

촉진제가 실리카와 카본블랙으로 충전된 천연고무 복합소재의 가황 특성에 미치는 영향

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Effects of Accelerators on the Vulcanization Properties of Silica vs. Carbon Black Filled Natural Rubber Compounds

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초록: 화학적 구조가 다른 thiuram계 TMTD(tetramethyl thiuram disulfide), DPTT(dipenta-methylene thiuram tetrasulfide), thiazole계 MBT(2-mercapto benzothiazole), MBTS(2,2-dithiobis(benzo-thiazole)), sulfenamide계 CBS(*n*-cyclohexyl benzothiazyl-2-sulfenamide), NOBS(*n*-oxydiethylene benzo-thiazyl-2-sulfenamide), 아연이 포함된 thiuram계 ZDBC(zinc di-*n*-butyl-dithiocarbamate)를 사용하여 각각의 촉진제가 실리카와 카본블랙으로 충전된 천연고무 복합소재의 가황 속도 및 가황 지수에 미치는 영향을 비교 평가하였다. 양 시스템에서 가황 속도는 thiuram계, thiazole계, sulfenamide계의 순서로 동일한 경향을 보였다. 각 촉진제에 대하여 실리카 컴파운드와 카본블랙 컴파운드에 비해 t_{s2} , t_{10} , t_{90} 에 도달하는 시간이 느리게 나타났으며 느린 가황 지수(CRI)를 나타내었다.

Abstract: Thiuram (DPTT, TMTD), thiazole (MBT, MBTS), sulfenamide (CBS, NOBS), and zinc containing thiuram (dithiocarbamate) (ZDBC) type accelerators were added into silica and carbon black filled natural rubber (NR) compounds. Their effects on vulcanization time and rate were compared. The vulcanization rate of thiuram type accelerator added compounds showed the fastest rate, followed by thiazole and sulfenamide types. Silica filled natural rubber (NR) compounds showed a slower vulcanization time (t_{s2} , t_{10} , t_{90}) and lower cure rate index (CRI) than carbon black filled ones upon each accelerator.

Keywords: accelerators, carbon black, silica, natural rubber, vulcanization time, rate.

Introduction

Goodyear-Hancock first discovered unaccelerated vulcanization of rubber.^{1,2} Later, organic accelerator, aniline, was first introduced by Oenslager in 1906.³ However, aniline was too toxic for use in rubber vulcanization. Later, reaction product of aniline with carbon disulfide such as thiocarbonyl was introduced in 1907.⁴ Subsequently carbon disulfide modification with aliphatic amines (e.g. dithiocarbamates), which thiuram type accelerators were introduced in 1919.⁵ And then delayed-action accelerators such as 2-mercaptobenzothiazole (MBT) and 2-mercaptobenzothiazole disulfide (or 2,2'-dithiobisbenzothiazole) (MBTS) were introduced in 1925.⁶⁻⁸ The first commercial benzothiazole sulfenamide (*N*-cyclohexylbenzothiazole-

2-sulfenamide), a delayed-action accelerator, was introduced by Harman in 1937.⁹ More delayed-action premature vulcanization inhibitor (PVI), *N*-(cyclohexylthio)phthalimide (CTP), was introduced in 1968.¹⁰ Studies on accelerator effects on vulcanization were focused mainly on carbon black (CB) filled systems. Coran summarized various types of accelerators and their roles in CB filled rubber compounds.⁵

After Thurn *et al.*¹¹ first discovered the use of silica in combination with bis(3-triethoxysilylpropyl) tetrasulfane (TESPT) and natural rubber (NR), Rauline patented this for practical 'green tire' application in 1992.¹² Since then, considerable efforts have been made on studies of silica-silane reinforcement in rubber compounds,¹³ silica dispersion,¹⁴⁻¹⁸ silica-silane reaction,^{14,15,19-27} silane-rubber reaction,²⁸⁻³⁰ zinc ion-,^{25,31-34} moisture-,^{35,36} temperature-,³⁷ and accelerator effects on vulcanization properties,^{38,39} effects of processing geometry,¹⁸ and effects of polymer blends.^{26,27,40,41}

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Comparing silica surface with carbon black, silica surface consists of Si-O bonds with hydroxyl groups (-OH), while carbon black mainly consists of C-C and C=C bonds. Silica particles exhibit a strong filler-filler interaction due to its polar ($\text{Si}^{+\delta}\text{-O}^{-\delta}$) character thus easily agglomerate each other, while CBs show a weak filler-filler interaction due to nonpolar (C-C) and weak polar (C=C) character thus show a good compatibility with a rubber chain, which contains double bonds.

