Experimental Study on the Curing Process of Styrene-Butadiene-Rubber —Progress of curing reaction under mold cooling stage—

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Abstract This is the second paper of a series that describes the curing process of styrene-butadiene-rubber packed in a cylindrical mold with inner diameter of 74.6 mm. Present paper mainly describes the curing process under the mold cooling stage. Sulfur was used as the curing agent and the sulfur concentration ranged from 1.0 to 5.0 weight percent. The mold temperature was controlled in two stages. The mold was heated at 414 K for 45 min. then switched off, and the mold was cooled by natural convection to the surroundings up to 75 min. Time-dependent radial distributions of the temperature profile and the crosslink density were measured in the cooling stage. It was confirmed that the curing reaction was related strongly to the temperature field. In the cooling stage, rubber temperature decreased in the outer zone whereas overshooted in the inner zone. The degree of cure at the rubber center reached to around 0.8 at time 45–60 min. elapsed after taking the heater off for sulfur concentration of 1 and 3 weight percent.

Keywords Styrene-butadiene-rubber, Curing process, Mold cooling stage, Sulfur concentration, Crosslink density

Introduction
Rubber materials are widely used in engineering processes and products. Curing process of thermosetting rubber usually consists of two fundamental roles. One is the crosslinking and the other the molding manufacturing. In the former process, formation of crosslinks is caused by chemical reactions and enhanced by heating the rubber. In recent years, there exists increasing demand for simulation-driven design which will cut down the cost and time required for product development, and many magnificent experimental and theoretical studies have been done from various perspectives\textsuperscript{1–5)}. In case of the rubber with relatively large dimensions, low thermal conductivity of the rubber leads to non-uniform distributions of the temperature history, which results in non-uniform cure state in the rubber. Since the mechanical properties of rubbers strongly depend on the crosslink density\textsuperscript{6)}, new attempts can be found for making a controlled gradient of the degree of cure in a thick rubber part\textsuperscript{7)}.

The authors have studied from experimental and theoretical viewpoints the sulfur curing process of styrene-butadiene-rubber (SBR) packed in a cylindrical mold\textsuperscript{8)}. Since the curing reaction is exothermic, we have made an attempt to cure SBR by effective use of heat generation in cure at the cooling stage. SBR sample packed in a cylindrical mold was press heated at 414 K for 45 min. then switched off, and the mold was cooled by natural convection to the surroundings for residual time selected from 0, 15, 30, 45, 60 and 75 min. We have taken the experimental data with different cooling time, and discussed the effects of cooling time on the progress of the curing process.

Sulfur curing is known to involve relatively large internal heat generation, but the curing process has not been completely analyzed and modeled\textsuperscript{9–12)} and experimental verifications of the models have been restricted to the sulfur concentration up to 2 weight percent at most. The present study was planned to study the progress of curing reaction in the mold cooling stage. The SBR packed in a cylindrical mold with sulfur concentrations of 3 and
5 weight percent were mainly tested and a new data set for sulfur of 1 weight percent was added to the previous result(s).

**Experimental**

**Methods**

Figure 1 illustrates the cylindrical mold and the positions of thermocouples for measuring the rubber temperatures. A steel pipe with inner diameter of 74.6 mm was used as the mold in which a rubber sample was packed. On the outer surface of the mold, a spiral semi-circular groove with diameter 3.2 mm was machined with 9 mm pitch, and four sheathed-heaters with 3.2 mm diameter, a–d, were embedded in the groove. On the outer surface of the mold, silicon coating layer was formed and a glass wool insulating material was rolled. The method described here provides one-dimensional radial heat conduction excepting for the upper and lower ends of the rubber. Four 1-mm-diameter sheathed thermocouples, A–D, were located in the mold as the wall thermocouples. Four 1-mm-diameter sheathed thermocouples were also equipped with the mold to control the heating wall temperatures. The top and bottom surfaces were the composite walls, each consisting of a Teflon sheet, a wood plate and a steel plate to which an auxiliary heater is embedded.

To measure the radial temperature profile in the rubber, eight thermocouples (rubber thermocouples) were located from the central axis to the heating wall at an interval of 5 mm. A thermocouple was also located at the central axis just below 60 mm from the mid-plane of the rubber to measure the temperature difference along the axis. All the thermocouples were led out through the mold and connected to a data logger, and all the temperature outputs were subsequently recorded to 0.1 K.

