# Binary Cure Systems of 1,6-Bis(*N,N'*-dibenzylthiocarbamoyldithio)-hexane and Benzothiazole Sulfenamides in Carbon Black-filled Natural Rubber Compounds

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Binary cure system is composed of different two cure accelerators, which can cause a synergy effect to delay the scorch time and to increase the cure rate. In this study, binary cure systems between 1,6-bis(*N,N'*-dibenzylthiocarbamoyldithio)-hexane (DBTH) and benzothiazole sulfenamides were investigated using carbon black-filled natural rubber compounds. *N*-Cyclohexyl-2-benzothiazole sulfenamide (CBS), *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS), and 2-(morpholinothio) benzothiazole (MOR) were employed as benzothiazole sulfenamides. The binary cure systems show scorch safty at high temperature. The binary cure systems have faster cure rate and better reversion resistance than the single cure system of the benzothiazole sulfenamides. DBTH is found to be more effective to decrease the viscosity of a compound than the benzothiazole sulfenamides. Physical properties of the vulcanizates with the binary cure system are better than those of the vulcanizates with the single one.

**Keywords :** Binary cure system, DBTH, Benzothiazole sulfenamide, Rubber compound.

## Introduction

In general, an accelerated sulfur cure system for a rubber compound is composed of sulfur, cure accelerator, zinc oxide, and fatty acid. Vulcanization process produces various crosslink structures of mono-, di-, and polysulfides. The network structure varies with the time and temperature of vulcanization. Polysulfide linkages are changed into mono- or difulfide linkage as the vulcanization is proceeding. Sulfide crosslinks of S-S and C-S bonds are relatively unstable. Especially, polysulfides are more unstable than mono- and disulfides.[1] Thus, the sulfur curing at high temperatures deteriorates the mechanical properties of rubbers due to reversion. Reversion occurs well in natural rubber (NR) compounds.[2-4] Curatives, especially sulfur, in a rubber vulcanizate affect postcuring.[5]

Crosslink type and degree of crosslink density of a rubber vulcanizate determine physical properties of the vulcanizate such as modulus, hardness, resilience, elongation at break, heat build-up, and so forth.[4] By increasing crosslink density, modulus, hardness, resilience, and abrasion resistance increase while elongation at break, heat build-up, and stress relaxation decrease. Stress relaxation, tensile strength, and resilience increase in proportion to the content of di- and polysulfides while fatigue and thermal aging resistance decrease.

Crosslink type and degree of crosslink density of a rubber vulcanizate are affected by type and content of a cure accelerator.[6-9] Binary cure system is composed of different two cure accelerators.[10-13] A good binary cure system leads to delay of scorch time and increase of cure rate compared to conventional single cure system. Polysulfide linkages have better dynamic property of a vulcanizate than mono- and disulfide ones but they are dissociated easily at high temperature. Bayer company recently introduced a new crosslinker, 1,6-bis(*N,N'*-dibenzylthiocarbamoyldithio)-hexane (DBTH, KA9188) for the production of highly reversion-stable vulcanizates of natural rubber (NR) and synthetic rubber.[14] In the previous work, we studied the synergy effect of DBTH on the properties of filled natural rubber (NR) compounds.[15]

## Experimental Section

Carbon black-filled natural rubber (NR) compounds were made of NR (SMR CV60), carbon black (N220), cure activators (stearic acid and ZnO), antidegradants (HPPD and wax), processing oil, and curatives (cure accelerator and sulfur). 6-Bis(*N,N'*-dibenzylthiocarbamoyldithio)-hexane (DBTH) and benzothiazole sulfenamides of *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS), *N-tert*-butyl-2-benzothiazole sulfenamide (TBBS), and 2-(morpholinothio) benzothiazole (MOR) were used as cure accelerators. The compounds without DBTH and containing DBTH were prepared. Contents of DBTH were 0.00 and 1.08 mmol (0.7 phr) of the rubber 100 g. Contents of the benzothiazole sulfenamides (CBS, TBBS, and MOR) were 0.00, 1.08, and 2.16 mmol of the rubber 100 g. Molecular weights of the cure accelerators are m/z 648, 264, 238, and 252 for DBTH, CBS, TBBS, and MOR, respectively. The formulations are given in Table 1.

