



Effect of Molecular Weight of Epoxidized Liquid Isoprene Rubber as a Processing aid on the Vulcanizate Structure of Silica Filled NR Compounds

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Abstract: In this study, epoxidized liquid isoprene rubber (E-LqIR) was used as a processing aid in a silica-filled natural rubber compound to improve the fuel efficiency, abrasion resistance, and oil migration problems of truck and bus radial tire tread. The wear resistance, fuel efficiency, and extraction resistance of the compound were evaluated according to the molecular weight of E-LqIR. Results of the evaluation showed that the E-LqIR compound had a lower chemical crosslink density than that of a treated distillate aromatic extract (TDAE) oil compound because of the sulfur consumption of E-LqIR. However, the filler-rubber interaction improved because of the reaction of E-LqIR with silica and crosslink with the base rubber by sulfur. As the molecular weight of E-LqIR increased, crosslink with sulfur was facilitated, and the filler-rubber interaction improved, resulting in improved abrasion resistance. The fuel efficiency performance of the E-LqIR compound was poorer than that of the TDAE oil compound because of the low chemical crosslink density and hysteresis loss at the free chain end of E-LqIR. However, the fuel efficiency performance improved as the molecular weight of E-LqIR increased.

Keywords: silica filled NR compound, epoxidized liquid isoprene rubber, wear resistance, low rolling resistance, extraction resistance

Introduction

Significant efforts have been made to increase the fuel efficiency and abrasion resistance of truck and bus radial (TBR) tires owing to the recent environmental regulations and emergence of electric vehicles.¹ Therefore, the partial replacement of carbon black used in TBR tire treads with a combination of silica and silane coupling agents to achieve increased fuel efficiency has attracted increased research attention.²⁻⁴ However, because the TBR tire treads are manufactured using NR as the base rubber, the resulting rubber compounds exhibit low silica-SCA-NR interactions owing to the interference of NR proteins and lipids. This results in poor abrasion resistance compared to compounds prepared using carbon black limit the application of silica in TBR tire tread compounds.^{5,6}

In addition, the recent emergence of autonomous driving technology has led to the expectation of automated cargo trucks to be operated 24 h a day. This poses another chal-

lenge for TBR tires that it would cause the migration of oils added as processing aids, thereby causing hardening of the tire material.^{7,8} To overcome this problem of oil migration, investigations concerning the use of liquid rubber as a new processing aid have recently gained traction. Similar research has been actively conducted considering PCR tires as the target application. Previous studies have confirmed the realization of processability improvement and resolution of oil-migration issues when using liquid rubber as the processing aid.⁹⁻¹¹ However, no previous studies have been reported concerning the application of liquid rubber to TBR tire treads, and no quantitative analysis of liquid rubber effects on the vulcanizate structure of tread compounds has been performed.

The reduced filler-rubber interactions of the silica filled NR compounds can be improved by introducing epoxide groups to NR, thereby promoting the chemical interactions between the silica hydroxyl and epoxide groups. This has been reported to improve the abrasion resistance of TBR tires.¹² Therefore, in this study, E-LqIRs, which act as cou-

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pling agents and processing aids, were applied to silica filled NR compounds for not only improving the problem associated with declining filler–rubber interactions but also solving the oil-migration problem. Furthermore, the effect of the E-LqIR molecular weight on the vulcanizate structure of compounds has been quantitatively analyzed by the vulcanizate structure analysis.

Materials and Experimental Methods

1. Materials

1.1 E-LqIR Polymerization and Epoxidation

All the chemicals were purged with nitrogen. Cyclohexane (99%, Samchun Chemical Co., Seoul, South Korea) was used as the organic solvent, and *n*-butyllithium (2.0 mol/L in cyclohexane, Sigma–Aldrich Corp., Seoul, South Korea) was the anionic initiator. Isoprene (99%, Samchun Chemical Co., Seoul, South Korea) was used as a monomer, and tetrahydrofuran (THF; 99%, Duksan General Chemical Co., Seoul, Korea) was used as a polar modifier to increase the reaction rate. In addition, *n*-octyl alcohol (99%, Yakuri Pure Chemicals Co. Ltd., Kyoto, Japan) was used as the termination agent.

LqIR was converted to the epoxidized form, i.e., E-LqIR, by using hydrogen peroxide (30 wt% in H₂O, Sigma–Aldrich Corp., Seoul, South Korea) and formic acid (98%, Sigma–Aldrich Corp., Seoul, South Korea).

1.2 Compounding

NR (Standard Vietnamese Rubber SVR-10, dirt content = 0.1 wt%; Astlett Rubber Inc., Oakville, ON, Canada) was used as the base rubber. Silica (Ultrasil 7000 GR, Evonik Industries AG, Essen, Germany), with a Brunauer–Emmett–Teller surface area of 160–175 m²/g, was used as the filler. Bis[3-(triethoxysilyl)propyl]-tetrasulfide (TESPT, Si-69; Evonik Korea Ltd., Seoul, Korea) was used as the silane coupling agent. ZnO and stearic acid (Sigma–Aldrich Corp., Seoul, South Korea) were used as activators, and N-(1,3-dimethyl butyl)-N-phenyl-p-phenylenediamine (6PPD, Kumho Petrochemical Co., Daejeon, Korea) was used as the anti-oxidant. Sulfur (Daejung Chemicals and Metals Co., Siheung, Korea) was used as the crosslinking agent. N-cyclohexylbenzothiazyl-2-sulfenamide (CBS; 98%, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) and 1,3-diphenylguanidine (DPG; 98%, Tokyo Chemical Industry Co., Ltd., Tokyo,

Japan) were used as the curing accelerators. N-(cyclohexylthio)phthalimide (PVI, Shandong Yanggu Huatai Chemical Co., Ltd., Liaocheng, China) was used as the prevulcanization inhibitor.

2. Measurements

Molecular weight and molecular weight distribution were measured using gel permeation chromatography (GPC) system (Shimadzu, Kyoto, Japan). The GPC system consisted of a solvent delivery unit, reflective index detector, and three types of Styragel columns: HT 6E (10 μm, 7.8 mm × 300 mm), HMW 7 column (15–20 μm, 7.8 mm × 300 mm), and HMW 6E column (15–20 μm 7.8 mm × 300 mm). Further, the measured molecular weight was corrected using a polyisoprene standard sample (Polyisoprene standard kit, Waters Corp., Milford, MA, USA).

The epoxide content of the ENR samples was determined using proton nuclear magnetic resonance spectroscopy (¹H NMR; Varian, Unity Plus 300, Garden State Scientific, Morristown, NJ, USA). Solutions of ENR (15 mg/mL) in deuterated chloroform (CDCl₃, Cambridge Isotope Laboratories, Inc., Andover, MA, USA) were prepared in 5-mm NMR tubes.

