1			
Sulfur					1			
MBTS					1.5			
TMTM					0.5			

Modulus and tensile strength (σ_b)

Stress–strain curves were obtained with a universal testing machine (KSU-05M-C, Kyoung Sung Testing Machine Co. Ltd., Ansan, Korea) at an extension speed of 500 mm/min. From these curves, the 100% modulus (E_{100}), 300% modulus (E_{300}), σ_b, and elongation at break of each vulcanizate were determined.

Tear strength

For the specimen manufactured with a die C of ASTM D 624, the maximum load (F) value was measured at an extension speed of 500 mm/min with the universal testing machine. This value divided by the specimen thickness (d) was recorded as the tear strength: G_t ($= F/d$).

Wear rate

Abrasion experiments were performed in an air atmosphere at room temperature with a knife abrasion tester.[14] The rotation speed of the rubber disk was controlled to 10 rpm to prevent heat generation due to frictional sliding. The applied normal loads on the surface of the specimen were 19.6 N. The wear rate was determined by the following equation: $W_R = W_L/n$, where W_R is the wear rate (g/revolution), W_L is the weight lost from the specimen by abrasion, and n is the rotation speed.

Morphology by scanning electron microscopy (SEM)

The dispersion state of ZnO in the rubber matrix was examined with SEM (Hitachi, model S-3000N, Tokyo, Japan). The surface of the cut section of the unfilled vulcanizates was treated with platinum.

Swelling ratio

Swelling tests were conducted to evaluate the degree of crosslinking of the vulcanizates. Three test pieces

($30 \times 5 \times 2$ mm^3) were left in toluene for 1, 2, 3, 6, 9, 12, and 24 h at 30°C in accordance with ASTM D 471-79. The swelling ratio was calculated by measurement of the weight before swelling (M_1) and the weight each hour (M_2) and with the following equation:

$$\text{Swelling ratio}(\%) = [(M_2 - M_1)/M_1] \times 100$$

RESULTS AND DISCUSSION

Unfilled system

Effect of nano-ZnO on the cure characteristics and mechanical properties of the unfilled compounds

The formulations for the contents of ZnO and nano-ZnO in the unfilled system are shown in Table I. In general, when diene rubbers, such as NR, BR, SBR, and NBR, are vulcanized with organic accelerators, 3.0–5.0 phr ZnO is added as an activator in combination with 1.0–2.0 phr stearic acid.[15]

Therefore, the content of ZnO was varied in the range 5.0–0 phr, and the content of stearic acid was fixed at 1.0 phr. In addition, nano-ZnO was used in the range 3.0–0.3 phr because of its small particle size, and we fixed the content of stearic acid at 0.1 phr. First, to evaluate the cure characteristics, the vulcanization curves of the test formulations were obtained by ODR, and the detailed results are shown in Figure 1 and Table II, respectively. For the UF-1–UF-3 compounds mixed with 5.0, 0.5, and 0 phr ZnO, respectively, the improvement of the maximum torque (T_{max}) value caused by increasing content of ZnO was caused by the fact that the Zn^{2+} ions in ZnO formed a chelate compound with the rubber–S$_{xy}$–accelerator (x,y = number of sulfur atom; S$_{xy}$ = S$_x$S$_y$; x: 1 ~ 8, y = 8-x) and, thus, made the vulcanization rate higher than that obtained with the free accelerator during the initial vulcanization and the fact that the polysulfides (S$_x$S$_y$) were more
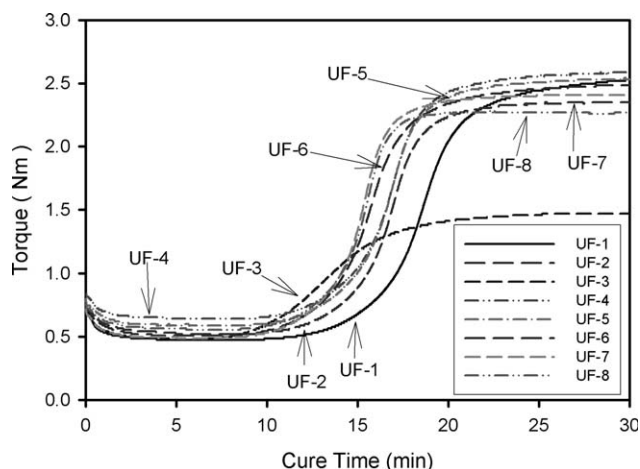
Figure 1 ODR curves of the NR/BR compounds for the unfilled system.