Mixing was performed in a Banbury type mixer at a rotor

**Table 1**. Formulations (phr)

| Compound No. | Without DBTH | Containing DBTH |
|---|---|---|
| SMR CV60[a] | 100.0 | 100.0 |
| N220[b] | 50.0 | 50.0 |
| ZnO | 5.0 | 5.0 |
| Stearic acid | 1.0 | 1.0 |
| HPPD[c] | 2.0 | 2.0 |
| Wax | 1.0 | 1.0 |
| Oil | 2.0 | 2.0 |
| Sulfur | 1.0 | 1.0 |
| DBTH[d] | 0.0 | 0.7 |
| Cure accelerator | Variable (CBS[e], TBBS[f], or MOR[g]) | |

[a]standard malaysian rubber. [b]carbon black. [c]*N*-phenyl-*N′*-(1,3-dimethylbutyl)-*p*-phenylenediamine. [d]1,6-bis(*N,N′*-dibenzylthiocarbamoyldithio)-hexane. [e]*N*-cyclohexyl-2-benzothiazole sulfenamide. [f]*N*-*tert*-butyl-2-benzothiazole sulfenamide. [g]2-(morpholinothio) benzothiazole

speed of 40 and 30 rpm for master batch (MB) and final mixing (FM) stages, respectively. The initial temperatures of the mixer were 110 and 80 °C for the MB and FM stages, respectively. The MB compounds were prepared as follow. (1) The rubber was loaded into the mixer and premixed for 0.5 min. (2) The carbon black and the ingredients (cure activators, antidegradants, and oil) were mixed for 3.0 min and the compounds were discharged. The FM compounds were prepared by mixing the curatives with the MB compounds for 1.5 min. Cure characteristics were obtained using a Flexsys rheometer (MDR 2000) at 180 °C. The vulcanizates were prepared by curing at 145 °C for 30 min. Physical properties of the vulcanizates were measured with the Universal Testing Machine (Instron 6021). Abrasion loss was measured according to ASTM 2228 with a Pico abrasion tester of BF Goodrich for 80 cycles.

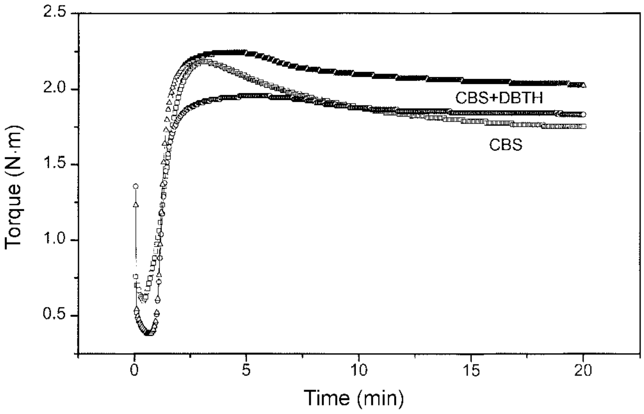


**Figure 1**. Rheocurves at 180 °C for the compounds containing CBS. Squares, circles, and triangles indicate the compounds containing CBS/DBTH of 2.16/0.0, 1.08/1.08, and 2.16/1.08 mmol, respectively.