The glass transition temperature (T_g) of the rubber was measured using differential scanning calorimetry (DSC-Q10, TA Instruments, USA). Rubber samples (3–6 mg) were measured from -80 to 100°C at a heating rate of 10°C/min.

The filler–filler interaction of the compound samples were determined using a rubber processing analyzer (RPA2000, Alpha Technologies, Hudson, OH, USA) according to the standard procedure given in ASTM D8059. The storage modulus (G') of the compounds after the 1st stage of mixing was measured at 60°C within a strain range of 0.01% to 40.04%. The storage modulus was high in the low strain region because silica agglomerates were not yet disintegrated, and decreased once higher strain was applied. The change in storage modulus ($\Delta G'$) was calculated by subtracting the value at a strain of 40.04% from that at 0.57%. This value describes the Payne effect, and represents the degree of filler–filler interaction. Thus, it was used as an indicator for the degree of filler dispersion within the rubber compounds.

The processability of the rubber was evaluated using the standard procedure given in ASTM D164. A Mooney viscometer (Vluchem IND Co., Seoul, Korea) was used to mea-

sure the torque as the rotor rotated at 2 rpm within a space filled with unvulcanized rubber. The sample was preheated to 100°C over 1 min, and the torque was measured as the rotor was rotated for 4 min.

For measuring bound rubber contents, after the first mixing stage, a sample of the compounds (0.2 ± 0.01 g) was placed on a filter paper and immersed in toluene (100 mL) for 6 days at 25°C to extract the unbound rubber. The toluene containing the extracted unbound rubber was cleaned with acetone and dried. The bound rubber content was computed based on the sample weights before and after the experiment as follows:

$$\text{Bound rubber content(\%)} = \frac{w_{fg} - w_t \left[\frac{m_f}{m_f + m_r} \right]}{w_t \left[\frac{m_r}{m_f + m_r} \right]} \times 100 \quad (1)$$

where w_{fg} is the weight of the filler and gel, w_t is the weight of the specimen, m_f is the weight fraction of the filler in the compounds, and m_r is the weight fraction of the polymer in the compounds.

The cure characteristics of the compounds were evaluated based on the minimum torque (T_{\min}), maximum torque (T_{\max}), scorch time (t_{10}), and optimal cure time (t_{90}) measured using a moving die rheometer (MDR, Myung Ji Co., Seoul, Korea) over 30 min at 150°C and a vibration angle of $\pm 1^\circ$.

For the crosslink density, vulcanizate specimens (10 mm \times 10 mm \times 2 mm) were sequentially immersed in tetrahydrofuran (THF, 99%, Samchun Chemical Co., Seoul, Korea) and n-hexane (95%, Samchun Chemical Co., Seoul, Korea) for 1 day each at 25°C to remove organic additives inside the specimens. The weight of the specimens was recorded. The specimens were immersed in toluene for 1 day at room temperature, and the swollen specimens were weighed. The total crosslink density was calculated using the Flory-Rehner equation as follows:

$$\nu = \frac{1}{2M_c} = -\frac{\ln(1-V_r) + V_r + \chi V_r^2}{2\rho_r V_s \left(V_r^{\frac{1}{3}} - 0.5 V_r \right)} \quad (2)$$

where ν is the crosslink density (mol/g), M_c is the average molecular weight between crosslink points (g/mol), V_r is the volume fraction of rubber in the swollen gel at equilibrium, V_s is the molar volume of solvent (cm^3/mol), ρ_r is the density of rubber sample (g/cm^3), and χ is the polymer-solvent interaction parameter. Further, the chemical crosslink density of

the unfilled compounds was calculated based on the Flory-Rehner equation (Equation (2)) and the Kraus equation (Equation (3)):

$$\frac{V_{r0}}{V_r} = 1 - m \left(\frac{\varphi}{1 - \varphi} \right) \quad (3)$$

where V_{r0} is the volume fraction of unfilled rubber in the swollen gel at equilibrium, V_r is the volume fraction of rubber in the swollen gel at equilibrium, and φ is the volume fraction of filler. Subsequently, the filler-rubber interaction was calculated as the difference between the total crosslink density (chemical crosslink density + filler-rubber interaction) and chemical crosslink density.

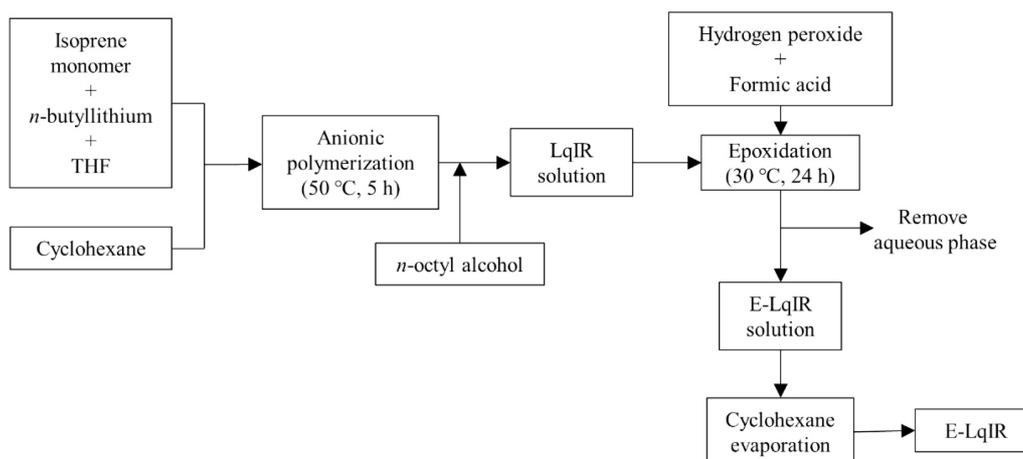
The mechanical properties of the vulcanizates, including tensile strength, modulus, and elongation at break, were evaluated. Dumbbell-shaped specimens (length = 100 mm; width = 25 mm) were tested at the speed of 500 mm/min using a universal testing machine (UTM, KSU-05M-C, KSU Co., Ansan, Korea) according to the standard procedure given in ATSM D 412.

Abrasion resistance was measured using an abrasion tester (DIN: Deutsche Industrie Normen, KSU Co., Ansan, Korea) according to the standard procedure given in DIN 53516. Cylindrical specimens (diameter = 16 mm; length = 8 mm) were tested, where an abrasive sheet was rotated on the surface of the specimen at 40 ± 1 rpm under load of 5 N. The mass loss was measured.