It has been known that hydroxyl group on silica surface chemically reacts with hydroxyl group in hydrolyzed silane via condensation reaction, and then forms a 3-dimensional network structure with a rubber chain.^{14,15} This, when applied in a tire tread compound, shows excellent wet and snow tractions, and low rolling resistance, which is a desirable property for fuel efficiency of an automobile. Technically advanced tire manufacturers, which overcome with silica dispersion, coupling reaction between silica-silane and silane-rubber chain, and processing technique, manufacture commercial green tires. Though these tires cost higher than conventional carbon black (CB) based tires, consumer purchases these types of tires due to traction safety and high gas mileage.

There were many studies on accelerator effects on vulcanization properties of CB filled rubber compounds.^{38,39,42-44} For example, Lorenz and Echte, and Scheele and Cherubim studied thiazole type accelerators on crosslinking rate in the NR

compound⁴² and NR & synthetic poly-1,5-dienes,⁴³ respectively. Morita and Young, and Bhathagar and Banerjee studied sulfenamide type accelerators on rate of sulfenamide-sulfur reaction and scorch delay reaction in the NR & SBR compound,^{44,45} respectively. However, there have been few published research reports on accelerator effects on silica filled rubber compounds.^{38,39,46} Moreover there were no studies on direct comparison between silica filled versus CB filled rubber compounds upon vulcanization properties.

In this study we compared vulcanization rate of silica/NR compounds and CB/NR compounds, which contain various accelerators. These accelerators consist of different chemical structure, i. e., thiuram type, TMTD (tetramethylthiuram disulfide) and DPTT (dipentamethylenethiuram tetrasulfide); thiazole type, MBT (2-mercaptobenzothiazole) and MBTS (2,2'-dithiobis(benzothiazole)); sulfenamide type, CBS (*n*-cyclohexylbenzothiazyl-2-sulfenamide) and NOBS (*n*-oxydiethylenbenzothiazyl-2-sulfenamide)]; and zinc ion containing thiuram type ZDBC (zinc di-*n*-butyldithiocarbamate)].

Experimental

Materials. The formulation and information of materials used in this study are summarized in Table 1.

Natural rubber (NR) used in this study was STR5 CV 50

Table 1. (a) Formulations (phr) and (b) Materials

(a)														
Materials	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10	T11	T12	T13	T14
NR ^a	100	→	→	→	→	→	→	→	→	→	→	→	→	→
Carbon black	40	→	→	→	→	→	→	-	-	-	-	-	-	-
Silica ^b	-	-	-	-	-	-	-	40	→	→	→	→	→	→
Silane	-	-	-	-	-	-	-	4	→	→	→	→	→	→
ZnO	5	→	→	→	→	→	→	→	→	→	→	→	→	→
Stearic Acid	2	→	→	→	→	→	→	→	→	→	→	→	→	→
PEG ^c	2	→	→	→	→	→	→	→	→	→	→	→	→	→
Sulfur	2	→	→	→	→	→	→	→	→	→	→	→	→	→
TMTD ^d	1	-	-	-	-	-	-	1	-	-	-	-	-	-
DPTT ^e	-	1	-	-	-	-	-	-	1	-	-	-	-	-
MBT ^f	-	-	1	-	-	-	-	-	-	1	-	-	-	-
MBTS ^g	-	-	-	1	-	-	-	-	-	-	1	-	-	-
CBS ^h	-	-	-	-	1	-	-	-	-	-	-	1	-	-
NOBS ⁱ	-	-	-	-	-	1	-	-	-	-	-	-	1	-
ZDBC ^j	-	-	-	-	-	-	1	-	-	-	-	-	-	1

^aNatural rubber. ^bTESPT (bis(3-triethoxy silyl propyl) tetrasulfane). ^cPoly(ethylene glycol). ^dTetramethyl thiuram disulfide. ^eDipenta-methylene thiuram tetrasulfide. ^f2-Mercapto benzothiazole. ^g2,2'-Dithiobis(benzothiazole). ^h*n*-Cyclohexyl benzothiazyl-2-sulfenamide. ⁱ*n*-Oxydiethylene benzothiazyl-2-sulfenamide. ^jZinc di-*n*-butyldithiocarbamate.