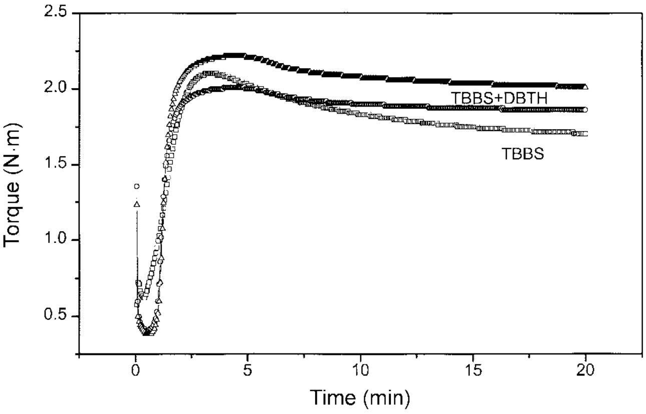


**Figure 2**. Rheocurves at 180 °C for the compounds containing TBBS. Squares, circles, and triangles indicate the compounds containing TBBS/DBTH of 2.16/0.0, 1.08/1.08, and 2.16/1.08 mmol, respectively.

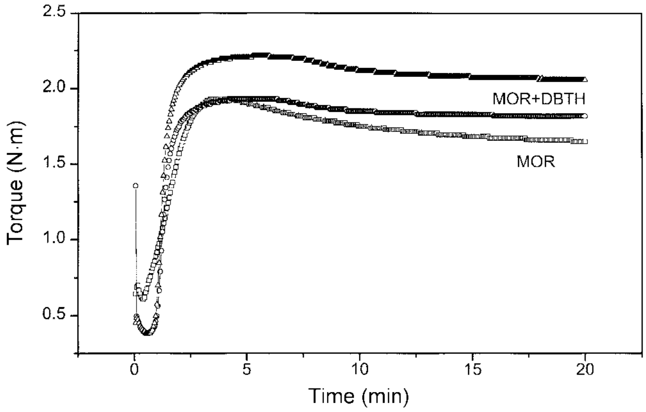


**Figure 3**. Rheocurves at 180 °C for the compounds containing MOR. Squares, circles, and triangles indicate the compounds containing MOR/DBTH of 2.16/0.0, 1.08/1.08, and 2.16/1.08 mmol, respectively.

## Results and Discussion

Cure accelerators were added with constant moles of 0.00, 1.08, and 2.16 mmol per 100 g rubber. The compounds containing and without DBTH were prepared. Figures 1, 2, and 3 are rheographs of the compounds with different benzothiazole sulfenamides of CBS, TBBS, and MOR, respectively. One can find easily the difference in rheocurves of the compounds containing and without DBTH. The detail data for the rheographs of CBS, TBBS, and MOR are summarized in Tables 2, 3, and 4, respectively. The minimum torque ($\mathbf{T_{min}}$) reflects the viscosity. The viscosity of the compound containing DBTH is lower than that of the compound without DBTH, irrespective of the benzothiazole sulfenamide types. The $\mathbf{T_{min}}$ of the compound containing DBTH is lower than that of the compound without DBTH by over 0.2 N·m. This implies that DBTH plays the role of a peptizing agent better than the benzothiazole sulfenamides. In general, a cure accelerator peptizes a rubber chain by radical capture of a rubber radical formed by shearing during the mixing. Three radicals can be formed from dissociation of DBTH, while two radicals can be formed from dissociation of the benzothiazole sulfenamides. One DBTH is dissociated to two radicals of dibenzylthiocarbamic acid (DBzCR) and one biradical of 1,6-hexanedithiol ($\cdot S-(CH_2)_6-S\cdot$, HDTR). The benzothiazole sulfenamide is dissociated to radicals of mer-

**Table 2**. Cure characteristics at 180 °C of the compounds containing CBS

| CBS/DBTH (mmol) | 2.16/0.0 | 1.08/1.08 | 2.16/1.08 |
|---|---|---|---|
| $\mathbf{T_{min}}$ (N·m) | 0.60 | 0.38 | 0.38 |
| $\mathbf{T_{max}}$ (N·m) | 2.16 | 1.96 | 2.24 |
| Delta torque (N·m) | 1.56 | 1.58 | 1.86 |
| $\mathbf{t_{min}}$ (min) | 0.39 | 0.65 | 0.65 |
| $\mathbf{t_{max}}$ (min) | 3.12 | 5.38 | 4.24 |
| $\mathbf{t_2}$ (min) | 0.52 | 0.87 | 0.87 |
| $\mathbf{t_{40}}$ (min) | 1.26 | 1.19 | 1.17 |
| $\mathbf{t_{90}}$ (min) | 2.09 | 1.99 | 1.79 |
| Cure rate (N·m/min)[a] | 0.89 | 1.24 | 1.78 |
| Reversion ratio (%)[b] | 27.2 | 8.2 | 11.8 |