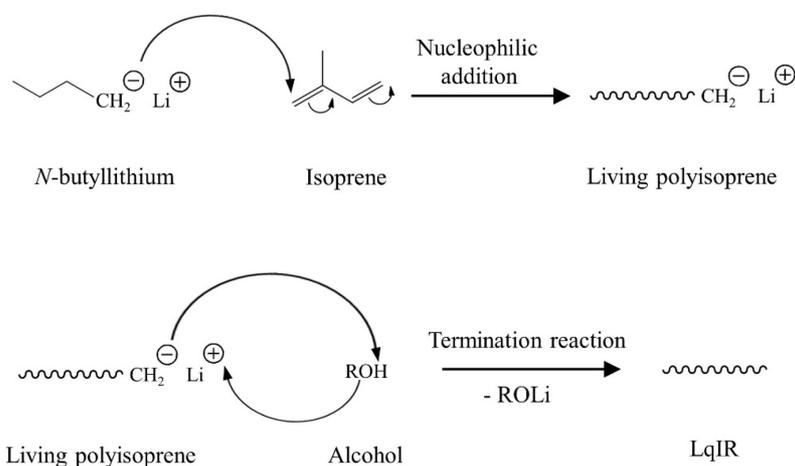
The dynamic viscoelastic properties of the compounds were evaluated by measuring the storage modulus (E'), loss modulus (E''), and $\tan \delta$ within a temperature range of -80 to 100°C at 0.2% strain and 10 Hz using a dynamic mechanical analyzer (DMA Q800, TA Instrument, New Castle, DE, USA).

3. Synthesis of Epoxidized Liquid Isoprene Rubbers

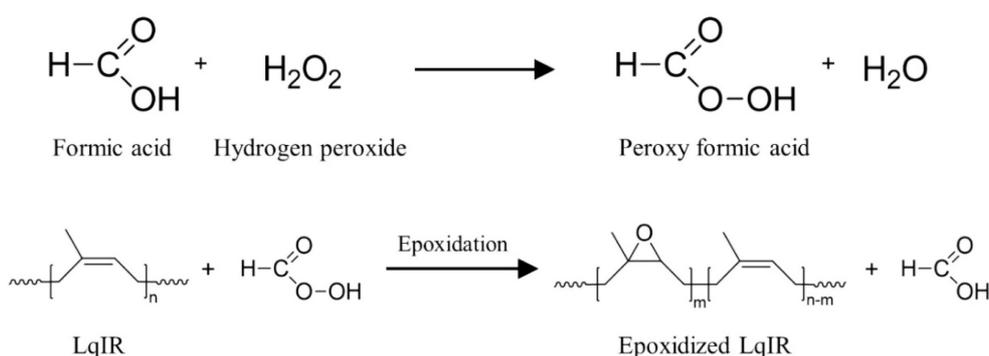
The whole synthesis process is shown in Scheme 1. At first, LqIR was synthesized by anionic polymerization in a nitrogen-purged reactor at 50°C. Cyclohexane and n-butyllithium were used as solvent and initiator, respectively. THF was added at a molar ratio of 0.25 relative to the initiator to accelerate the reaction.¹³ Subsequently, isoprene was introduced into the reactor under nitrogen atmosphere. The polymerization of LqIR lasted 5 h, and then the reaction was terminated by adding n-octyl alcohol (1.2 M; in excess with respect to the initiator) (Scheme 2). LqIR of different molec-



Scheme 1. Schematic flow chart of the E-LqIR synthesis process.



Scheme 2. Polymerization of LqIR.



Scheme 3. Epoxidation of LqIR.

ular weights was synthesized by adjusting the initiator to isoprene monomer ratio. After terminating the reaction, the LqIR solution was removed from the reactor and placed in a three-necked round-bottom flask along with aqueous hydrogen peroxide and formic acid. The heterogeneous solution containing the cyclohexane and aqueous phases was

stirred at a speed of 1000 rpm using a high speed stirrer at 30°C and allowed to react at the suspension interface for 24 h (Scheme 3).¹⁴ After the epoxidation reaction, the aqueous phase containing hydrogen peroxide and formic acid was removed to prevent residual reaction, and the E-LqIRs were obtained by evaporating cyclohexane from the E-LqIR solu-

Table 1. Formulation of the Compounds (phr)

	TDAE oil	E-3k	E-14k	E-22k
NR	100	100	100	100
Silica (Ultrasil 7000GR)	55	55	55	55
TESPT ¹⁾	4.4	4.4	4.4	4.4
TDAE oil	10	-	-	-
E-LqIR ²⁾	-	10	10	10
ZnO	4	4	4	4
Stearic acid	3	3	3	3
6PPD	2	2	2	2
TMQ	1	1	1	1
Sulfur	1.5	1.5	1.5	1.5
CBS	1.5	1.5	1.5	1.5
DPG	1.06	1.06	1.06	1.06
PVI	0.3	0.3	0.3	0.3

¹⁾The amount of silane coupling agents was calculated as 8 wt% of the weight of silica.

²⁾E-LqIRs with different molecular weight was used.

tion using a vacuum evaporator. The macrostructures and microstructures of the E-LqIRs were analyzed by GPC and ¹H NMR spectroscopy, and T_g was measured using DSC.

4. Preparation of Rubber Compounds and Vulcanizates

Compounds were manufactured using an internal mixer (300cc, Mirae Scientific Instruments Inc., Gwangju, Korea) based on the formulations presented in Table 1. The fill factor was 80% of the mixer volume. The input unit was parts per hundred rubber (phr), and the compounds were proportional to the amount of rubber added.

The mixing procedure is outlined in Table 2, where the initial temperatures of the first and second stages were 100 and 50°C, respectively, and the dump temperature ranges were 150 to 155°C and 80 to 90°C, respectively. After mixing was complete in each stage, the compounds were formed into

sheets using a two-roll mill. The vulcanizates were prepared by pressing the compound in a hydraulic press at 150°C for an optimal curing time (t_{90}).

Results and Discussion

1. Synthesis of Epoxidized LqIR

The results of GPC, DSC, and ¹H NMR analyses of E-LqIR are presented in Figure 1 and Table 3. As described in the previous section, E-LqIRs were synthesized using LqIRs of different molecular weights to determine the molecular-weight effect of E-LqIRs on the TBR tread compound. The results of the GPC analysis exhibit the E-LqIR M_n values of 3815, 14,253, and 22,098 g/mol. The corresponding T_g values of these E-LqIRs equal -69.03, -60.55, and -58.96°C, respectively, as obtained by DSC. As can be realized, the T_g values increase with increasing molecular weight owing to chain-mobility restrictions.^{15,16} The results of the ¹H NMR measurements reveal the presence of signals in the 4.6-4.8, 4.8-5, and 5-5.2 ppm range owing to the presence of olefinic

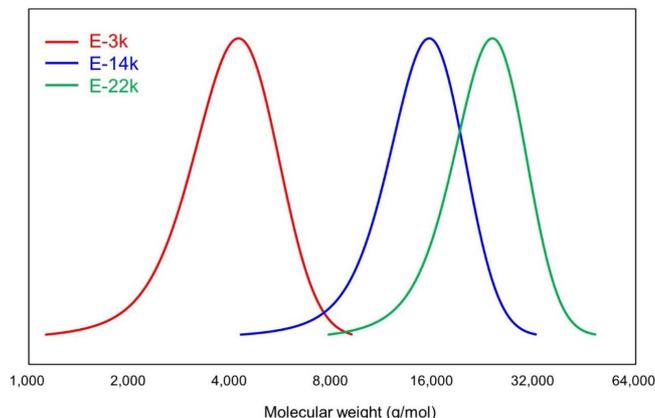


Figure 1. Gel permeation chromatography (GPC) curves of E-LqIRs.

