A Benzoxazole Sulfenamide Accelerator: Synthesis, Structure, Property, and Implication in Rubber Vulcanization Mechanism

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ABSTRACT: A benzoxazole sulfenamide and its related zinc compound were synthesized and characterized, which are shown to be useful accelerators for sulfur vulcanization. In comparison with the benzothiazole accelerator, the benzoxazole sulfenamide revealed nearly no reversion, an improved feature that is desirable for tire industry. Through the synthesis of the zinc complex **9**, which was assumed to be an accelerator-activator for vulcanization, the study aimed to shed some light on the vulcanization mechanism. The crystal structure of the zinc complex **9** showed that two benzoxazole-2-thiol ligands were attached to the zinc center in different isomeric forms, with one in the *thio* form (linked via sulfur atom) while the other in *thio–keto* form (linked via nitrogen atom). Lack of the vulcanization accelerator activity from **9** led to the assumption that the sulfurating species might be zinc complexes containing only one benzoxazole-2-thiol ligand. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39699.

INTRODUCTION

Vulcanization is a chemical process[1] that converts a soft and tacky rubber into harder and more durable materials with greatly improved resistance to wear and abrasion.[2] In the tire industry, the economically most important method remains to be the sulfur vulcanization in the presence of various vulcanization accelerators.[3] Thiazoles such as mercaptobenzothiazole (MBT) **1** and its sulfenamide derivatives **3** are among the accelerators of highest economic importance. Rostek et al.[4] showed that the fragment ─N═C─S─ (indicated by the dotted circle in **1** and **3**, Scheme 1) is a structural requirement for accelerator activity in sulfur vulcanization. The nitrogen atom in that fragment is assumed to act as hydrogen acceptor during the vulcanization and crosslinking reactions.[2,5] The assumption is consistent with the experimental observation that sulfur becomes attached to the rubber hydrocarbon at allylic position.[6] For tire applications, benzothiazolesulfenamide **3** is typically preferred over **1**, as the former provides desirable "scorch time" which allows the processing of rubber mixture at high temperature before noticeable vulcanization occurs.[2,7] As a consequence of vulcanization, the crosslink density is increased to a certain level within the rubber species, which is accompanied with increasing mechanical properties. The rubber system using **3**, however, often exhibits weakness in terms of reversion stability, meaning that the crosslink density could decrease after passing the vulcanization optimum.[8]

Although many efforts have been devoted to understand the vulcanization reaction,[1] there are still questions about the nature and formation of the active sulfurating agent. In vulcanization using **3b** (e.g., N-*tert*-butyl-2-benzothiazolesulfenamide (TBBS) if R═ *t*-butyl), the first few steps are believed to involve thermal cleavage of S─N bond in **3b** (at vulcanization temperature, 140–180°C), liberating 2-mercaptobenzothiazole **1** that readily reacts with zinc oxide to produce **5** (Scheme 2).[9,10] The compound **5** can be further transformed to **6**, which is thought to be produced *in situ*. Compound **5** is not an activator, as its mixture with sulfur and zinc oxide does not cure rubber after heating for 60 min at 140°C.[11] The mixture of amine complex **6** (R═cyclohexyl) with sulfur and zinc oxide, however, rapidly vulcanizes the *cis*-polyisoprene rubber at 140°C.[11] Although the amine complex **6** is widely assumed to be an active sulfurating species for rubber cross-linking,[9] its crystal structure has not

been determined. The *t*-butylamine derivative (i.e., R= t-butyl in **6**) has been synthesized,[12] but its accelerator activity is not known in literature. It should be noted that the complex **6**, synthesized by reaction of the ammonium complex **5**·(NH$_3$)$_2$ with an amine,[12] could not be obtained by direct reaction of **5** with an amine. Poor reactivity of **5** with a primary amine raises the question that how effectively the **6** can be formed in the absence of ammonium.

Despite intense interests in developing benzothiazole-based accelerators **1** and **3**,[2,13] little attention has been paid to the benzoxazole analogues **2**[14,15] and **4**.[16,17] Earlier study by Sebrell et al. shows that **2** exhibits much lower accelerating power than **1**.[15] Khanra et al. report that **4a** is much less active than **3a**, although the former gives a slightly shorter "scorch time" at 150°C.[17] While few examples of **4** are briefly mentioned in the patent literatures,[16,18] their accelerator properties have not been carefully examined. Stemming from our general interests in developing benzoxazole materials,[19,20] we decide to synthesize **4b** and to examine its potential applications for vulcanization accelerator. The choice of **4b** avoids the accelerators containing secondary amines, which can react with nitrogen oxides to form suspected carcinogenic nitrosamines.[21] In comparison with the current industrial accelerator TBBS (**3b** where NRR' = NH (t-Bu)), the corresponding **4b** exhibits similar "scorch delay." In addition, the cure curve of sulfenamide **4b** (NRR' = NH(t-Bu)) shows nearly no reversion, in contrast to thiazole derivative **3b** whose cure curves exhibit significant reversion.[15,17]

EXPERIMENTAL

Materials
Natural rubber (SMR CV60) was purchased from Akrochem. Sulfur (Harwich), zinc oxide (Akrochem), stearic acid (Harwick), TBBS (Flexsys America), 2-mercaptobenzoxazole (Fisher), zinc acetate dihydrate (Fisher), *tert*-butylamine (Aldrich) were used as received.