Styrene-butadiene-rubber (SBR) was used as the polymer. Key ingredients include sulfur as the curing agent, carbon blacks as the reinforced agent. Ingredients of the compounded rubber are listed in Table 1, where sulfur concentrations of 1, 3 and 5 weight percent were prepared. In the present paper, S denotes the sulfur weight percent. To locate the rubber thermocouples at the prescribed positions, rubber sheets with 1 and 2 mm thick were rolled up with rubber thermocouples and packed in the mold.

After each experiment was terminated, the rubber sample was brought out quickly from the mold then immersed in ice water. Then a thin rubber sheet with 5 mm thick was sliced just below the rubber thermocouples to perform the swelling test. As shown in Fig. 2, eight test pieces were cut out at an interval of 5 mm from the sliced sheet. Each test piece has dimensions of 3 mm × 3 mm × 5 mm and swelling test with toluene was conducted. Crosslink density \( [RX] \) was evaluated from the equation proposed by Flory.

![Figure 1. Cylindrical mold and positions of rubber thermocouples.](image)

### Table 1. Ingredients of styrene-butadiene-rubber.

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer (SBR)</td>
<td>53.8 52.7 51.6</td>
</tr>
<tr>
<td>Cure agent (Sulfur)</td>
<td>1.0 3.0 5.0</td>
</tr>
<tr>
<td>Vulcanization accelerator</td>
<td>0.9 0.9 0.9</td>
</tr>
<tr>
<td>Reinforcing agent (Carbon black)</td>
<td>31.9 31.2 30.6</td>
</tr>
<tr>
<td>Softner</td>
<td>8.0 7.8 7.6</td>
</tr>
<tr>
<td>Activator (1)</td>
<td>2.6 2.5 2.5</td>
</tr>
<tr>
<td>Activator (2)</td>
<td>0.5 0.5 0.5</td>
</tr>
<tr>
<td>Antioxidant (1)</td>
<td>0.5 0.5 0.5</td>
</tr>
<tr>
<td>Antioxidant (2)</td>
<td>0.3 0.3 0.3</td>
</tr>
<tr>
<td>Antideteriorant</td>
<td>0.3 0.5 0.5</td>
</tr>
</tbody>
</table>
and Rehner\textsuperscript{13,14}) using the measured results of the swelling test. The crosslink densities at fully cured conditions $[RX]_0$ were obtained from our preliminary experiments as $6.20 \times 10^{-4}$, $1.75 \times 10^{-3}$ and $5.42 \times 10^{-3}$ mol/cm$^3$ for $S=1$, 3 and 5 percent, respectively.

**Theoretical Background**

We discuss about the SBR curing process in the mold cooling stage using the prediction model proposed by the authors\textsuperscript{8}). Heat conduction equation with constant physical properties can be expressed in the cylindrical coordinates as

$$c T_0 \frac{\partial T}{\partial t} = \lambda \frac{\partial}{\partial r} \left( \frac{r \partial T}{\partial r} \right) + \frac{dQ}{dT}$$

subject to

$$T = T_{\text{init}} \quad \text{for} \quad t = 0$$

$$T = T_w(\tau) \quad \text{for} \quad \tau > 0 \quad \text{and} \quad r = r_c$$

$$\frac{\partial T}{\partial r} = 0 \quad \text{for} \quad \tau > 0 \quad \text{and} \quad r = 0$$

where $r$ is the radial coordinate, $t$ the elapsed time, $\rho$ the density, $c$ the specific heat, $\lambda$ the thermal conductivity, $T_w(\tau)$ the heating wall temperature and $T_{\text{init}}$ the initial rubber temperature. The second term of the right hand side of equation (1) shows the effect of internal heat generation due to the curing reaction expressed as

$$\frac{dQ}{dT} = \rho \Delta H d\epsilon/dt$$

where $Q$ is the internal heat generation, $\Delta H$ the heat of reaction and $\epsilon$ the degree of cure.

Method for estimating $d\epsilon/dt$ in equation (3) has been proposed by Onishi and Fukutani\textsuperscript{12}). A set of reactions is treated as the chain one which includes CBS thermal decomposition as shown in Fig. 3, where $\alpha$ is the effective accelerator, $N$ is the mercapt of accelerator, $M$ is the polysulfide, $RN$ is the polysulfide of rubber, $R^*$ is the active point of rubber, and $RX$ is the crosslink site. The model extracts fundamental reactions and the chemical process is simply expressed by a set of the following five chemical reactions.

$$k_1 : \alpha \rightarrow N$$

$$k_2 : N + \alpha \rightarrow M$$

$$k_3 : M \rightarrow RN + N$$

$$k_4 : RN \rightarrow R^* + N$$

$$k_5 : R^* \rightarrow RX$$

The rate constants $k_1$–$k_5$ were derived from the analysis of the isothermal curing data set with sulfur concentration of 1 weight percent obtained using an oscillating rheometer in the range from 403 to 483 K at an interval of 10 K\textsuperscript{8}). Therefore model calculated values in the present paper will be shown only for $S=1$ percent.