easily broken, whereas each sulfur fragment (S_x and S_y) was used for the vulcanization, which thus increased the degree of crosslinking.[16] On the other hand, the decrease of scorch time (t_{10}) and t_{90} brought about by the decrease in the ZnO content was judged to be caused by the fact that the decomposition time of ZnO decreased during the combination process between the rubber and S_{xy}–accelerator because of the decrease in the Zn^{2+} content.[15]

In addition, when nano-ZnO was used, the same tendency was also seen as that in the case of ZnO. Even when the nano-ZnO content was decreased to 3.0, 1.5, and 1.0 phr, as in the case of the UF-4–UF-6 compounds, the T_{max} values were similar to those observed when 5.0 phr ZnO (UF-1 compound) was used, and when 1.0 phr nano-ZnO was used, t_{90} of the UF-6 compound decreased by 180 s compared to that of the UF-1 compound. In particular, the T_{max} and E_{300} values of the UF-6 compound were 2.49 Nm and 1.617 MPa, which were similar to those observed for the compound with 5.0 phr conventional ZnO, that is, 2.53 Nm and 1.723 MPa, respectively. The UF-4–UF-8 compounds with nano-ZnO

showed higher minimum torque (T_{min}) values than the UF-1–UF-3 compounds. This was due to the small amount of stearic acid applied to the compounds, which caused a reduced lubrication effect.

The stress–strain curves and mechanical properties of the UF-1–UF-8 compounds are shown in Figure 2 and Table II, respectively. From the results of the UF-1–UF-3 compounds, the decrease in ZnO content led to decreases in E_{100} and E_{300} and an increase of the elongation at break. This was due to the decrease in the crosslink density of the compounds.[17] Such a kind of trend was also shown in the UF-4–7 compounds, in which nano-ZnO was used.

Figure 3 shows the tear strength and wear rate of the compounds according to the content of ZnO and nano-ZnO in the unfilled system. The more the content of ZnO decreased, the more the tear strength increased. Without ZnO, the tear strength of the UF-3 compound was the highest. This was caused by the increase in the elongation at break. When the same amount of nano-ZnO was used, excellent tear strength was observed, as compared to when conventional ZnO was used. This was because the crack growth was prevented more effectively by the presence of a lot of nanosized particles of ZnO. In the previous studies, with carbon black as the filler, there were contradictory opinions regarding the evaluation of the wear resistance as a function of the content of nano-ZnO, but according to this study, with the unfilled system, the compounds with conventional ZnO showed better wear resistance than those with nano-ZnO. For the UF-1–3 compounds mixed with ZnO, a higher amount of stearic acid was used than for the UF-4–8 compounds mixed with nano-ZnO, that is, 1.0 phr versus 0.1 phr; so the increased lubrication caused the slip of a knife abrader on the surface of the specimen during abrasion. Accordingly, the compounds mixed with conventional ZnO showed that the lower ZnO content was, the lower its wear rate was, but the compounds mixed with nano-ZnO showed that the lower nano-ZnO content was, the higher its wear rate was; that

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TABLE II
Cure Characteristics and Mechanical Properties of the Unfilled System