Table 1. Continued

(b)	
Materials (trade name)	Manufacture
NR (STR5 CV50)	Pan Rubber (Thailand)
Carbon black (N220)	OCI (S. Korea)
Silica (LK955-1)	Shangdong Link Silica (China)
Silane (Si-69)	Evonik (Germany)
Stearic acid	Suria Chem. (China)
ZnO	Hanil Chemical Ind. (S. Korea)
PEG (KONION)	Green Chemical (S. Korea)
Sulfur (MIDAS SP 325)	Miwon commercial (S. Korea)
TMTD (TT)	Shandong Shanxian Chemical (China)
DPTT	Shandong Shanxian Chemical (China)
MBT (M)	Shandong Shanxian Chemical (China)
MBTS (DM)	Shandong Shanxian Chemical (China)
CBS (CZ)	Shandong Shanxian Chemical (China)
NOBS (NBS)	Shandong Shanxian Chemical (China)
ZDBC	Linkwell Rubber Chemicals (China)

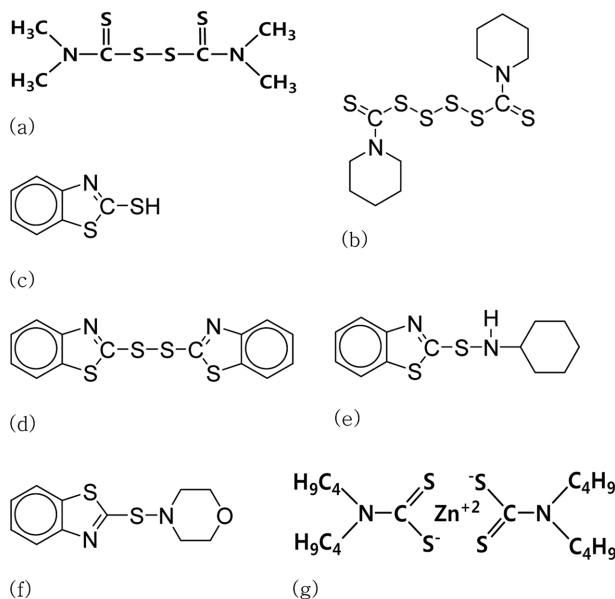


Figure 1. Chemical structures of accelerators: (a) TMTD (tetramethyl thiuram disulfide); (b) DPTT (dipenta-methylene thiuram tetrasulfide); (c) MBT (2-mercapto benzothiazole); (d) MBTS (2,2'-dithiobis(benzothiazole)); (e) CBS (*n*-cyclohexyl benzothiazyl-2-sulfenamide); (f) NOBS (*n*-oxidiethylene benzothiazyl-2-sulfenamide); (g) ZDBC (zinc di-*n*-butylthiocarbamate).

grade with Mooney viscosity (ML1+4(100 °C)) 50 supplied by Pan Rubber Co., Ltd. (Thailand). Carbon black used was N220 grade with average particle size 20~25 nm and BET surface

area 100~120 m²/g produced by OCI Co., Ltd. (S. Korea). Silica used was LK955-1 grade with average particle size 15 nm and BET surface area 160~190 m²/g produced by Shangdong Link Silica Co., Ltd. (China). Coupling agent used was Si-69 [bis(3-triethoxysilylpropyl) tetrasulfane (TESPT)] supplied by Evonik Degussa (Germany). Various additives including activators (ZnO, stearic acid, and PEG), curing agent (Sulfur), and accelerators (TMTD, DPTT, MBT, MBTS, CBS, NOBS, and ZDBC) were used. Chemical structures of each accelerator are shown in Figure 1.