Table 2. Mixing Procedure Used to Manufacture the Compounds and Vulcanizates

	Time (min:s)	Action
1st Stage	0:00-1:30	NR mastication (initial temp.: 100°C)
	1:30-2:40	Add silica 1/2, TESPT 1/2, and oil or E-LqIRs 1/2
	2:40-3:40	Add remaining silica, TESPT, and oil or E-LqIRs
	3:40-5:30	Add ZnO, St/A, 6PPD, and TMQ
	5:30	Ram up
	5:30-7:30	Extra mixing and dump (dump temp.: 150-155°C)
2nd Stage	0:00-0:30	Master batch from first stage (initial temp.: 50°C)
	0:30-2:30	Curatives and dump (dump temp.: 80-90°C)

Table 3. Characteristics of E-LqIRs

	E-3k	E-14k	E-22k
Mn (g/mol)	3815	14,253	22,098
Polydispersity	1.1	1.08	1.07
T_g (°C)	-69.03	-60.55	-58.96
3,4-addition (mol%)	13.5	12.5	11.6
1,4-addition (mol%)	73.1	75.0	75.5
Epoxide contents (mol%)	13.4	12.5	12.9
Functionality (Epoxide/Chain)	7.3	25.4	40.6

methine protons corresponding to the 3,4-, 1,2-, 1,4- addition units of polyisoprene, respectively. The signals corresponding to epoxy methane protons were observed at 2.7 ppm.^{17,18} Moreover, signals corresponding to the presence of n-octyl alcohol, added as a reaction terminator for LqIR, were observed at 3.6 ppm. The epoxide contents in the three E-LqIRs were calculated as the areas under the peaks observed in the 4.6-4.8, 5-5.2, and 2.7 ppm range (Equation 4). These calculated epoxide contents equal 13.4, 12.5, and 12.9 mol%, respectively, and they are nearly identical.

$$\text{Epoxide contents (mol\%)} = \frac{A_{2.7}}{A_{2.7} + A_{5.0-5.2} + A_{4.6-4.8}/2} \times 100 \quad (4)$$

The functionality—the number of epoxide groups for every E-LqIR chain—was calculated using the results of GPC and NMR analyses. The average unit number of chains was calculated (Equation 5) using the molecular weights of the isoprene unit (68.12 g/mol) and its epoxidized variant (84.12 g/mol) as well as Mn. Subsequently, the average number of epoxide groups per chain (Equation 6) was calculated using the epoxide contents obtained using Equation (4).

Chain unit number =

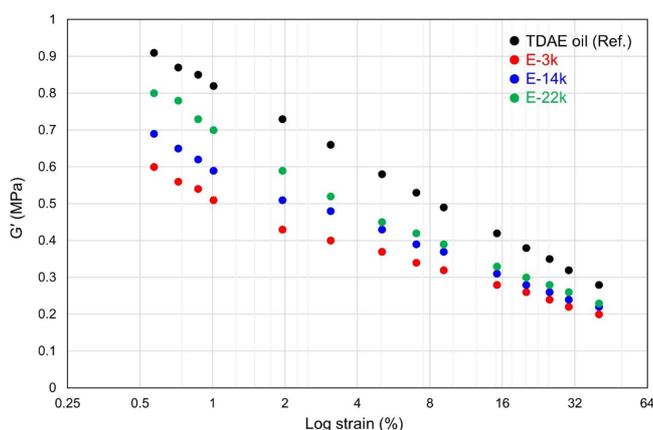
$$\frac{M_n}{\left(68.12 \times \left(1 - \frac{\text{epoxide contents}}{100}\right) + 84.12 \times \frac{\text{epoxide contents}}{100}\right)} \quad (5)$$

Functionality (Epoxide/Chain) =

$$\text{Chain unit number} \times \frac{\text{epoxide contents}}{100} \quad (6)$$

2. Payne effect

The results of the Payne-effect analysis, presented in Figure 2 and Table 4, demonstrate the presence of filler–filler interactions in the uncured compounds.¹⁹ In general, the storage modulus (G') reduces with increasing strain amplitude

**Figure 2.** The strain dependences of the shear storage modulus (G') for the compounds.**Table 4.** Payne Effect Results

Compounds	TDAE oil	E-3k	E-14k	E-22k
$\Delta G'$ (0.57-40.04%, MPa)	0.63	0.40	0.47	0.57

due to the breakdown of the filler–filler network; however, a high $\Delta G'$ value represents a strong filler–filler interaction. Accordingly, in this study, the degree of silica dispersion was determined based on the results of the Payne-effect analysis because a low Payne effect value indicates superior silica dispersion within a compound. The results of this study reveal that the Payne-effect values of E-LqIRs are smaller compared to those of the TDAE oil because the epoxide group in E-LqIR covers the silica surface. These results confirm that silica dispersion can be improved by decreasing the molecular weight of the E-LqIRs. Therefore, the findings of this study indicate that the excellent flow properties of the low molecular weight E-LqIR make it suitable for use as a processing aid in TBR tire tread.