The density $\rho$ was determined as $1.165 \times 10^3$ kg/m$^3$ using the mixing-rule. The thermal conductivity $\lambda$ was measured using the cured rubber at 293 K and the result was 0.33 W/mK. DSC measurements of the specific heat capacity $c$ and that of the heat of reaction $\Delta H$ for the rubber compound were performed in the range from 293 to 453 K, and the results were $c = 1.84 \times 10^3$ and $\Delta H = 1.23 \times 10^4$ J/kg. Heat conduction equation (1) was reduced to systems of simultaneous algebraic equations by a control-volume-based, finite difference procedure. Number of control volumes was 37 and time step of 0.5 sec. was chosen after some trials.

Figure 4 is an example of the effect of the internal heat generation rate on the curing process of SBR with 45 min. mold heating at 414 K and subsequent mold cooling. In Fig. 4, the internal heat generation rate $dQ/dt$ and the crosslink density $[RX]$ are shown for the case with sulfur concentration of 1 weight percent. It can be seen from Fig.
that the curing reaction occurs after $\tau=45$ min. without mold heating, especially the reaction begins in the inner zone ($r<20$ mm). The induction time is shorter for nearer the heating wall (larger $r$) due to faster heat penetration. For example, they are almost 8 min. for $r=37.3$ mm (heating wall surface) and 65 min. for $r=0$ mm (rubber center). The result at $r=37.3$ mm, where the rubber temperature reaches 414 K quickly, clearly indicates that it requires a certain amount of time and temperature to produce the internal heat generation. The $\text{d}Q/\text{d}\tau$ at each radial position shows a sharp increase and takes a maximum then decreases moderately. The crosslink density $[RX]$ increases rapidly just after the onset of the curing, then approaches gradually to a constant value as shown in the lower part of Fig. 4.

Table 2 summarizes the numerical results of the electric power consumption along with the rubber states at $r=0$ mm for the elapsed time of 45, 80 and 120 min. Two conditions were simulated. One is the 180 min. mold heating at 414 K corresponding to the conditions of A1 and A2. The other is the 45 min. mold heating at 414 K and subsequent 135 min. mold cooling, corresponding to the conditions of B1 and B2. In the conditions of A1 and B1, curing reactions with heat of reaction of 0 J/kg were attempted in order to study the effect of internal heat generation. In Table 2, the power consumption for A1 is 18 kJ larger than that for A2 and the difference almost agrees with the heat of reaction in the rubber sample. Effects of internal heat generation in the cooling stage can be found by comparing the results of B1 and B2. It can be found that the rubber temperature and the degree of cure at $\tau=80$ min. are 8.0 K and 0.18 higher for

### Table 2. Electric power consumption and rubber states at $r=0$ mm for $\tau=45$, 80, and 120 min. Sulfur concentration of 1 weight percent.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Heat of reaction J/kg</th>
<th>Power consumption kJ</th>
<th>Rubber temperature and degree of cure at $r=0$</th>
<th>Elapsed time minutes</th>
<th>Temperature $^\circ$C</th>
<th>Degree of cure -</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>0</td>
<td>260</td>
<td></td>
<td>45</td>
<td>103.8</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>130.5</td>
<td>0.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120</td>
<td>137.9</td>
<td>0.99</td>
</tr>
<tr>
<td>A2</td>
<td>$1.23 \times 10^4$</td>
<td>242</td>
<td></td>
<td>45</td>
<td>104.4</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>138.1</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120</td>
<td>139.9</td>
<td>0.99</td>
</tr>
<tr>
<td>B1</td>
<td>0</td>
<td>226</td>
<td></td>
<td>45</td>
<td>103.8</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>126.5</td>
<td>0.38</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>120</td>
<td>127.5</td>
<td>0.96</td>
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<tr>
<td>B2</td>
<td>$1.23 \times 10^4$</td>
<td>221</td>
<td></td>
<td>45</td>
<td>104.4</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>80</td>
<td>134.5</td>
<td>0.57</td>
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<td></td>
<td></td>
<td>120</td>
<td>128.7</td>
<td>0.99</td>
</tr>
</tbody>
</table>
B2 than for B1. At $\tau=120$ min., however, the curing process for the two cases seem to be almost completed. Comparison of the results for A2 and B2 with and without mold cooling stage shows that the power consumption for B2 is 21 kJ lower than A2. At $\tau=80$ and 120 min., the rubber temperatures for A2 are 3.6 K and 11.2 K higher than those for B2, respectively. At $\tau=80$ min., the degree of cure for A2 is 0.09 higher than for B2, whereas at $\tau=120$ min. little difference of the degree of cure can be found. Therefore it may be possible to make an effective use of heat of reaction for reducing power input to the mold.