Mixing. For masterbatch1 (MB1) mixings, 1.6 L Banbury mixer (model: BS-B16S) which consists of tangential type rotors manufactured by Bongshin Casting & Machinery Co., Ltd. (S. Korea) was used. This is an internal mixer. The rotor speed and temperature was set at 43 rpm and 120 °C, respectively. For processing of the MB2 compound two-roll mill, which was manufactured by Daewong Machinery Co., Ltd. (S. Korea), was used. The roll mill speed and ratio between front and rear was set to 19 rpm and 1:1.2, respectively. For MB1 mixing, NR, silica (or CB), coupling agent, zinc oxide, stearic acid, and PEG-4000 were added into the internal mixer for 12 min. For MB2 mixing, MB1 compound, sulfur, and accelerators (TMTD, DPTT, MBT, MBTS, CBS, NOBS, and ZDBC) were added into the two-roll mill for 5 min.

Cure Characterization. Vulcanization properties, t_{s2} , t_{10} , t_{90} , T_{min} , and T_{max} , were measured using an oscillating disk cure rheometer (DRM-100), which was manufactured by Daekyung Co., Ltd. (S. Korea), at 160 °C for 20 min following ASTM D2084 method. Cure rate index (CRI) was calculated following eq. (1).

$$CRI = \frac{100}{(t_{90} - t_{s2})} \quad (1)$$

where t_{s2} was the scorch point, and t_{90} was the time to reach 90% of full cure defined as $T_{max} - T_{min}$.

Results and Discussion

Cure Characterization. The vulcanization properties, t_{s2} , t_{10} , t_{90} , and CRI, of accelerator added compounds are summarized in Table 2.

Figures 2 through 5 show rheometer graph of thiuram (TMTD/DPTT), thiazole (MBT/MBTS), sulfenamide (CBS/NOBS), and zinc containing thiuram (dithiocarbamate) (ZDBC) accelerator added compounds, respectively.

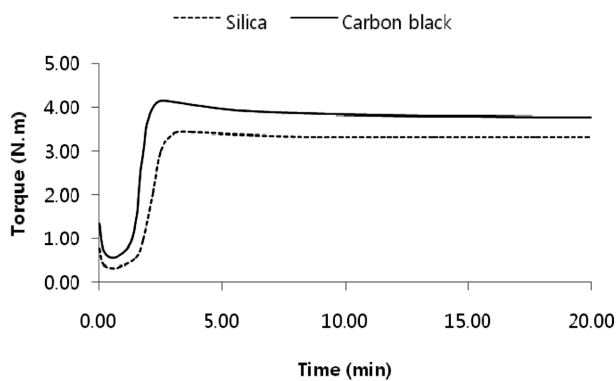
Thiuram type accelerator added system showed the fastest

Table 2. Vulcanization Time (t_{s2} , t_{10} , and t_{90}) and CRI of Accelerator Added Silica and Carbon Black Filled NR Compounds

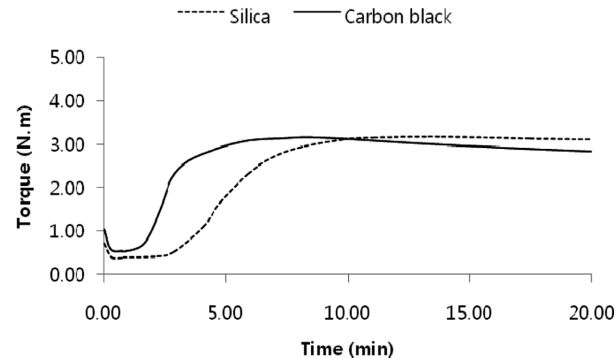
	t_{s2} (sec)		t_{10} (sec)		t_{90} (sec)		CRI	
	Silica	CB	Silica	CB	Silica	CB	Silica	CB
TMTD	93	74	98	80	161	126	1.47	1.92
DPTT	101	88	106	92	213	178	0.89	1.11
MBT	87	60	91	66	447	254	0.28	0.52
MBTS	202	106	212	108	500	274	0.34	0.60
CBS	292	134	319	151	568	269	0.36	0.74
NOBS	295	158	319	175	656	332	0.28	0.57
ZDBC	62	63	64	61	556	120	1.37	1.75

CB: Carbon black.