[a] Cure rate = ($\mathbf{T_{90}}$−$\mathbf{T_2}$)/($\mathbf{t_{90}}$− $\mathbf{t_2}$). [b] Reversion ratio (%) at 20 min = 100 × ($\mathbf{T_{max}}$−$\mathbf{T_{20min}}$)/( $\mathbf{T_{max}}$−$\mathbf{T_{min}}$)

**Table 3**. Cure characteristics at 180 °C of the compounds containing TBBS

| TBBS/DBTH (mmol) | 2.16/0.0 | 1.08/1.08 | 2.16/1.08 |
|---|---|---|---|
| $\mathbf{T_{min}}$ (N·m) | 0.62 | 0.41 | 0.38 |
| $\mathbf{T_{max}}$ (N·m) | 2.10 | 2.01 | 2.22 |
| Delta torque (N·m) | 1.48 | 1.60 | 1.84 |
| $\mathbf{t_{min}}$ (min) | 0.37 | 0.53 | 0.58 |
| $\mathbf{t_{max}}$ (min) | 3.36 | 4.41 | 4.43 |
| $\mathbf{t_2}$ (min) | 0.46 | 0.81 | 0.84 |
| $\mathbf{t_{40}}$ (min) | 1.25 | 1.16 | 1.21 |
| $\mathbf{t_{90}}$ (min) | 2.22 | 1.87 | 1.93 |
| Cure rate (N·m/min)[a] | 0.74 | 1.33 | 1.49 |
| Reversion ratio (%)[b] | 26.4 | 9.4 | 11.4 |

[a] Cure rate = ($\mathbf{T_{90}}$−$\mathbf{T_2}$)/( $\mathbf{t_{90}}$−$\mathbf{t_2}$). [b] Reversion ratio (%) at 20 min = 100 × ($\mathbf{T_{max}}$−$\mathbf{T_{20min}}$)/( $\mathbf{T_{max}}$−$\mathbf{T_{min}}$)

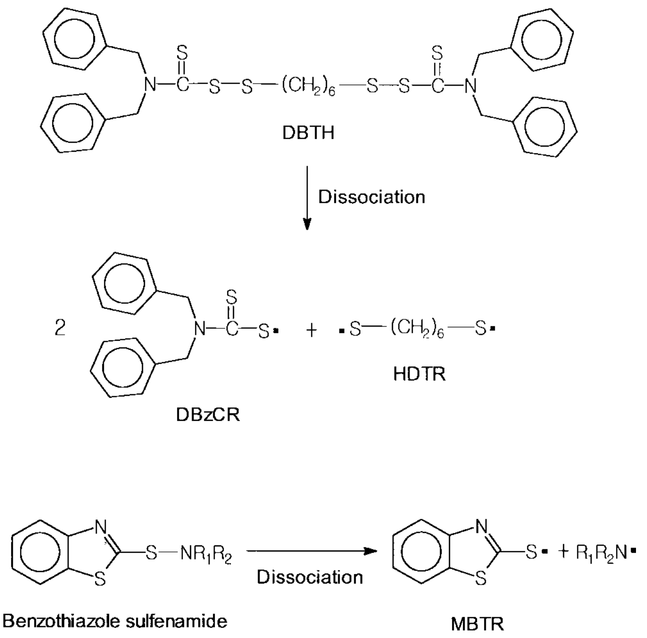
**Table 4**. Cure characteristics at 180 °C of the compounds containing MOR