3. Cure Characteristics and Mooney Viscosity

Figure 3 and Table 5 present the results of Mooney viscosity and bound rubber content measurements, as well as the cure characteristics determined in this study using MDR. The low molecular weight of E-LqIR facilitates silica dispersion, thereby resulting in low Mooney viscosity and T_{\min} values. Furthermore, the observed low bound rubber content could be attributed to the decrease in occluded rubber content.²⁰ In terms of cure characteristics, the E-LqIR compounds demonstrated small ΔT values owing to the increase sulfur consumption by their double bonds compared to TDAE oil. Furthermore, an increase in the E-LqIR molecular

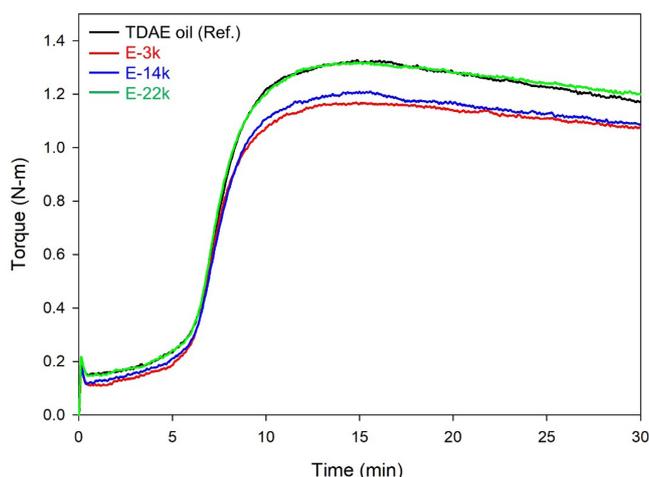


Figure 3. Compounds cure characteristics by MDR at 150°C.

Table 5. Cure Characteristics and Mooney Viscosity of the Compounds

Compounds	TDAE oil	E-3k	E-14k	E-22k
Mooney viscosity (ML ₁₊₄ @100°C)	50.2	44.9	49.1	52
Bound rubber contents (%)	31.7	23.5	27.9	28.8
T _{min} (N-m)	0.15	0.11	0.12	0.15
T _{max} (N-m)	1.33	1.17	1.21	1.32
ΔT (N-m)	1.18	1.06	1.09	1.17

weight causes an increase in the silica covering by E-LqIRs. This limits the accelerator adsorption effect by silica. In addition, increase in the E-LqIR molecular weight increases the co-vulcanization points of E-LqIR with NR by sulfur. This results are the attainment of high ΔT values as shown in the case of E-LqIR compound.

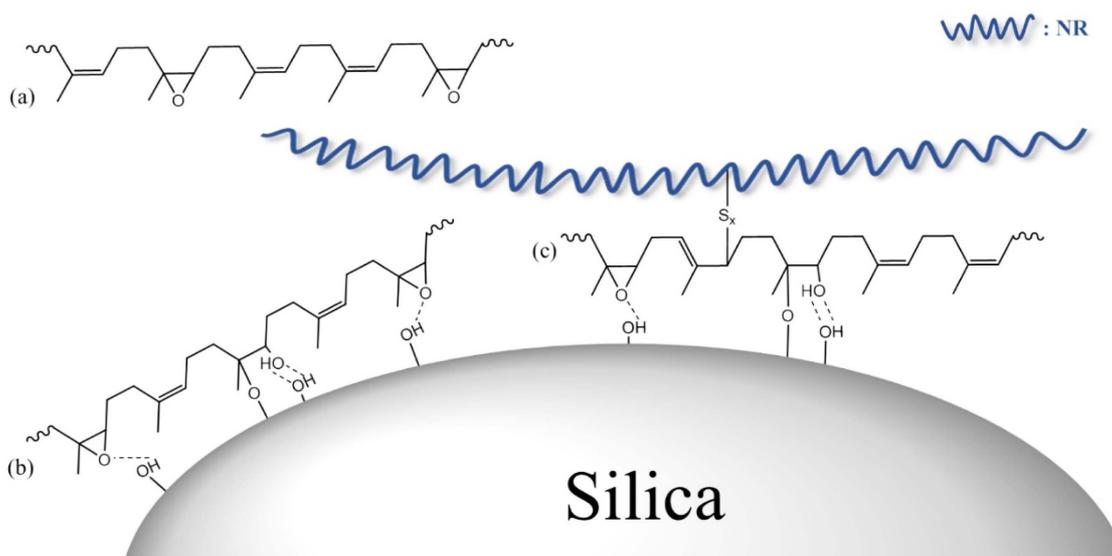


Figure 4. The proposed mechanism of silica filled NR compound vulcanizates with epoxidized LqIRs (E-LqIRs); (a) E-LqIRs without interaction with silica and rubber, (b) E-LqIRs as a silica covering agent, and (c) E-LqIRs as a coupling agent by sulfur.

4. Crosslink Density and Vulcanizate Structure Analysis

Figure 4 illustrates the E-LqIR interactions that can be observed in the silica filled NR vulcanizates that contain E-LqIRs. The E-LqIRs that do not interact with rubber or silica (Fig. 4(a)) act as lubricants. Owing to the absence of interactions, these E-LqIRs can be extracted during the pretreatment stage of swelling tests. On the other hand, the E-LqIRs that form hydrogen bond and the direct silica–epoxy bonds with the silica hydroxyl groups act as silica-covering agents (Fig. 4(b)). Therefore, these E-LqIRs cannot be extracted during the pretreatment stage of swelling tests.²¹ In addition, some E-LqIRs that interact with silica can be coupled with NR through crosslinks with sulfur, and these E-LqIRs can act as coupling agents (Fig. 4(c)).²²

During the pretreatment stage of swelling tests, the organic

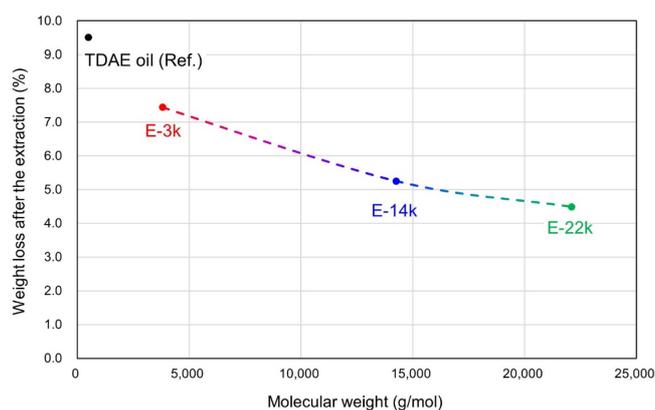


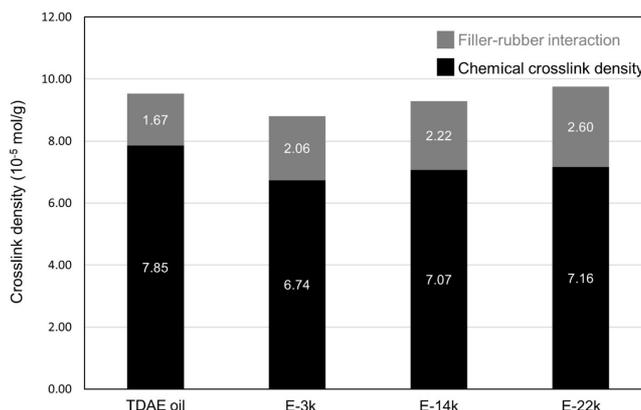
Figure 5. Weight loss after extraction according to molecular weight of E-LqIRs.