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|	UF-1	UF-2	UF-3	UF-4	UF-5	UF-6	UF-7	UF-8
T_{min} (Nm)	0.47	0.52	0.47	0.64	0.60	0.51	0.49	0.55
T_{max} (Nm)	2.53	2.35	1.47	2.61	2.54	2.49	2.41	2.28
t_{10} (s)	895	809	562	801	795	741	726	736
t_{90} (s)	1318	1138	1087	1176	1153	1138	1029	1009
σ_b (MPa)	2.350	2.333	3.105	1.968	2.355	2.371	2.472	3.217
E_{100} (MPa)	0.892	0.736	0.484	0.861	0.846	0.843	0.764	0.729
E_{300} (MPa)	1.723	1.401	0.759	1.738	1.697	1.617	1.473	1.376
Elongation (%)	450.0	575.5	1675.4	355.4	457.4	495.1	581.9	833.0
Swelling ratio (%)	365.1	410.2	680.2	360.3	362.4	384.5	389.9	501.7
Tear strength (kgf/cm)	16.28	19.31	22.24	17.48	18.18	20.51	21.24	26.66
Wear rate ($\times 10^{-4}$ mg/revolution)	2.20	1.20	1.16	2.97	3.10	3.13	3.19	0.87
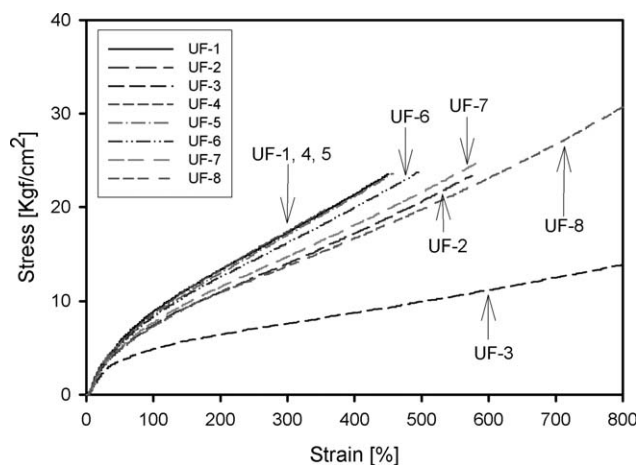
Figure 2 Stress–strain curves of the NR/BR compounds for the unfilled system.

is, there was a decreasing wear resistance. This could be explained by the fact that, in the compounds mixed with conventional ZnO, the lower the ZnO content was, the greater the lubrication effect of stearic acid was; this, thus, caused causing an increase in the degree of slipping on the surface. However, in the compounds mixed with nano-ZnO, the small amount of stearic acid did not act effectively as a lubricant. When the lubrication effect was minor, the reinforcing effect by nano-ZnO was emphasized, so the wear resistance decreased as the content of nano-ZnO decreased.

Swelling ratio and SEM morphology of the unfilled compounds

The cure characteristics and mechanical properties of the unfilled compounds confirmed that t_{90} of the compounds mixed with nano-ZnO decreased, whereas E_{100} and E_{300} increased. Only at 20 wt % nano-ZnO content did ZnO show cure characteristics and mechanical properties of the same level or
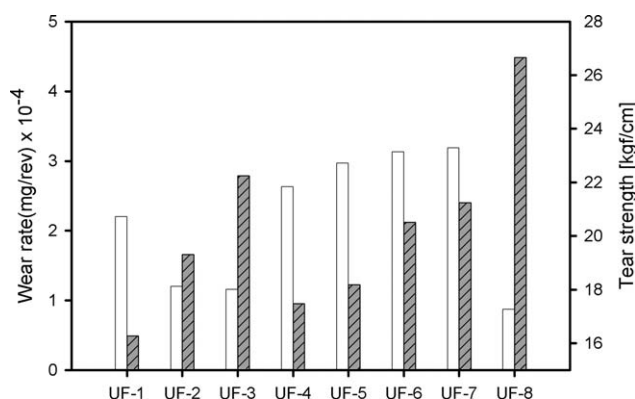

Figure 3 Tear strength and wear rate of the NR/BR compounds for the unfilled system.

higher. Figure 4 shows the swelling ratios of the UF-1–UF-8 compounds. At higher swelling ratios, the solvent penetrated into the rubber matrix more easily, which means that the degree of crosslinking was low. In the unfilled system, the swelling ratios of the compounds were in the order: UF-4 < UF-5 < UF-1 < UF-6 < UF-7 < UF-2 < UF-8 < UF-3. This precisely corresponded to the T_{max} value of the cure characteristics, which was influenced by the degree of crosslinking. For the UF-4 and UF-5 compounds, although the contents of nano-ZnO were less than that of ZnO in the UF-1 compound, the degree of crosslinking was high because of the increased specific surface area.