| MOR/DBTH (mmol) | 2.16/0.0 | 1.08/1.08 | 2.16/1.08 |
|---|---|---|---|
| $\mathbf{T_{min}}$ (N·m) | 0.61 | 0.38 | 0.38 |
| $\mathbf{T_{max}}$ (N·m) | 1.93 | 1.93 | 2.22 |
| Delta torque (N·m) | 1.32 | 1.55 | 1.84 |
| $\mathbf{t_{min}}$ (min) | 0.37 | 0.57 | 0.57 |
| $\mathbf{t_{max}}$ (min) | 3.97 | 5.32 | 5.61 |
| $\mathbf{t_2}$ (min) | 0.47 | 0.82 | 0.82 |
| $\mathbf{t_{40}}$ (min) | 1.63 | 1.15 | 1.19 |
| $\mathbf{t_{90}}$ (min) | 2.54 | 2.05 | 2.06 |
| Cure rate (N·m/min)[a] | 0.56 | 1.11 | 1.31 |
| Reversion ratio (%)[b] | 21.2 | 7.1 | 8.7 |

[a] Cure rate = ($\mathbf{T_{90}}$−$\mathbf{T_2}$)/($\mathbf{t_{90}}$−$\mathbf{t_2}$). [b] Reversion ratio (%) at 20 min = 100 × ($\mathbf{T_{max}}$−$\mathbf{T_{20min}}$)/($\mathbf{T_{max}}$−$\mathbf{T_{min}}$)

captobenzothiazole (MBTR) and the rest amine as shown in Scheme 1.

Delta torque is the difference of the maximum torque ($\mathbf{T_{max}}$) and minimum torque ($\mathbf{T_{min}}$). The delta torque reflects the crosslink density since the delta torque begins to increase from the minimum torque point by crosslinking reactions. The larger the delta torque, the higher the crosslink density.



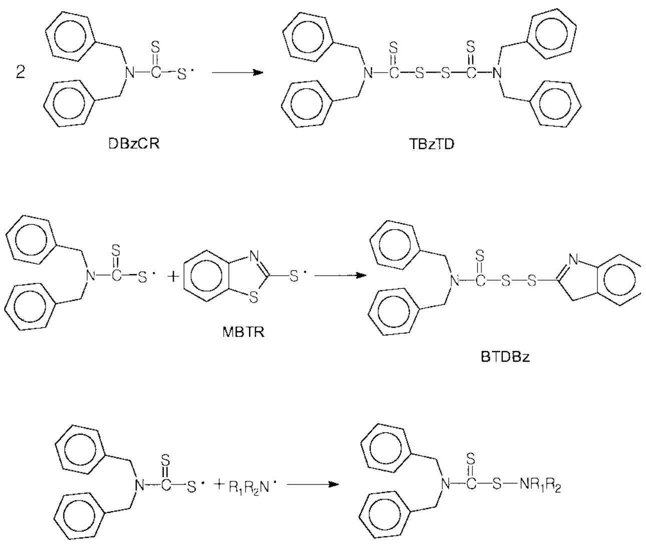
**Scheme 1**

Delta torque of the compound containing DBTH is higher than that of the compound without DBTH when the total cure accelerator content is the same. The increased delta torque of the compound containing DBTH may be due to the crosslink formation by HDTR. Difference in the delta torques of the compounds containing and without DBTH increases as basicity of the amine of benzothiazole sulfenamide decreases. Differences in the delta torques are 0.02, 0.12, and 0.23 N·m for the compounds with CBS, TBBS, and MOR, respectively. Gas basicities of cyclohexyl amine (CBS), *tert*-butyl amine (TBBS), and morpholine (MOR) are 893, 891, and 885 kJ/mol, respectively.[16]