Synthesis of N-tert-2-Butyl-Benzoxazole Sulfenamide (7)
The 2-mercaptobenzoxazole (2.5 g, 0.0165 mol) and sodium hydroxide (1.3 g, 0.0325 mol) were dissolved in 70 mL of water, and then 27 mL of an aqueous solution containing 18 mL (0.169 mol) of *tert*-butylamine was added.[22] To this solution at room temperature, 55 mL of water containing 8.4 g (0.033 mol) of iodine and 4.6 g of potassium iodide was added drop by drop with stirring until constant brown color developed. The precipitate was filtered off, washed with water and dried in a vacuum oven for overnight (90%). The compound had mp 55–56°C. While the ^{1}H NMR of **7** in CD$_3$OD (Figure 1) gave the signals at 7.51 (m, 2H,), 7.28 (m, 2H,), and 1.18 (s, 9H), the ^{1}H NMR of **7** in CDCl$_3$ (300 MHz) revealed more details: 7.62 (d, 1H, J = 6.2 Hz), 7.61 (d, 1H, J = 7.0 Hz), 7.28 (t, 1H, J = 6.2 Hz), 7.24 (t, 1H, J ≈ 7.0 Hz), 3.11 (s, 1H, —NH—), 1.24 (s, 9H). ^{13}C NMR (CDCl$_3$, 300 MHz) δ 168.5, 151.4, 141.8, 123.9, 123.5, 118.5, 109.6, 55.1, 28.7.

Synthesis of Zinc Bis(benzoxazole-2-thiolate) (8)
The 2-mercaptobenzoxazole (1.51 g, 10 mmol) and potassium hydroxide (0.56 g, 10 mmol) were added to 35 mL of ethanol. The mixture was heated until it became homogeneous. To this
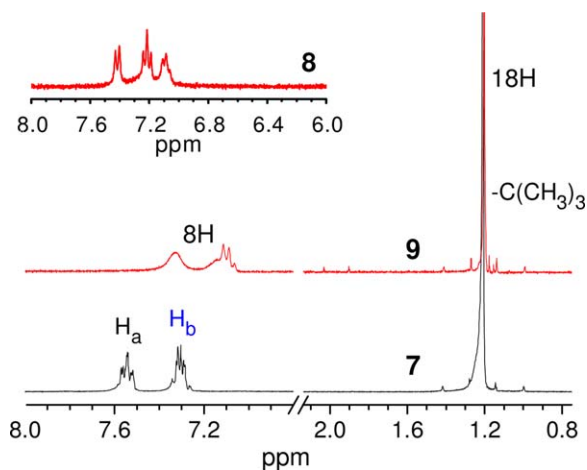
Figure 1. ^{1}H NMR of benzoxazole derivatives **7**, **8** and **9** in CD$_3$OD. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solution, an ethanol solution (40 mL) of zinc acetate dihydrate (1.09 g, 4.97 mmol) was added. The mixture was allowed to cool, and the precipitate was filtered off, washed with ethanol, and dried in a vacuum oven for overnight (71%). ^{1}H NMR of **8** (in CD$_3$OD, 300 MHz): 7.41 (d, 2H, J = 7.2 Hz), 7.22 (t, 4H, J = 7.2 Hz), 7.10 (d, 2H, J = 7.2 Hz).

Synthesis of Tert-Butylamine Complex of Zinc Benzoxazole-2-Thiolate (9)
Zinc bis(benzoxazole-2-thiolate) (1.0 g, 2.73 mmol) and *tert*-butylamine (4 mL, 38 mmol) was added to 40 mL of acetone. The mixture was stirred until it became homogeneous. The yellow solution was then evaporated in vacuum. The complex was partially dissociated during crystallization, $(Ar\text{-}S)_2Zn(NH_2\text{-}Bu^t)_2 \rightleftharpoons (Ar\text{-}S)_2Zn(NH_2\text{-}Bu^t) + NH_2\text{-}Bu^t$ and a small amount of amine (~2%) could be added to suppress the dissociation. The crude solid product was recrystallized from a mixture of methylene dichloride and hexanes (1 : 4 ratio by volume) which contains 2% amine, giving white crystalline (plate-like) (0.75 g, 61%). The acetone/hexanes (1 : 4 ratio) could also be used for recrystallization. ^{1}H NMR of **9** (in CD$_3$OD, 300 MHz): 1.20 (s, 18H), 7.0–7.2 (br, 4H), 7.23–7.43 (br, 4H).