Figure 5 shows the SEM images of the UF-1 and UF-2 compounds mixed with ZnO and the UF-6 and UF-7 compounds mixed with nano-ZnO, respectively. As shown in Figure 5(a,b), corresponding to the UF-1 and UF-2 compounds, the size of the particles is large compared to that shown in Figure 5(c,d), corresponding to the UF-6 and UF-7 compounds. In particular, Figure 5(d) shows a large number of particles of nano-ZnO and an excellent degree of dispersion compared to Figure 5(b). This was due to the nano-ZnO, which was surface-treated with alkyl silane for improved dispersion.

Therefore, with a reduction in size and an increase in the surface area of the ZnO nanoparticles, they effectively formed the complex with accelerator, sulfur, and rubber and were easily dispersed into the matrix, instead of forming agglomerates on the surface.[17]

Silica-filled system

Effect of the content of stearic acid on the cure characteristics and mechanical properties of the silica-filled compounds

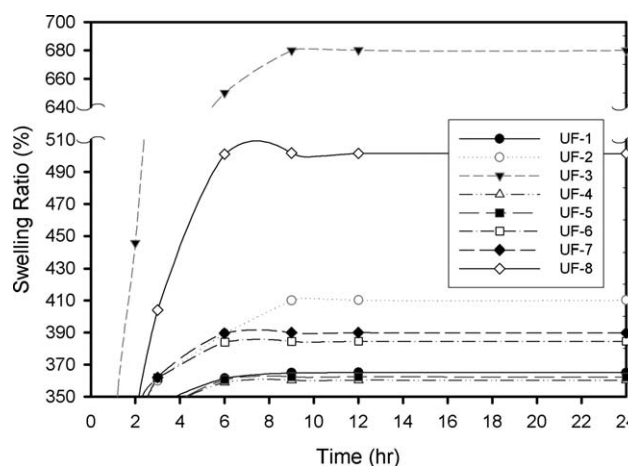According to the evaluation of nano-ZnO in the unfilled system, around 1.0 phr was the minimum