For the compounds without DBTH, the delta torque of the compound containing CBS is higher than that of the compound containing TBBS or MOR and the delta torque of the compound containing TBBS is higher than that of the compound containing MOR. This also follows the order of the gas basicity. The cure rate also has an order of CBS > TBBS > MOR as shown in Tables 2-4. The cure rate was calculated by dividing the difference between the torques at $\mathbf{t_{90}}$ and $\mathbf{t_2}$ ($\mathbf{T_{90}}$-$\mathbf{T_2}$) by the difference between the times of $\mathbf{t_{90}}$ and $\mathbf{t_2}$ ($\mathbf{t_{90}}$-$\mathbf{t_2}$). The cure rates at 180 °C are 0.89, 0.74, 0.56 N·m/min for CBS, TBBS, and MOR, respectively. These imply that CBS is more efficient accelerator than TBBS or MOR. However, the reversion resistance property is worse for CBS than for TBBS or MOR. Reversion ratio at 20 min was calculated by dividing the difference between the maximum torque and the torque at 20 min ($\mathbf{T_{max}}$-$\mathbf{T_{20min}}$) by the delta torque. The results are summarized in Tables 2-4. The reversion ratios are 27.2, 26.4, and 21.2% for CBS, TBBS, and MOR, respectively. This implies that the vulcanizate containing CBS has more polysulfide linkages than the compound containing TBBS or MOR.

Cure characteristics of rubber compounds with accelerated sulfur cure systems containing benzothiazole sulfenamides were studied by several groups.[17,18] Morita and Young[17] studied cure characteristics of rubber comounds containing CBS, TBBS, or MOR and reported that scorch time of the compound containing CBS was faster than that of the compound containing TBBS or MOR and the cure rate became faster as the cure accelerator content increased. Ignatz-Hoover and Kuhls[18] studied correlation between variation of the cure characteristics with the accelerator type and the bond length of Zn-N in zinc complex composed of zinc oxide, fatty acid, and benzothiazole sulfenamides using AM1 semi-empirical calculations. They found that the scorch time increased as the Zn-N bond length increased. The Zn-N bond lengths were 4.402, 4.437, and 4.465 Å for CBS, TBBS, and MOR, respectively.[18]

Scorch time (**$t_2$**) becomes slower by adding DBTH. This may be the recombination reactions between the radicals formed from DBTH and benzothiazole sulfenamide as shown in Scheme 2. Two DBzCR formed from DBTH can be combined to form tetrabenzylthiuram disulfide (TBzTD). The DBzCR can also react with MBTR or the amine radical to produce benzothiazolylthiodibenzylthiocarbamate (BTDBz) or anothr carbamate including amine, respectively. These recombination reactions result in inhibition of the reaction of the cure accelerators and ZnO/zinc stearate to form zinc complex. For accelerated sulfur cure system, crosslinking reaction is occurred through activated zinc complex including chemical bond between zinc and accelerator.[19-21] The reaction to prevent from formation of the zinc complex of the benzothiazole sulfenamide leads to slow scorch time resulting from delay of crosslinking reaction,. Though the scorch time is delayed by adding DBTH, the **$t_{40}$** and **$t_{90}$** become faster by adding DBTH. The cure rate is also faster for the compound containing DBTH than for the compound without DBTH. Improvement of the scorch safety and the faster cure rate can be explained by the synergy effect of DBTH with benzothiazole sulfenamide as shown in Schemes 1 and 2. Datta and coworkers[22,23] studied the synergy effect of binary cure accelerator system and reported that synergistic combinations produced monosulfidic linkages, enhanced the cure rate, and reduced the scorch time.