Table 6. Crosslink Densities of the Vulcanizates (Unit, 10^{-5} mol/g)

Compounds	TDAE oil	E-3k	E-14k	E-22k
Weight loss after the extraction (wt%)	9.51	7.43	5.25	4.49
Weight loss after the extraction 10phr in TDAE oil and E-LqIRs (%)	100	62.0	21.8	7.8
Total crosslink density (Chemical crosslink density + Filler-rubber interaction)	9.52	8.80	9.29	9.76
Chemical crosslink density	7.85	6.74	7.07	7.16
Filler-rubber interaction	1.67	2.06	2.22	2.60

matter present in the vulcanizates is extracted using two different organic solvents—THF and n-hexane. Figure 5 and Table 6 present the amounts of extracted organic matter. The proportion of 10 phr of TDAE oil in the vulcanizate equals to 5.44 wt%. The TDAE oil represents the highest amount of organic matter extracted at 9.51% (10 phr of TDAE oil (5.44 wt%) along with additives, such as stearic acid, 6PPD, and TMQ (4.07 wt%)). This is because the TDAE oil can be easily extracted using organic solvents, as it does not form a chemical bond with other materials in the compound. However, the E-LqIRs are more resistant to extraction owing to the increased interactions between the epoxide groups and silica. Assuming complete extraction of TDAE oil along with that of the same amount of additives, the amount of E-LqIR that can be extracted decreases from 62% to 21.8% to 7.8% with increasing molecular weight. This confirms the high extraction resistance of E-LqIRs. Thus, it is confirmed that the larger the molecular weight of E-LqIRs, the more unlikely is the occurrence of problems associated with processing-aid migration.⁸

To investigate the effect of E-LqIR molecular weight on the rubber compound vulcanizate structures containing different filler contents, the total crosslink density was calculated as the sum of the filler–rubber interactions and the chemical crosslink density observed by vulcanizate structure analysis.²¹⁻³⁰ The results obtained are presented in Figure 6 and Table 6. The chemical crosslink density of the compound with added E-LqIRs is lower than that of the compound containing TDAE oil. This can be attributed to the additional consumption of sulfur by the E-LqIR double bonds. On the other hand, a greater number of filler–rubber interactions occur in the vulcanizates containing E-LqIR owing to the presence of sulfur, which makes the E-LqIRs as coupling agents. The results of the vulcanizate structure analysis reveals that a high molecular weight of E-LqIR facilitates easy crosslink with sulfur, thereby increasing the filler–rubber interaction. In addition, without extraction, as the amount of E-LqIR covering the silica without extraction increased,

**Figure 6.** Crosslink densities of the vulcanizates.

it was confirmed that the chemical crosslink was increased due to the decrease of the accelerator adsorbed to the silica along with the entanglement of the E-LqIR.

5. Mechanical Properties and DIN Abrasion Loss

Figure 7 and Table 7 list the mechanical properties of E-LqIR compounds manufactured in this study. In the stress-strain curve, the modulus demonstrates the same trend as the change in the crosslink density of the compounds. The E-3k

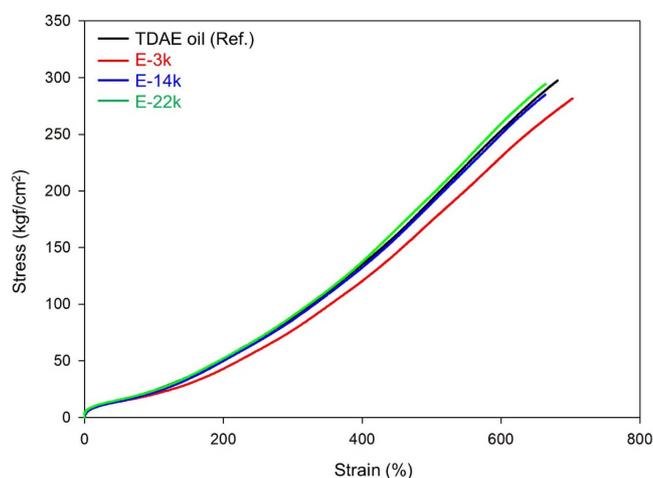
**Figure 7.** Stress-strain curves of the vulcanizates.

Table 7. Mechanical Properties of the Vulcanizates

Compounds	TDAE oil	E-3k	E-14k	E-22k
$M_{100\%}$ (kgf/cm ²)	23.8	20.5	22.1	23.6
$M_{300\%}$ (kgf/cm ²)	88.5	72.0	86.0	89.5
Elongation at break (%)	680	720	660	660
Tensile strength (kgf/cm ²)	298	282	285	294
DIN abrasion loss (mg)	152.0	140.4	138.8	133.3

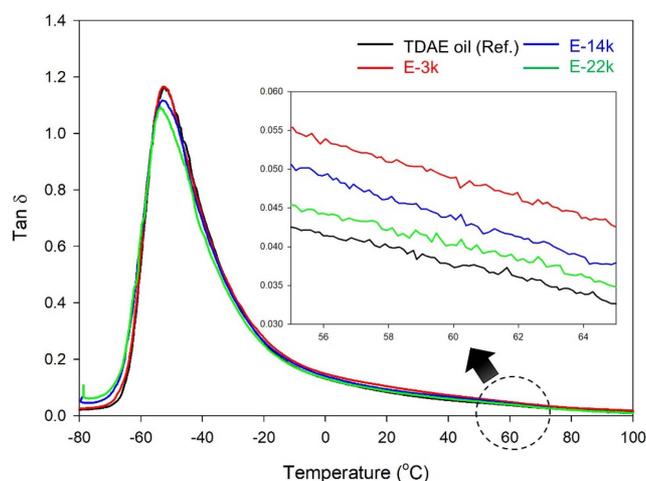
compound demonstrates the lowest modulus owing to the sulfur consumption by E-LqIR. With increase in molecular weight to E-14k and E-22k, the corresponding modulus value was observed to increase owing to increases in chemical crosslink density and filler–rubber interactions.

The abrasion resistance of the compounds was evaluated by performing the DIN abrasion tests, and the results obtained are described in Table 7. Evidently, the E-LqIR compounds with high filler–rubber interactions exhibit superior abrasion resistance compared to those containing TDAE oil.^{12,31} In addition, because the filler–rubber interactions improve with increase in the E-LqIR molecular weight, the E-22k compound demonstrates the highest abrasion resistance.