Figure 4 Swelling ratio as a function of the immersion time for the unfilled system.
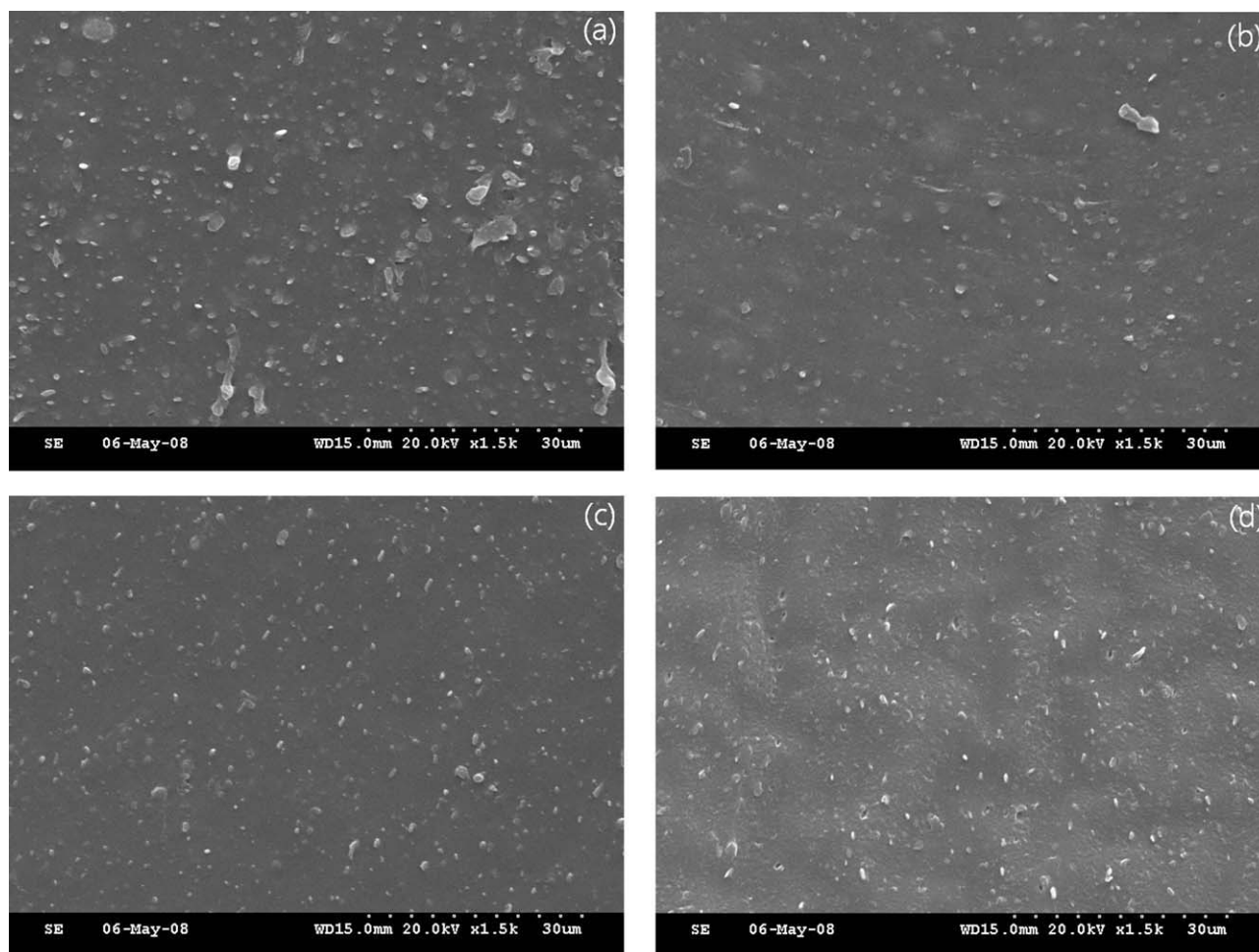
Figure 5 SEM images of the NR/BR compounds for the unfilled system: (a) UF-1, (b) UF-2, (c) UF-6, and (d) UF-7.

content of nano-ZnO that could provide equivalent cure characteristics and mechanical properties compared to those observed when 5.0 phr conventional ZnO was used. In the silica-filled system, we evaluated the influence on the cure characteristics and mechanical properties of the amount of stearic acid by increasing it from 0.1 to 0.3 phr while fixing the content of nano-ZnO at 1.0 phr in the NR/BR compounds filled with 35 phr silica. The formulations of the Z-2–Z-4 compounds are listed in Table III. The cure curves of the test formulations and the corresponding results are shown in Figure 6 and Table IV, respectively. In the silica-filled system, as compared to the Z-1 compound, the use of 1.0 phr nano-ZnO and 0.1 phr stearic acid (Z-2 compound) resulted in decreases of t_{10} and t_{90} by 15 and 29 s, respectively, and an increase in the T_{max} value by 0.09 Nm. In the unfilled system, the T_{max} value of the UF-6 compound decreased by 0.04 Nm when 1.0 phr nano-ZnO was used, as compared to that of the UF-1 compound when 5.0 phr ZnO was used. This means that the effect of nano-ZnO was more pro-

nounced in the silica-filled system. This was judged to be caused by the improvement in the degree of dispersion of the nano-ZnO by the PEG-4000 used as a dispersing agent for the dispersion of silica in the rubber matrix.