**Scheme 2**

Since polysulfides are more unstable than mono- and disulfides, the sulfur curing at high temperatures deteriorates the mechanical properties of rubbers due to reversion. Reversion is decrease of the crosslink density by dissociation of the existing crosslinks. The reversion ratio of the compound containing DBTH is much lower than that of the compound without DBTH. The reversion resistance is improved by about three times when the total cure accelerator content is the same. When the total cure accelerator content is the same of 2.16 mmol, the reversion ratios of the compounds containing DBTH are 8.2, 9.4, and 7.1% for CBS, TBBS, and MOR, respectively, while for the compounds without DBTH are 27.2, 26.4, and 21.2%, respectively. And even the compounds containing the benzothiazole sulfenamide of 2.16 mmol and DBTH of 1.08 mmol (total cure accelerator content is 3.24 mmol) have better reversion resistance by over twice. This means that DBTH produces mono- or disulfide rather than polysulfides. This may be due to formation of shorter sulfur crosslinks by DBzCR and TBzTD formed from DBTH. The DBzCR and TBzTD act as a sulfur donor to produce lower rank sulfur crosslinks.[24]

Physical properties of the vulcanizates are summarized in Tables 5-7. Moduli of the vulcanizates containing DBTH are higher than those of the vulcanizates without DBTH. This is

**Table 5**. Physical properties of the vulcanizates containing CBS

| CBS/DBTH (mmol) | 2.16/0.0 | 1.08/1.08 | 2.16/1.08 |
|---|---|---|---|
| 100% Modulus (kg/cm$^2$) | 19.9 | 27.4 | 31.4 |
| 300% Modulus (kg/cm$^2$) | 105.3 | 129.0 | 145.7 |
| Tensile strength (kg/cm$^2$) | 289.7 | 299.7 | 301.1 |
| Elongation at break (%) | 615.2 | 564.8 | 539.1 |
| Heat build-up (°C) | 37.3 | 26.4 | 25.5 |
| Abrasion loss (mg) | 30 | 27 | 25 |

**Table 6**. Physical properties of the vulcanizates containing TBBS

| TBBS/DBTH (mmol) | 2.16/0.0 | 1.08/1.08 | 2.16/1.08 |
|---|---|---|---|
| 100% Modulus (kg/cm$^2$) | 20.1 | 28.6 | 30.3 |
| 300% Modulus (kg/cm$^2$) | 105.4 | 133.4 | 137.6 |
| Tensile strength (kg/cm$^2$) | 287.4 | 304.3 | 310.9 |
| Elongation at break (%) | 626.4 | 578.0 | 567.4 |
| Heat build-up (°C) | 37.2 | 28.0 | 25.3 |
| Abrasion loss (mg) | 29 | 26 | 24 |

**Table 7**. Physical properties of the vulcanizates containing MOR

| MOR/DBTH (mmol) | 2.16/0.0 | 1.08/1.08 | 2.16/1.08 |
|---|---|---|---|
| 100% Modulus (kg/cm$^2$) | 18.5 | 27.7 | 31.4 |
| 300% Modulus (kg/cm$^2$) | 98.4 | 127.0 | 142.9 |
| Tensile strength (kg/cm$^2$) | 278.5 | 304.1 | 305.3 |
| Elongation at break (%) | 615.8 | 594.3 | 547.4 |
| Heat build-up (°C) | 37.4 | 26.5 | 24.1 |
| Abrasion loss (mg) | 30 | 28 | 26 |

due to the crosslink density. Modulus of a vulcanizate is a propotional physical property to the crosslink density.[25] Crosslink density of the vulcanizate containing DBTH is higher than that of the vulcanizate without DBTH as discussed previously. The elongation at break becomes shorter by adding DBTH. This is also due to the crosslink density. The elongation at break is an inversely propotional physical property to the crosslink density.[25] Though the elongation at break of the vulcanizate containing DBTH is shorter than that of the vulcanizate without DBTH, the tensile strength of the former is higher than that of the latter. This may be due to the long crosslinkers (-S-$(CH_2)_6$-S-)[14] formed from HDTR. The heat build-up and wear property is also improved by adding DBTH. This can be also explained with the increased crosslink density.

## Conclusion

Binary cure system composed of DBTH and benzothiazole sulfenamide shows a synergy effect of the delayed scorch time, fast cure rate, and high crosslink density. By adding DBTH, viscosity of the compound is decreased and the delta torque is increased. The compound containing DBTH has better reversion resistance than the compound without DBTH. Physical properties are also improved by adding DBTH.

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