6. Dynamic Viscoelastic Properties

Tan δ at 60°C indicates the rolling resistance (RR) of a tire,³² whereas the loss modulus E'' at 0°C indicates of the corresponding wet grip performance.^{33,34} Rubber compounds typically exhibit high values of tan δ at temperatures near T_g owing to the hysteresis of the rubber chains.³¹ In addition, the value of E'' at 0°C decreases with improvement of silica-dispersion.³⁵ On the other hand, the value of tan δ at 60°C is seldom affected by the rubber chain hysteresis and low values of tan δ are observed under conditions of excellent silica dispersion and high crosslink density.^{36,37} In tire tread compounds manufactured using liquid rubber as a processing aid. The value of tan δ of the vulcanizates is greatly affected by the hysteresis loss from the chain end of the liquid rubber.^{9,38,39}

Figure 8 and Table 8 present the dynamic viscoelastic properties of these compound. Evidently, the E-LqIR containing compounds exhibit a higher value of tan δ at 60°C compared to those containing TDAE oil. This can be attributed to the low chemical crosslink density and hysteresis loss at the E-LqIR chain end. On the other hand, an increase in the E-LqIR molecular weight causes a reduction in the value of

**Figure 8.** Temperature dependences of tan δ for vulcanizates.**Table 8.** Viscoelastic Properties of Vulcanizates

Compounds	TDAE oil	E-3k	E-14k	E-22k
T_g (°C)	-52.3	-52.6	-53.0	-53.6
E'' at 0°C (MPa)	1.60	2.00	1.51	1.44
Tan δ at 60°C	0.037	0.049	0.044	0.040

tan δ at 60°C owing to the decrease in the number of E-LqIR chain ends and the increase in crosslink density. Furthermore, the improvement in silica dispersion in the E-LqIR containing compounds over the TDAE oil containing counterpart causes the value of E'' at 0°C to decrease in the former. However, the E-3k compound demonstrates a higher value of E'' at 0°C compared to the TDAE-oil containing counterpart owing to hysteresis loss at the chain end of the E-LqIR. In addition, E-14k and E-22k compounds demonstrate comparatively lower values of E'' at 0°C owing to a decrease in the number of chain ends of E-LqIR. This confirms their inferior wet grip performance compared to the TDAE oil compound.

Conclusions

In this study, the effect of the molecular weight of E-LqIRs applied as a processing aid to the silica filled NR compound on the compound properties was investigated. For the compound with E-LqIRs, chemical interactions were formed with the hydroxyl group of silica by the introduced epoxide group, which improved the silica dispersion compared to that of the TDAE oil compound. With smaller molecular weight of E-LqIRs, E-LqIRs can better perform the role as a processing aid, leading to excellent silica dispersion. In addition, with interaction of E-LqIRs with silica and rubber, extraction resistance is increased compared to that of the TDAE oil

compound, confirming feasibility of improvement in the problem of processing aid migration of tires. The result shows that the higher the molecular weight of E-LqIRs, interactions with silica and rubber can be easily formed, leading to a significant improvement in the extraction resistance with increasing molecular weight. As a result of the vulcanizate structure analysis, with increasing molecular weight of E-LqIRs, more silica surface was easily covered. Hence, the accelerators adsorbed to the silica surface decreased, leading to an increase in the chemical crosslink density. In addition, with increasing coupling with NR by sulfur, the filler-rubber interactions increased. Therefore, as the molecular weight of E-LqIRs increased, the abrasion resistance was improved with increasing filler-rubber interactions.

As a result of analysis of dynamic viscoelastic properties, compared to the properties of TDAE oil compound, E-LqIRs consumed sulfur and had a low chemical crosslink density, so E-LqIRs compounds showed a high $\tan \delta$ at 60°C value due to hysteresis loss at the E-LqIRs chain ends. On the other hand, as the molecular weight of E-LqIRs increased, the $\tan \delta$ at 60°C value decreased due to an increase in crosslink density and a decrease in the number of chain ends of E-LqIRs.

The results obtained in this study confirm that the use of high molecular weight E-LqIRs in tire tread compounds does not justify their role as processing aids. However, their inclusion significantly enhances the extraction resistance, abrasion resistance, and fuel efficiency of the final compound owing to increased filler-rubber interactions and reduced number of E-LqIR chain ends.

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References

1. B. Rodgers, "Tire Engineering: An Introduction", CRC Press: Boca Raton, FL, USA (2020).
2. V. D. Veiga, T. M. Rossignol, J. D. S. Crespo, and L. N. Carli, "Tire tread compounds with reduced rolling resistance and improved wet grip", *Journal of Applied Polymer Science* **134**, 39 (2017).
3. S. S. Sarkawi, W. K. Dierkes, and J. W. M. Noordermeer, "Natural Rubber-Silica Combinations for Low Rolling Resistance Truck Tyre Treads", *Rubber World* **2012**, 26 (2012).
4. M.-J. Wang, P. Zhang, and K. Mahmud, "Carbon—Silica Dual Phase Filler, a new Generation Reinforcing Agent for Rubber: Part IX. Application to Truck Tire Tread Compound", *Rubber Chem. Technol.*, **74**, 1, 124 (2001).
5. S. S. Sarkawi, W. K. Dierkes, and J. W. M. Noordermeer, "Morphology of silica-reinforced natural rubber: The effect of silane coupling agent", *Rubber Chem. Technol.*, **88**, 3, 359 (2015).
6. W. Dierkes, K. Sengloyluan, W. Kaewsakul, J. Noordermeer, K. Sahakaro, and A. Blume, "New Approaches to Increase the Compatibility of Natural Rubber and Silica for Reduction of Rolling Resistance of Truck and Bus Tires", *ITEC in Focus: Green Tire* **2019**, 25 (2019).
7. T. Nakazono and A. Matsumoto, "Mechanical properties and thermal aging behavior of styrene-butadiene rubbers vulcanized using liquid diene polymers as the plasticizer", *J. Appl.* **118**, 4, 2314 (2010).
8. T. Kataoka, P. B. Zetterlund, and B. Yamada, "Effects of storage and service on tire performance: Oil component content and swelling behavior", *Rubber Chem. Technol.*, **76**, 507 (2003).
9. D. Kim, B. Ahn, K. Kim, J. Y. Lee, I. J. Kim, and W. Kim, "Effects of Molecular Weight of Functionalized Liquid Butadiene Rubber as a Processing Aid on the Properties of SSB/ Silica Compounds", *Polymers*, **13**, 850 (2021).
10. M. Gruendken, "Liquid rubber for safer and faster tires", Tire technology EXPO 2018, Hannover, Germany (2018).
11. K. Ikeda, "Bio Liquid Polymer for Winter Tires", Tire Technology EXPO 2018, Hannover, Germany (2018).
12. G. Ryu, D. Kim, S. Song, K. Hwang, B. Ahn, and W. Kim, "Effect of Epoxide Content on the Vulcanizate Structure of Silica-Filled Epoxidized Natural Rubber (ENR) Compounds", *Polymers*, **13**, 1862 (2021).
13. H. Hsieh and R. P. Quirk, "Anionic polymerization: principles and practical applications", CRC Press (1996).
14. Y. Zhao, B. Huang, H. Cong, H. Shao, and A. Du, "Epoxidation of high trans-1,4-polyisoprene and its properties", *Journal of Applied Polymer Science*, **107**, 2986 (2008).
15. C. G. Robertson and C. M. Roland, "Glass transition and interfacial segmental dynamics in polymer-particle composite", *Rubber Chemistry and Technology*, **81**, 506 (2008).
16. M. G. Abiad, M. T. Carvajal, and O. H. Campanella, "A review on methods and theories to describe the glass transition phenomenon: applications in food and pharmaceutical products", *Food Engineering Reviews*, **1**, 105 (2009).
17. D. Chen, H. Shao, W. Yao, and B. Huang, "Fourier transform infrared spectral analysis of polyisoprene of a different microstructure", *International Journal of Polymer Science* (2013).