In the Z-2–Z-4 compounds, t_{10} and t_{90} increased when the stearic acid content was increased from 0.1 to 0.3 phr. This was judged to be caused by the increase in the formation time of zinc stearate through the reaction of ZnO and stearic acid because of the increase in the content of stearic acid.[11] On the contrary, the T_{max} value decreased by 0.07 Nm by the lubrication effect when the content of stearic acid increased from 0.1 to 0.3 phr.

The stress–strain curves of the Z-2–4 compounds are shown in Figure 7. E_{100} and E_{300} of the Z-2 compound were improved by 1.229 and 2.214 Nm, respectively, as compared to those of the Z-1 compound. This was judged to be caused by the improvement in the degree of crosslinking. When the stearic acid content was increased from 0.1 to 0.3 phr, decreases were observed in σ_b, tear strength,

TABLE III
Experimental Formulations of the NR/BR Compounds for the Silica-Filled System (phr)

	Z-1	Z-2	Z-3	Z-4	Z-5	Z-6	Z-7	Z-8	Z-9
NR (SMR-3L)					20				
HSR (KHS-68)					10				
BR (KBR-01)					70				
Silica (Zeosil-155)					35				
Coupling agent (Si-69)					2				
PEG-4000					2				
ZnO	5.0	—	—	—	—	—	—	—	—
Nano-ZnO	—	1.0	1.0	1.0	3.0	1.5	0.5	0.3	0.1
Stearic acid	1.0	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.1
Naugard 445					1				
W-1500					1				
Sulfur					1				
MBTS					1.5				
TMTM					0.5				

E_{100}, and E_{300}. This was the same tendency observed for the T_{max} value among the cure characteristics results; namely, it was judged to be caused by the increase in the lubrication effect of stearic acid

Effect of the content of nano-ZnO on the cure characteristics and mechanical properties of the silica-filled system

Table III shows the formulations of the Z-2 and Z-5–Z-9 compounds with various nano-ZnO contents in the silica-filled system. The content of stearic acid for the compounds was restricted to 0.1 phr based on the previous test result. The cure curves and corresponding results are shown in Figure 6 and Table IV, respectively. We compared the cure characteristics of the Z-1 compound with those of the Z-2 and Z-5–Z-9 compounds containing 1.0, 3.0, 1.5, 0.5, 0.3, and 0.1 phr nano-ZnO. The T_{max} value of the Z-5 compound was improved by 0.17 Nm compared to that of the Z-1 compound by an increase in the degree of crosslinking. For the Z-9 compound, the amount of ZnO required to activate the vulcanization accelerator was too limited to show any vulcanization acceleration effect and improvement of the T_{max} value. As the content of nano-ZnO in the compounds was increased from 0.3 to 3.0 phr, t_{10} and t_{90} increased. This was judged to be because the increase in the content of nano-ZnO increased the degradation time of ZnO in the chelate formation process with rubber–S_x–accelerator because of the increase in the concentration of Zn^{2+}.[12]

In particular, the T_{max} value of the Z-2 compound was improved by 0.09 Nm, and t_{10} and t_{90} decreased by 15 and 29 s, respectively, compared to those of the Z-1 compound. A value of 1.0 phr was the content of nano-ZnO that had the most excellent t_{90} under the conditions exceeding the T_{max} value of the Z-1 compound.

The stress–strain curves and mechanical properties of the Z-2 and Z-5–Z-9 compounds are shown in Figure 7 and Table IV, respectively. E_{100} and E_{300} of the Z-5 compound were improved by 0.671 and 2.390 Nm, respectively, compared to those of the Z-1 compound. On the contrary, for the Z-8 compound, E_{100} and E_{300} decreased by 0.071 and 0.698 Nm, respectively. This means that 0.3 phr nano-ZnO was too small to show any effect on the improvement in the degree of crosslinking compared to 5.0 phr of ZnO.