Compounding
Natural rubber masterbatch was made by masticating natural rubber (SMR CV60) in a Brabender internal mixer (speed: 50 rpm; temperature 55°C; loading chute: manual + 5 kg). If applicable, zinc oxide and/or stearic acid were also mixed with rubber in the mastication process. Natural rubber was mixed for 1.3 min, and the mixture was mixed for additional 2 min after addition of zinc oxide/stearic acid. Sulfur and/or accelerators were then mixed with the masterbatch on a two roll mill (roll speed: front 12 rpm, rear 10 rpm; temperature: 120°C).

Cure Characterization
Vulcanization kinetics was determined from rheometer curves using an Alpha Moving Die Rheometer (MDR) 2000 at 140°C. Parameters of cure curves are shown in Table I.

Table I. Cure Parameters of Different Accelerators at 140°C

Cure system	Maximum torque (dNm)	Torque increment ($\Delta M = M_{max} - M_{min}$)	ts2 (min)[a]	t90 (min)[b]	Cure rate index[c]
S only	1.2	0.33	–	–	–
MBO,[d] ZnO	2.0	1.63	–	–	–
TBBS, ZnO	7.3	6.72	21.4	32.6	8.9
7, ZnO	4.1	3.65	37.3	60.6	4.3
7, Stearic acid	1.0	0.68	–	–	–
7, ZnO, Stearic acid	3.9	3.67	26.3	56.7	3.3
Zinc salt **8**	0.8	0.28	–	–	–
Zinc salt **8**, ZnO, Stearic acid	2	1.68	–	–	–
Zinc complex **9**	1.3	0.75	–	–	–
Zinc complex **9**, ZnO	3.9	3.54	17.8	36.7	5.3
Zinc complex **9**, Stearic acid	0.9	0.57	–	–	–
Zinc complex **9**, ZnO, stearic acid	4.3	4.03	18.4	45.4	3.7

[a] ts2: time when cure curve reaches 2 torque units increase above minimum torque (scorch time).
[b] t90: time when cure curve reaches 90% of full cure. t90 is generally the time when most physical properties of a vulcanizate reach optimal results.
[c] Cure rate index: 100/(t90 − ts2).
[d] MBO: 2-mercaptobenzoxazole.

RESULTS AND DISCUSSION

### Synthesis of Benzoxazole-2-Sulfenamides and Related Zinc Complexes

The desirable benzoxazole-2-sulfenamide **7** (Scheme 3) was synthesized from benzoxazole-2-thiol **2** and *tert*-butyl amine in high yield, by using a literature procedure for a similar compound.[22] The ^{1}H NMR spectrum of **7** detected four aromatic protons in anticipated two doublet and two triplet (in CDCl$_3$), confirming its structure. Bis(benzoxazole-2-ylthio)zinc **8** was also prepared from **2** by reaction with base followed by treatment with zinc acetate Zn(OAc)$_2$.

The amine complex was conveniently prepared by reaction of **8** with *tert*-butylamine to give crystalline product. The synthesis of the amine complexes **9** appeared to be simpler than its zinc benzothiazole-2-thiolate (**6**), where the corresponding zinc complex of *t*-butylamine was prepared by substitution from the ammonium complex of zinc benzothiazole-2-thiolate (Ar−S−Zn(NH$_3$)$_2$−S−Ar → Ar−S−Zn(NH$_2$-Bu)$_2$−S−Ar.[12] During recrystallization, the amine complex **9** was found to partially dissociate, similarly as observed from its thiazole analogue **6**.[12] A small amount of *tert*-butylamine (~2%) could be used to suppress the dissociation. Crystal structure analysis showed that the resulting crystals had the structure **9** (Figure 2), not **10**. Interestingly, two benzoxazole-2-thiolates in **9** adopted different structures, with one in the *thio* form, while the other in the isomeric *thio-keto* form. The tetra-coordinated zinc adopts a tetrahedral geometry, with bonding length 2.013 Å for Zn(1)-N(2), 2.059 Å for Zn(1)-N(4), and 2.283 Å for Zn(1)-S(1).

Rubber Curing Study

To study vulcanization characteristics, moving disk rheometer (MDR) was used to measure the cure curves of natural rubber in the presence of benzoxazole accelerators. As shown in Figure 3, the addition of sulfenamide **7** significantly increased the curing rate of the NR/sulfur mixture, revealing its accelerator activ-