TMTD

**Figure 2.** Cure characteristics of the CB/NR and silica/NR vulcanizates accelerated with thiuram (TMTD) accelerators.

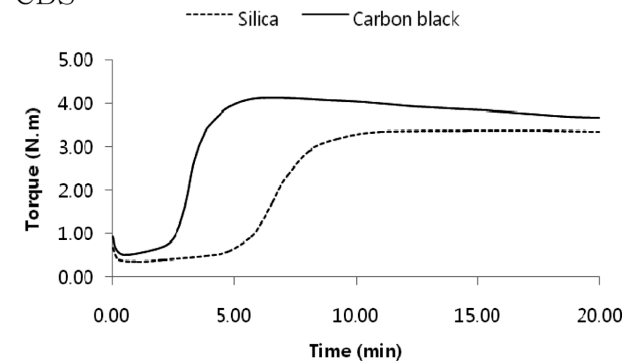
MBTS

**Figure 3.** Cure characteristics of the CB/NR and silica/NR vulcanizates accelerated with thiazole (MBTS) accelerators.

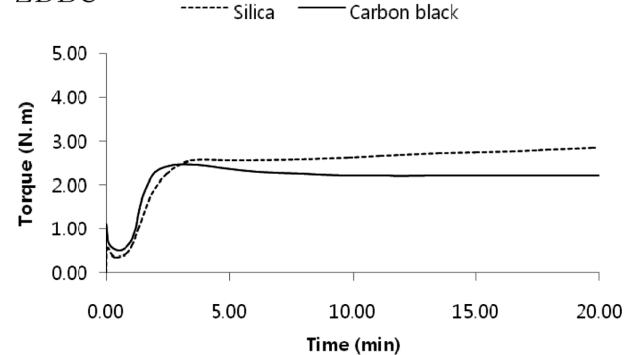
rate and followed by thiazole and sulfenamide type.

Effects of Thiuram Type Accelerators (TMTD, DPTT). When TMTD was added, the silica filled compound showed longer t_{s2} , t_{10} , and t_{90} (93, 98, 161 sec) and lower CRI (1.47) values compared to the CB filled one t_{s2} , t_{10} , and t_{90} (74, 80,

CBS

**Figure 4.** Cure characteristics of the CB/NR and silica/NR vulcanizates accelerated with sulfenamide (CBS) accelerators.

ZDBC

**Figure 5.** Cure characteristics of the CB/NR and silica/NR vulcanizates accelerated with zinc ion containing thiuram (dithiocarbamate) (ZDBC) accelerator.

126 sec), and CRI (1.92), respectively.

When DPTT was added, the silica filled compound showed longer t_{s2} , t_{10} , and t_{90} (101, 106, 213 sec) and lower CRI (0.89) compared to the CB filled one (t_{s2} , t_{10} , t_{90} (88, 92, 178 sec), CRI (1.11)), respectively.

Overall, when thiuram type accelerators, TMTD and DPTT, were added into the silica filled NR compounds, they showed longer vulcanization time (t_{s2} , t_{10} , and t_{90}) and slower vulcanization rate than the CB filled ones, respectively. Also, TMTD added compounds showed faster vulcanization rate (CRI) and shorter vulcanization time (t_{s2} , t_{10} , and t_{90}) than DPTT added ones in both silica and CB filled systems. We observed a trend that a compound showed fast cure proportionally related to high CRI values.

Effects of Thiazole Type Accelerators (MBT, MBTS). When MBT was added into the silica filled compound, it showed longer t_{s2} , t_{10} , and t_{90} (87, 91, 447 sec) and lower CRI (0.28) compared to the CB filled one (t_{s2} , t_{10} , t_{90} (66, 66, 254 sec), CRI (0.52)), respectively. When MBTS was added, the silica filled compounds showed longer t_{s2} , t_{10} , and t_{90} (202, 212, 500 sec) and lower CRI (0.34) compared to the CB filled one (t_{s2} , t_{10} , t_{90} (106, 108, 274 sec), CRI (0.60)), respectively.