In particular, E_{100} and E_{300} of the Z-2 compound were improved by 1.229 and 2.214 Nm, respectively, compared to those of the Z-1 compound. As the content of nano-ZnO increased from 0.1 phr (Z-9 compound) to 3.0 phr (Z-5 compound), E_{100} and E_{300} were improved, but the elongation at break decreased. The improvement in the mechanical properties may have been due to the increase in the degree of crosslinking because of the better
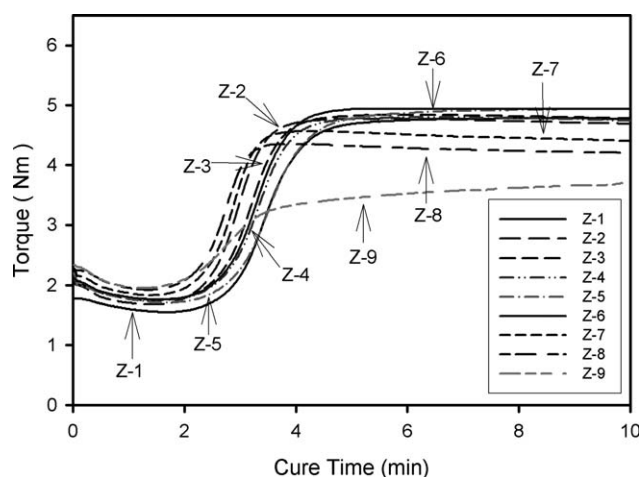

Figure 6 Cure characteristics of the NR/BR compounds for the silica-filled system.

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TABLE IV
Cure Characteristics and Mechanical Properties of the NR/BR Compounds for the Silica-Filled System

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	Z-1	Z-2	Z-3	Z-4	Z-5	Z-6	Z-7	Z-8	Z-9
T_{min} (Nm)	1.55	1.81	1.75	1.75	1.72	1.76	1.83	1.92	1.95
T_{max} (Nm)	4.78	4.87	4.84	4.80	4.95	4.93	4.56	4.35	3.84
t_{10} (s)	163	148	149	155	165	154	133	126	124
t_{90} (s)	256	227	228	239	268	240	196	186	515
σ_b (MPa)	12.52	14.36	12.19	11.38	12.29	12.99	11.44	16.24	13.05
Tear strength (kgf/cm)	63.59	68.90	66.56	62.45	67.32	63.72	66.64	62.06	60.38
E_{100} (MPa)	2.485	3.714	3.384	3.199	3.156	2.927	2.708	2.414	2.088
E_{300} (MPa)	7.261	9.475	9.204	8.848	9.651	9.565	7.652	6.563	5.458
Elongation (%)	455.4	431.6	392.0	378.7	369.0	383.5	436.0	625.1	646.6

dispersion and the increase in the surface area of the nano-ZnO.[17]

In the silica-filled system, the effect of nano-ZnO on the cure characteristics and mechanical properties were compared with that of the unfilled system. The T_{min} and T_{max} values were increased by the increase in the viscosity of the silica-filled compounds. t_{10} and t_{90} significantly decreased because of the heat conduction of the fillers. σ_b, E_{100}, E_{300}, and tear strength were greatly improved. This was mainly because of the effects of strain amplification[18] and hysteresis of the vulcanizates by the inclusion of silica fillers.

When the same amount of nano-ZnO with a particle size of 70 nm, instead of conventional ZnO, was used in carbon-black-filled systems,[13,17] T_{max}, σ_b, E_{100}, and E_{300} were improved, as in the case of the silica-filled system; however, t_{10} and t_{90} also increased. In the carbon-black-filled system, 1.0 phr was the minimum amount of nano-ZnO that provided equivalent cure characteristics and mechanical properties to those obtained when 5.0 phr ZnO was used, but the T_{max} value was low. This means that the degree of dispersion of nano-ZnO was low in the carbon-black-filled system. Wang and Chen[13] used a nano-ZnO master batch to increase the degree of dispersion; as a result, the use of 1.0 phr nano-ZnO showed a T_{max} value at the same level as the use of 5.0 phr conventional ZnO. In addition, elongation increased by 60%, which, thus, caused an increase in σ_b by 50%. However, t_{90} increased to 254 s compared to 202 s when 5.0 phr conventional ZnO was used.