ity. It should be pointed out that the sulfenamide **7** is structurally similar to the commercial accelerator TBBS (**4b** where −NRR' = −NH(t-Bu)), which is widely used in the tire manufacture for rubber curing. In comparison with TBBS, the curing curve of **7** exhibited nearly the same "scorch delay," a valuable feature to prevent prevulcanization. Although the vulcanization activity of **7** was lower than that of TBBS, the curing curve of **7** did not reveal "a reversion" (a decrease in modulus after reaching a maximum), in sharp contrast to TBBS and mercaptobenzoxazole **2**.[15] The study also pointed to that the reactivity of benzoxazolesulfenamide **4b** was only moderately lower than benzothiazolesulfenamide **3b**, in sharp contrast to the thiol compounds where the accelerator activity of **2** is dramatically lower than **1**.[17] Interestingly, when using the mixture of TBBS and **7** (1 : 1 ratio), the curing curve showed quite different characteristics, revealing an earlier start of vulcanization with similar curing rate as TBBS. The result pointed to the existence of the synergistic effect between TBBS and **7**. The
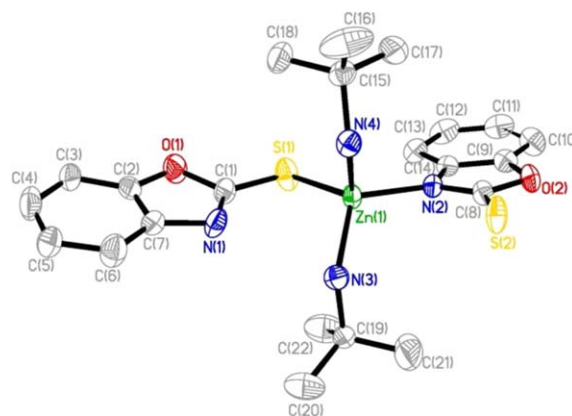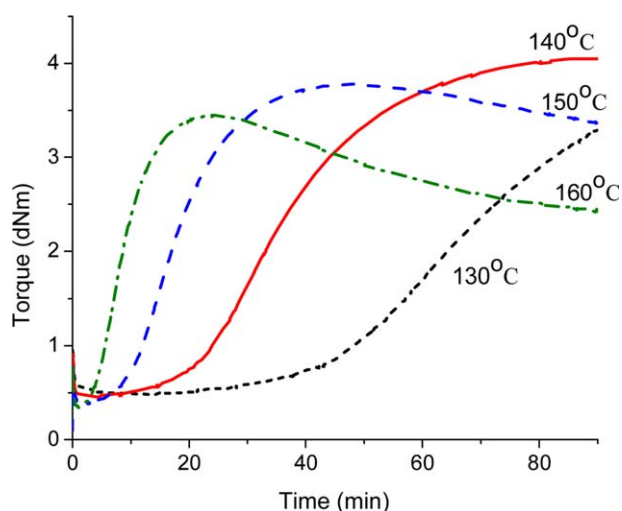

Figure 2. Crystal structure of zinc complex **9**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
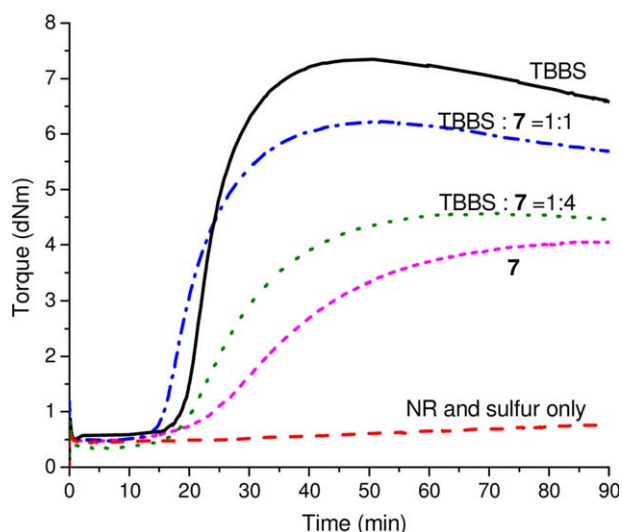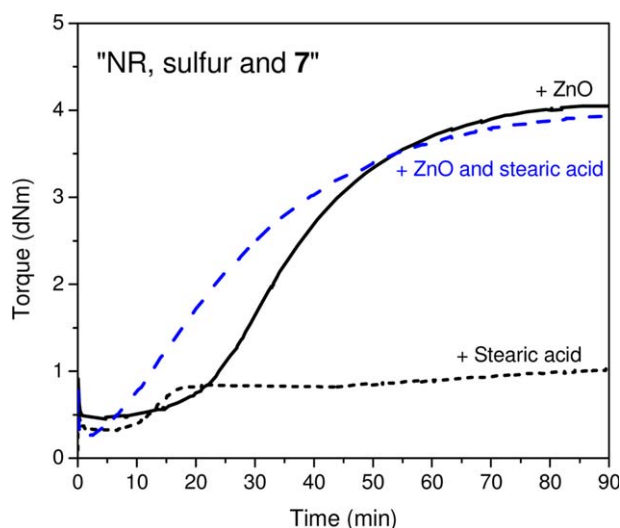
Figure 3. Cure characteristic curves of compound **7** at 140°C. The sample composition is shown in Table II. In the control experiment, only natural rubber (NR) and sulfur are used. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
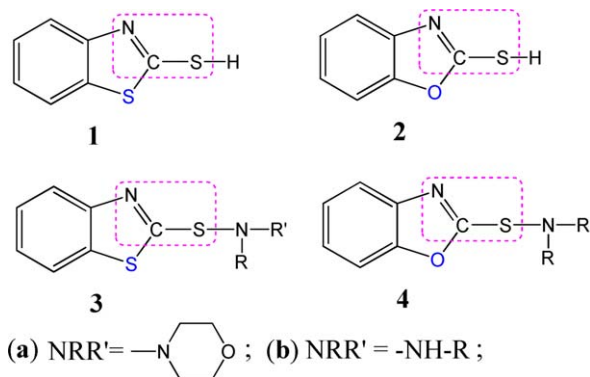