Overall, when thiazole type accelerators, MBT and MBTS, were added, the silica filled NR compounds showed longer vulcanization time and slower vulcanization rate than the CB filled ones, respectively.

MBT vs. MBTS. The effects and mechanisms of MBT and MBTS in CB/NR compounds as well as in silica/NR were reviewed.^{38,39}

As MBTS transformed into MBT, the MBTS absorbed energy until the S-S bond in its chain dissociated,⁴ and then transformed into two MBTs.⁴⁷⁻⁵⁰ The zinc ion attracted MBTs and formed a ligand structure with double bonds in rubber chain and sulfur atom. And then further reacted with sulfur atom and formed a covalent bond with rubber chain.⁵¹

MBTS showed longer delay time (less scorch) and faster cure rate than MBT. This was because the MBT reacted with sulfur faster than the MBTS due to energy absorption stage of MBTS to split into two molecules of MBT as described previously.⁴⁷⁻⁵⁰

Effects of Sulfenamide Type Accelerators (CBS, NOBS). When CBS was added, the silica filled compound showed longer t_{s2} , t_{10} , and t_{90} (292, 319, 568 sec) and lower CRI (0.36) compared to the CB filled one (t_{s2} , t_{10} , t_{90} (134, 151, 269 sec), CRI (0.74)), respectively. When NOBS was added, the silica filled compounds showed the same trend as shown in the case of CBS, i.e. longer t_{s2} , t_{10} , and t_{90} (295, 319, 656 sec) and lower CRI (0.28) compared to the CB filled one (t_{s2} , t_{10} , t_{90} (158, 175, 332 sec), CRI (0.57)), respectively.

Overall, when sulfenamide type accelerators, CBS and NOBS, were added into the silica filled NR compounds, they

showed longer vulcanization time (t_{s2} , t_{10} , t_{90}) and slower vulcanization rate (CRI) than the CB filled ones, respectively. Also, CBS added compounds showed faster vulcanization rate (CRI) and shorter vulcanization time (t_{s2} , t_{10} , and t_{90}) than NOBS added ones in both silica and CB filled systems.

Effects of Zinc Ion Containing Thiuram (Dithiocarbamate) Type Accelerator (ZDBC). When ZDBC was added, the silica filled compound showed longer t_{s2} , t_{10} , and t_{90} (62, 64, 135 sec) and lower CRI (1.37) compared to the CB filled one (t_{s2} , t_{10} , t_{90} (63, 61, 120 sec), CRI (1.75)), respectively. Zinc ion containing dithiocarbamate accelerators were known for a fast cure rate and excellent crosslinking density in CB filled NR compounds.⁵ There were several research reports on effects of zinc ion on crosslinking density and rate.^{3,5,25,33,34,52-54} The two main roles of zinc ion in a rubber compound were reaction initiation and accelerated vulcanization. Zinc ion acted as a reaction initiator via formation of a polar bond with silanol groups on silica surface as explained by Norman.⁵³

During vulcanization, the zinc ion formed a ligand structure with polar molecules such as amines, acids, and esters, thus increased the vulcanization rate of the compound as explained by Bateman *et al.*³ and Kim *et al.*^{28-32,38} In this research, we observed that the addition of zinc ion containing accelerator (ZDBC) reduced the initiation time (t_{s2}), however, showed a marching behavior compared to the non zinc ion accelerators (TMTD, DPTT, MBT, MBTS, CBS, NOBS). This matched with the explanations of Sae-Oui *et al.* and others.⁵⁵⁻⁵⁸ The structure of thiuram type accelerators (TMTD, DPTT), which consists of thiuram group (-NC(=S)S-), was similar compared to that of the ZDBC (see Figure 1).

There were several research reports on the exchange interaction of a zinc ion with hydroxyl group and amine group in an accelerator. Polar zinc ions were adsorbed on the silica surface, and thus this made increased time to reach the equilibrium point, thus the compound showed a marching behavior.⁵⁵⁻⁵⁸ We presumed that the ZDBC adsorbed on silanol group on silica surface less affected sulfurs and double bonds in rubber chain compared to CB filled system thus showed a marching behavior.