18. O. Hayashi, T. Takahashi, H. Kurihara, and H. Ueno, "Monomer unit sequence distribution in partly-epoxidized trans-1, 4-polyisoprene", *Polymer Journal*, **13**, 215 (1981).
19. A. R. Payne and R. E. Whittaker, "Low Strain Dynamic Properties of Filled Rubbers", *Rubber Chem. Technol.*, **44**, 440 (1971).
20. Y. Yue, H. Zhang, Z. Zhang, and Y. Chen, "Polymer-Filler Interaction of Fumed Silica Filled Polydimethylsiloxane Investigated by Bound Rubber", *Compos. Sci. Technol.*, **86**, 1 (2013).
21. B. Ahn, N. Kim, K. Kim, I. J. Kim, H. J. Kim, C. H. Kang, J.-Y. Lee, and W. Kim, "Effect of the functional group of silanes on the modification of silica surface and the physical properties of solution styrene-butadiene rubber/silica composites", *Compos. Interfaces*, **26**, 585 (2019).
22. G. Ryu, D. Kim, S. Song, K. Hwang, and W. Kim, "Effect of the Epoxide Contents of Liquid Isoprene Rubber as a Processing Aid on the Properties of Silica-Filled Natural Rubber Compounds", *Polymers*, **13**, 3026 (2021).
23. J.-Y. Lee, B. Ahn, W. Kim, H. Moon, H.-J. Paik, and W. Kim, "The effect of accelerator contents on the vulcanizate structures of SSBR/silica vulcanizates", *Compos. Interfaces*, **24**, 563 (2017).
24. N. Park, B. Ahn, J.-Y. Lee, W. Kim, H. Moon, and W. Kim, "Effect of organosilane agents on the vulcanizate structure and physical properties of silica-filled solution styrene butadiene rubber compounds", *Compos. Interfaces*, **25**, 259 (2017).
25. B. Ahn, N. Park, D. Kim, and W. Kim, "Influence of end-functionalized solution styrene-butadiene rubber on silica-filled vulcanizates with various silica-silane systems", *Rubber Chem. Technol.*, **92**, 364 (2019).
26. B. Ahn, J.-Y. Lee, D. Kim, I. J. Kim, S. Han, and W. Kim, "Effects of silane agents and curing temperatures on vulcanizate structures", *Rubber Chem. Technol.*, **93**, 414 (2020).
27. I. J. Kim, B. Ahn, D. Kim, H. J. Lee, H. J. Kim, and W. Kim, "Vulcanizate structures and mechanical properties of rubber compounds with silica and carbon black binary filler systems", *Rubber Chem. Technol.*, **94**, 339 (2020).
28. I. J. Kim, D. Kim, B. Ahn, H. J. Lee, H. J. Kim, and W. Kim, "Vulcanizate Structures of SBR Compounds with Silica and Carbon Black Binary Filler Systems at Different Curing Temperatures", *Polymers*, **12**, 2343 (2020).
29. I. J. Kim, D. Kim, B. Ahn, H. Lee, H. Kim, and W. Kim, "Vulcanizate Structures of NR Compounds with Silica and Carbon Black Binary Filler Systems at Different Curing Temperatures", *Elast. Compos.*, **56**, 20 (2021).
30. S. Han, D. Kim, S. Kim, J. Kim, D. Mun, K. Morita, and W. Kim, "Effect of Silane and Sulfur Variation on the Vulcanizate Structure of Silica-Filled Styrene-Butadiene Rubber Compounds", *Elast. Compos.*, **56**, 32 (2021).
31. M.-J. Wang, "Effect of polymer-filler and filler-filler interactions on dynamic properties of filled vulcanizates", *Rubber Chem. Technol.*, **71**, 520 (1998).
32. S. Han, W.-S. Kim, D.-Y. Mun, B. Ahn, and W. Kim, "Effect of coupling agents on the vulcanizate structure of carbon black filled natural rubber", *Compos. Interfaces*, **27**, 355 (2020).
33. S. Maghami, "Silica-Filled Tire Tread Compounds: An Investigation into the Viscoelastic Properties of the Rubber Compounds and Their Relation to Tire Performance", Ph.D. Thesis, University of Twente, Enschede, The Netherlands, (2016).
34. K. Suchiva, C. Sirisinha, P. Sae-Oui, and P. Thapthong, "Development of tyre tread compounds for good wet-grip: Effects of rubber type", In Proceedings of the IOP Conference Series: Materials Science and Engineering, Bangkok, Thailand, 17-21 December 2018; Volume 526, doi:10.1088/1757-899x/526/1/012035.
35. R. Yang, Y. Song, and Q. Zheng, "Payne effect of silica-filled styrene-butadiene rubber", *Polymer*, **116**, 304 (2017).
36. P. Thavamani and A. K. Bhowmick, "Dynamic Mechanical Properties of Hydrogenated Nitrile Rubber: Effect of Cross-Link Density, Curing System, Filler and Resin", *J. Mater. Sci.*, **27**, 3243 (1992).
37. S. Ahankari and K. K. Kar, "Processing of styrene butadiene rubber-carbon black nanocomposites with gradation of cross-link density: Static and dynamic mechanical characterization", *Mater. Sci. Eng. A*, **491**, 454 (2008).
38. T. Kitamura, D. F. Lawson, K. Morita, and Y. Ozawa, "Anionic Polymerization Initiators and Reduced Hysteresis Products Therefrom", U.S. Patent 5,393,721, 28 February 1995.
39. V. P. Sierra, J. Wagemann, C. Van De Pol, N. Kendziorra, K. Herzog, C. Recker, and N. Mueller, "Rubber Blend with Improved Rolling Resistance Behavior", U.S. Patent 9,080,042, 14 July 2015.