Figure 5. Effect of cure rate on rubber sample (natural rubber: 100 Phr; sulfur: 2.4 Phr; compound **7** :0.6 Phr) in the presence of different activators at 140°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

increasing curing activity of **7**, in the presence of TBBS, also suggests that the accelerator activity of **7** could be further improved. The cure behavior of **7**, in the sample of "rubber + ZnO + sulfur," was also examined at different temperatures (Figure 4). As expected, the cure onset occurred at an earlier time when the temperature was raised. The cure density, which is proportional to the torque force, appeared to be increased when temperature was decreasing from 160 to 140°C. In summary, benzoxazole-2-sulfenamide compound exhibited significant accelerator activity for rubber curing, and further improvement of its activity could lead to a new class of vulcanization accelerators.

The effect of different activators on the cure rate was further examined (Figure 5). As anticipated, zinc oxide is the most

Table II. Composition of a Typical Rubber Vulcanizate

Ingredient	Phr (parts per hundred parts rubber)
Natural rubber (NR)	100
Zinc oxide	5.0
Sulfur	2.4
Accelerator (TBBS, **7**, **8** or **9**)	0.6
Stearic acid (if added)	2
DPG (if added)	0.4

effective activator for vulcanization, when the sample has a composition shown in Table II. When stearic acid (2 Phr) was added to the sample, the accelerator activity of **7** appeared to be decreased overall to repeatedly give less crosslinking formation. The presence of stearic acid, however, increased the rate in the early reaction (before 20 min, during the delay period), which

Figure 4. Cure characteristic curves of **7** at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
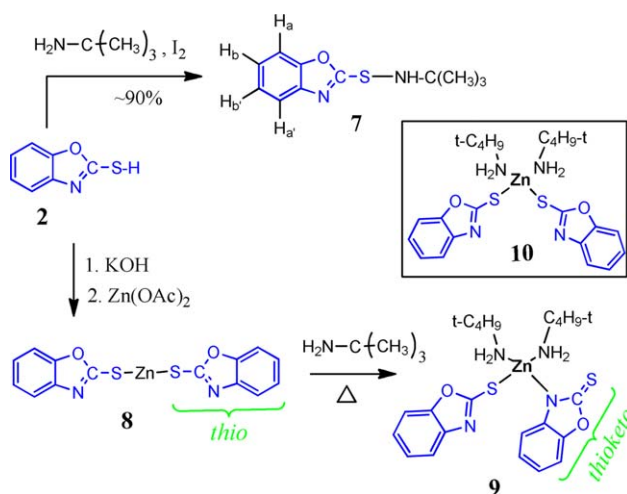