Silanization Reaction. Silica-silane added system undergoes either direct or two major reaction steps.

When silica-silane were added into a rubber compound, alkoxy silane first hydrolyzed with water molecule and then the hydroxyl group in the hydrolyzed silane reacted with hydroxyl group on silica surface and then condensation reaction took place, then silane chemically bonded on the silica surface as

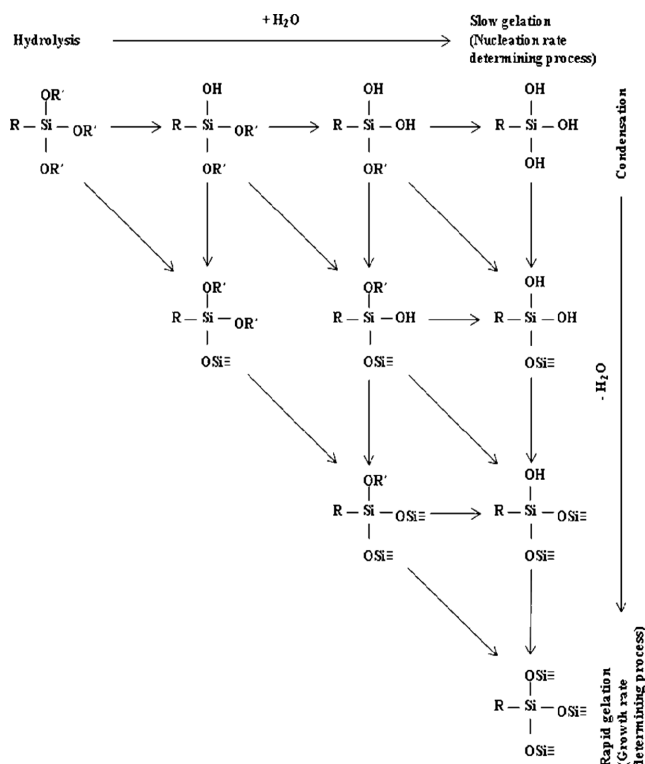


Figure 6. Schematic presentation of hydrolysis and condensation reaction of a trialkoxy silane [redraw from 59].

shown in Figure 6.⁵⁹ Second, the other side of silane, which consists of sulfur group, chemically reacted with double bond in a rubber chain. At this stage the S₈ ring opened and then vulcanized with double bond in rubber chain as found in the CB system. And then they formed a 3-dimensional network structure between silica and rubber chain.^{14,21,35-37,60}

Overall, comparing the silica/NR and the CB/NR compounds with various accelerators, the t_{s2} , t_{10} , and t_{90} values of the silica filled compounds showed longer than those of the CB filled ones, respectively. This was due to polar characteristic of silica surface⁵³ and water molecules in the compound.^{59,61} Accelerator was adsorbed on the silica surface due to its polar characteristic, so not all accelerators participate in the vulcanization reaction. As a result, the delayed vulcanization reaction was occurred. Thus, the reaction of alkoxy group of silane and silanol group of silica should be optimized in mixing step. Our experimental results of vulcanization rate matched with the descriptions above. This experimental result was the first direct comparison between the silica/NR compound and the CB/NR one under the same recipe with respect to vulcanization time and rate according to various accelerators.

Conclusions

Various accelerators, thiuram (TMTD, DPTT), thiazole (MBT, MBTS), sulfenamide (CBS, NOBS), and zinc ion containing thiuram (dithio-carbamate) (ZDBC), were added into the silica filled and CB filled NR compounds and then the vulcanization time and rate of each compound were compared. The vulcanization rate of thiuram type accelerator added compounds showed the fastest rate and then followed by thiazole and sulfenamide type. The t_{s2} and t_{10} (delay time) of the silica filled compounds showed longer than that of the CB filled ones, respectively. The vulcanization rate (CRI) of the silica filled compounds showed lower than that of the CB filled ones. This was due to delayed action of polar accelerators adsorbed on polar silica surface.

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