In the silica-filled system, the content of minimum nano-ZnO was 1.0 phr, and in this case, the T_{max} value increased by 2%, compared to when 5.0 phr conventional ZnO was used. This means that there was no problem of the improper dispersion of nano-ZnO, unlike in the case of the carbon black system. Additionally, in the silica-filled system, the compound mixing time could be reduced by removal of the master batch process used in the carbon black system. In addition, σ_b was improved by 12%, and the elongation appeared to be similar to that

observed when 5.0 phr ZnO was used. Improvements in E_{100} and E_{300} were also observed. t_{90} was 227 s when 1.0 phr nano-ZnO was used; however, it was 256 s when 5.0 phr ZnO was used. This was judged to be caused by the fact that the available surface area of the nano-ZnO was increased compared to when the nano-ZnO was used in the carbon-black-filled compounds. This was due to the excellent dispersion effect of the dispersing agent used in the silica-filled compounds.

CONCLUSIONS

The effects of nano-ZnO on the cure characteristics and mechanical properties of the unfilled NR/BR compounds were evaluated. As the content of nano-ZnO increased, the cure characteristics and mechanical properties were increased, and the elongation at break and tear strength decreased. In particular, compared to the amount of conventional ZnO, only 20 wt % nano-ZnO was enough to obtain similar cure characteristics and mechanical properties because the increase in the available surface area of nano-ZnO led to an increase in the degree of crosslinking of the vulcanizates.
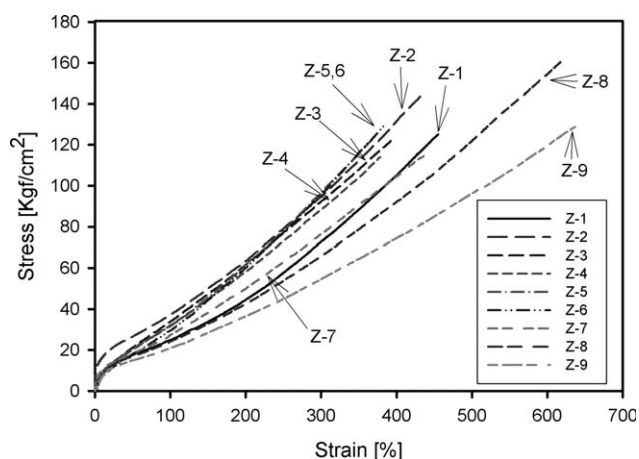

Figure 7 Stress–strain curves of the NR/BR compounds for the silica-filled system.

In the unfilled system, when the lubrication effect of stearic acid was dominant, the wear resistance of the compounds increased with decreasing amount of ZnO; however, when the reinforcing effect of nano-ZnO was dominant, the wear resistance of the compounds decreased with decreasing amount of nano-ZnO.

In the silica-filled system, the effect of nano-ZnO was more pronounced than in the unfilled system because of the improvement of the dispersion of nano-ZnO by a dispersing agent for silica in the rubber matrix. When the content of stearic acid increased from 0.1 to 0.3 phr in the compound, the mechanical properties decreased. This was due to the increase of the lubrication effect caused by the increased amount of stearic acid.

Compared to that of nano-ZnO used in the carbon black system, when 1.0 phr of nano-ZnO was used in the silica-filled system, the cure characteristics and mechanical properties were improved. This was due to the fact that the available surface area of nano-ZnO increased by the dispersing agent used for the dispersion of silica in the silica-filled system.

In the silica-filled NR/BR compounds, we judged that 1.0 phr nano-ZnO was suitable for reducing the amount of zinc, which was the goal of this study. Accordingly, 1.0 and 0.1 phr were the most appropriate contents of nano-ZnO and stearic acid, respectively. In addition, the use of nano-ZnO enabled a reduced t_{90} and improved mechanical properties.

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