Scheme 1. Structures of sulfonamides 1–4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
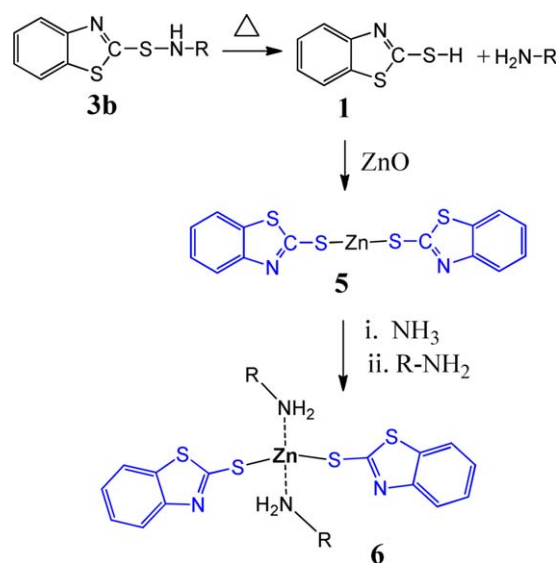
Scheme 2. Structure and formation of **6**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
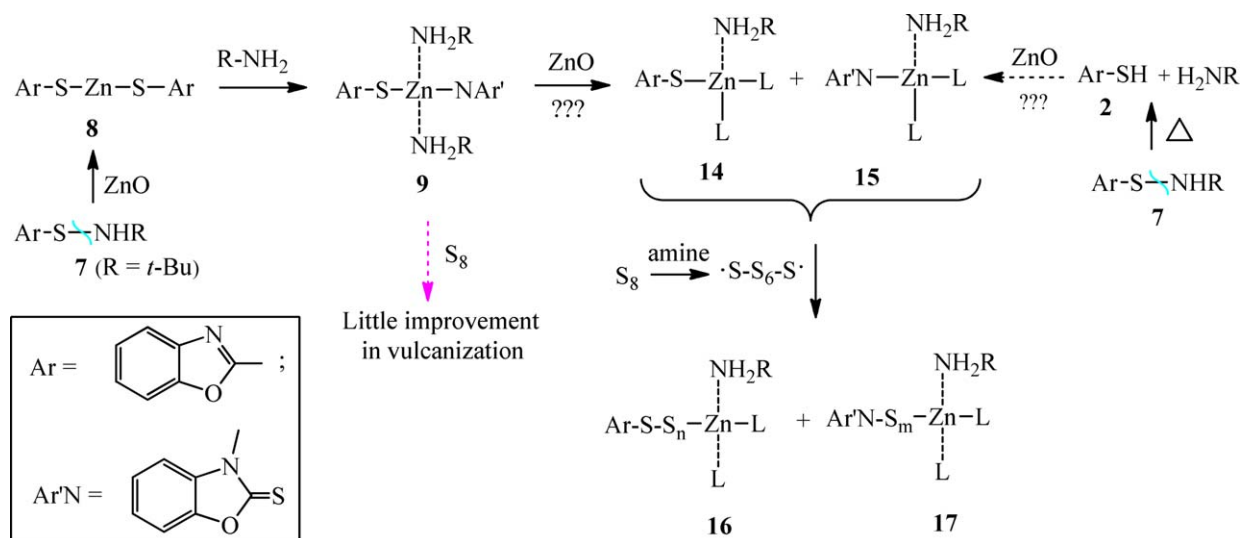

Scheme 3. Synthesis of benzoxazole derivatives **7–9**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

is similarly observed in the rubber system using thiazole analogue **3b**.[23]

The test samples for Figure 3 were consisting of natural rubber, zinc oxide, sulfur, and accelerator (see Table II). Other carbon-containing ingredients (e.g., carbon black, oil, stearic acid, and antidegradent) were not used in order to simplify the task for structural characterization of the resulting rubber after curing. During the curing process, an important question is the chain structure of the curing rubber, which determines the physical property of the final rubber product. ^{13}C NMR was thus acquired from the cured samples by using benzoxazole **7** as vulcanization accelerator. The major signals were detected at 134.7, 125.2, 31.9, 26.1, 23.0 ppm, attributing to the polymer backbone.[24] The inset in Figure 6 shows the minor signals arising from the crossing-linking reaction. In both cured samples, the

characteristic signal at ~56.8 ppm is detected as minor signal,[25] indicating that the vulcanization is occurring at the indicated position in **11**. Two minor signals at 39.7 and 44.4 ppm were also detected, which indicates the presence of the structure **12** with mono sulfur bridge.

Possible Vulcanization Mechanism

Because the cured rubber by using **7** had the similar chemical structure as that by using TBBS accelerator, we assume that the curing process followed the same vulcanization mechanism. To shed light on the curing mechanism, one important step is to identify the active sulfurating species. In analogy to the process proposed for benzothiazole sulfenamide **3**,[1] the possible route to the active sulfurating species for benzoxazole sulfonamide **4** is shown in Scheme 4. In the presence of ZnO, the sulfur–nitrogen bond in **7** is assumed to be cleaved under thermal conditions, forming zinc compound **8** and releasing amine. The chemical process of **7**→**8** might be similar as its thiazol

Scheme 4. Possible routes to the formation of the active sulfurating agents in the rubber system. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
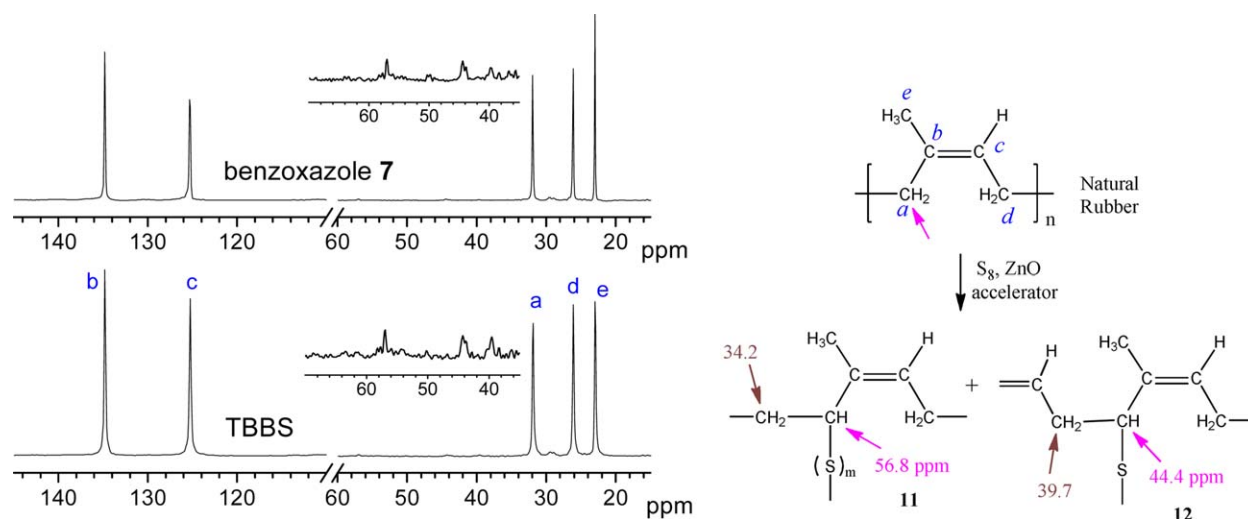
Figure 6. CPMAS ^{13}C NMR of cured rubber by using benzoxazole **7** (top) or TBBS (bottom) as vulcanization accelerator (cure time: 90 min). The inset shows the enlarged region for 35–70 ppm. The chemical shifts of natural rubber are assigned by using the reference.[24,25] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

analogue (**3** → **5**). One step toward understanding the vulcanization process is to examine the cure activity of **8** and **9**.

To confirm the assumption, the corresponding zinc compounds **8** and **9** were thus used to compare their rubber cure behavior. When being used with natural rubber and sulfur, zinc compound **8** exhibited nearly no observable vulcanization activity [Figure 7(a)]. Addition of ZnO or "ZnO and stearic acid" showed only little improvement. The small vulcanization activity might be attributed to "zinc oxide and stearic acid," which are known to have minor vulcanization activity.[2] When the zinc complex **9** was used alone, little accelerator activity was observed [Figure 7(b)]. In sharp contrast to **8**, addition of zinc oxide to **9** drastically increased the accelerator activity in vulcanization. In addition, the onset of curing by using **9** occurred earlier than that by using either **7** or **8** (Figures 3 and 7), indicating that **9** can be converted to an active species more readily in the vulcanization process.

Comparison of cure curves [Figures 3 and 7(b)] showed that the benzoxazole-based sulfenamide **7** (a specific member of **4b**) appeared to exhibit "no reversion" at 140°C [i.e., the system holds the torque level (or crosslinking density) after reaching the vulcanization optimum], revealing some advantage over the benzothiazole-based **3b** (e.g., TBBS when R=*t*-Bu). The trend was further verified by examining the cure characteristics on an extended time scale (from 90 to 150 min, Figure 8). The impact of benzoxazole on reversion in sulfenamide (**3b** vs. **4b**) appears to be opposite to that observed in the thiols (**1** vs. **2**), as the vulcanization using **2** is reported to exhibit more significant reversion than **1**.[15] While sulfenamide **7** exhibited lower accelerator activity than TBBS, its accelerator activity could be increased by addition of a small amount of amine (diphenyguanidine (DPG), 0.4 Phr) (see curve "**7**+DPG+ZnO" in Figure 8). Interestingly, the addition of DPG dramatically increased the curing activity of zinc compound **8** (Figure 8), while the
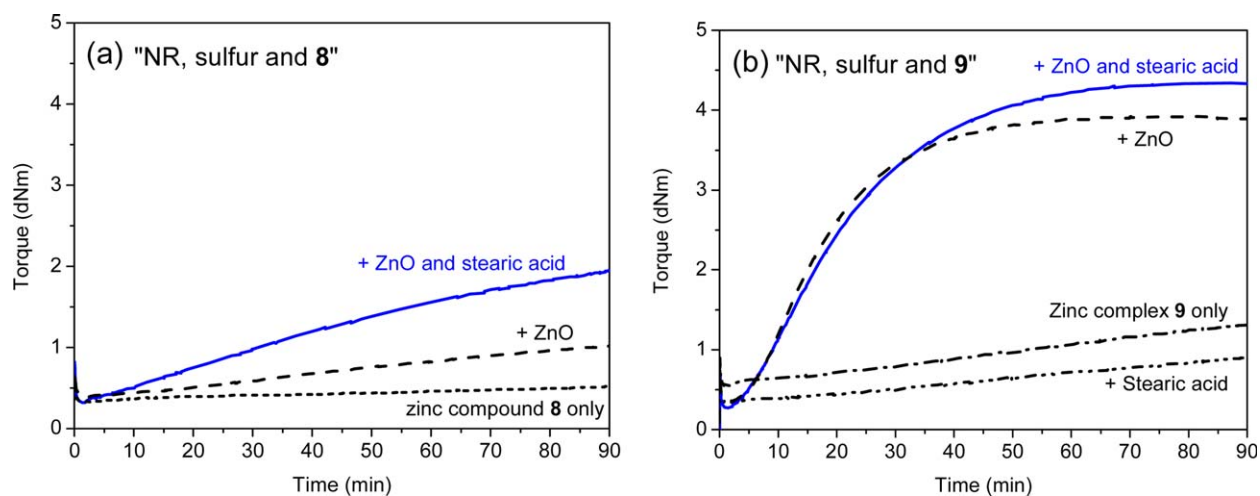
Figure 7. Effect of zinc compounds **8** (a) and **9** (b) on cure rate of rubber compound (100 NR + 2.4 sulfur) at 140°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
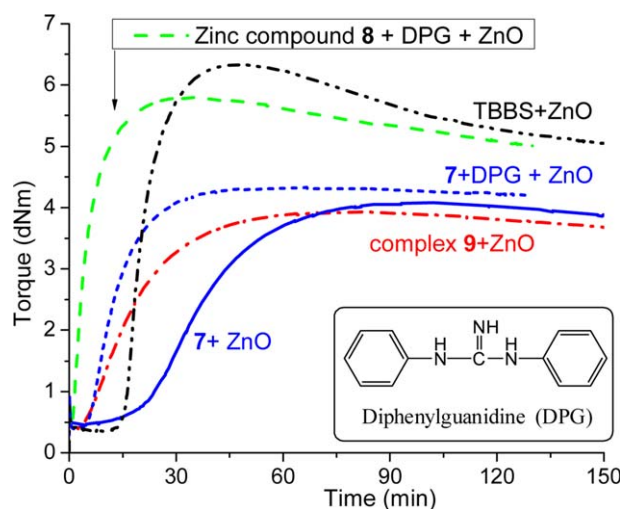
Figure 8. Comparison of cure characteristic curves by using different accelerators at 140°C (using the rubber composition in the Table II). The inset shows the structure of diphenylguanidine (DPG). The amount of amine (diphenylguanidine, DPG) used was 0.4 Phr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compound **8** exhibited nearly no accelerator activity [Figure 7(a)]. The result suggests that the accelerator activity of benzoxazole-based sulfenamide could be significantly increased if it is coupled with a suitable amine.

The experimental evidences shed some light on the vulcanization process. Because the amine complex **9** alone did not exhibit noticeable accelerator activity [Figure 7(b)], the real sulfurating species must be associated with other chemical species. The required addition of ZnO to **9** led us to assume the possible formation of **14** and **15** where each zinc is attached to only one benzoxazole ligand (Scheme 4). The assumption is consistent with the literature report that direct reaction of ligand **2** with zinc sulfate can give the complexes with a 1 : 1 metal-to-ligand molar ratio, on the basis of elemental analysis and vibrational spectral analysis.[26,27] The proposed **14** and **15** had only one amine ligand, which is consistent with the observation that the amine ligand on **9** tends to dissociate during the recrystallization process.

In summary, we have synthesized a new benzoxazole-2-sulfenamide (compound **7**), and examined its potential use as vulcanization accelerator. In comparison with the current commercial benzothiazolesulfenamide (TBBS), compound **7** revealed similar "scorch time," a desirable "delayed vulcanization." Interestingly, the curve of benzoxazole-2-sulfenamide **7** exhibited a long plateau at 140°C, indicating the less danger of over-vulcanization, while the curve of using TBBS exhibited a notable reversion. The study thus shows that the benzoxazole sulfenamide could be practically useful chemical for vulcanization accelerator applications.

The crystal structure of amine complex **9** reveals that the benzoxazole-2-thiolate ligand is attached to Zn(II) in two different isomeric forms (i.e., *thio-* or *thioketo*-forms, see Figure 2). The complex **9** is ruled out to be an effective active sulfurating

species, since the additional ZnO is required for the complex **9** to exhibit the accelerator function. In conjunction with other evidences, the zinc complexes **14** and/or **15** are proposed to be potential sulfurating species in the rubber system (Scheme 4). It should be noted that **14** and **15** could be formed directly from "**7** + ZnO," without necessarily going through the zinc compounds **8** and **9**. For benzothiazole sulfenamide **3b**, the proposed mechanism removes the concern that the amine complex **6** is synthesized by reaction of the ammonium complex **5**·(NH$_3$)$_2$ with an amine (not **5** with amine).[12] It should also be noted that the zinc complexes **9** and **15** includes the —N—C≡S fragment, which is common in the fast curing dithiocarbamates accelerator such as zinc dimethyldithiocarbamate (Me$_2$N—C(=S)—S)$_2$Zn.[13] Further study should be carried out, if possible, to determine whether *thio* or *thio-keto* ligand in the zinc complex plays a more significant role in the vulcanization process.

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