Results and Discussion

Prior to the curing experiments with mold cooling stage, experiments with continuous 180 min. mold heating at 414 K were conducted. Figure 5 compares the measured temperature profiles between S=1 and 5 percent, where symbols present the measured rubber temperatures and short-dash lines show the heating wall temperatures. In Fig. 5(a) solid lines represent the prediction from our previous study for S=1 percent$^8$ and in Fig. 5(b) short-dash lines connect the measured data. The measured rubber temperature shows a typical transient temperature field until the uniform rubber temperature almost equal to the heating wall value is observed. The elapsed times to reach these conditions are about $\tau=80$ and 75 min. for S=1 and 5 percent, respectively. Then the rubber temperatures exceed the heating wall values about 1 K for S=1 percent. For S=5 percent, the rubber temperature at $r=0$ mm takes a maximum of 429 K then gradually decreases. The difference in the maximum rubber temperature between the two may be caused by the effect of internal heat generation due to the curing reaction. Initial temperature rise in the region $r>30$ mm for S=5 percent seems to be slightly slower than that for S=1 percent. This may be caused by the instantaneous delay in operating the electric power input to the mold.

Figure 6 shows the results of S=1 percent for 45 min. mold heating at 414 K and subsequent mold cooling, where symbols present the measured data and solid lines show the predicted values. The temperature field is shown on the coordinates of $T$ and $\tau$ in Fig. 6(a), and that on $T$ and $r$ in Fig. 6(b). In Fig. 6(a), in the region $\tau$ larger than 45 min., the rubber temperature $T_R$ at $r=35$ mm decreases monotonically, while that at $r=0$ mm increases and takes a maximum at $\tau=90$ min. then decreases. An overall inspection of Figs. 6(b) and 6(c) indicates that the curing reaction is strongly related to the temperature history. For example, at $\tau=45$ min., despite the rubber temperature ranges from 380 to 414 K, the crosslink density $[RX]$ less than $r=25$ mm is negligible small. In the region after $\tau=45$ min., the rubber temperature in the inner zone increased and the reaction proceeds, and finally almost uniform $[RX]$ value of $6\times10^{-4}$ mol/cm$^3$ is obtained at $\tau=120$ min. where the negative rubber temperature gradient $dT/dr$ can be observed as shown in Fig. 6(b). The predictions of $T_R$ and $[RX]$ almost agree well with the measurements.

Figure 7 shows the temperature profiles of S=3 and 5 percent, where symbols present the measured temperatures and dash-dot lines connect the data points. Effects of sulfur concentration on the rubber temperature history in the
inner region $r<20\text{mm}$ show the following characteristics. At $\tau=45\text{min.}$, the rubber temperature takes in the range from 370 to 390K regardless of the sulfur concentration as shown in Figs. 6(a), 7(a) and 7(b). After $\tau=45\text{min.}$, the temperatures monotonically increase and reach an almost uniform value at an elapsed time around 70 min., taking slightly shorter time for S=5 percent than for S=1 and 3 percent data. After the uniform temperature field is obtained it can be seen from Fig. 6(b) and right hand parts of Figs. 7(a) and 7(b) that the negative temperature gradient $dT/dr$ is formed and, for example, the gradient at $t=90\text{min.}$ for S=5 percent is larger than the other two conditions.

Figure 8 plots the profiles of the crosslink density for S=3 and 5 percent for 45 min. mold heating and subsequent mold cooling, where symbols present the experimental results and dash-dot lines connect the data points. As expected, the crosslink density in the inner zone increases after $r=45\text{min.}$ where the decreasing wall temperature field exists as shown in Fig. 7. We focus the increase in the crosslink density $\Delta[RX]$ at $r=0\text{mm}$ from $\tau=45\text{to} 90\text{min.}$ in conjunction with Fig. 6(c), the $\Delta[RX]$ values are $5.1\times10^{-4}$, $1.30\times10^{-3}$ and $1.50\times10^{-3}\text{mol/cm}^3$ for S=1, 3 and 5 percent, respectively. If we introduce the change of the degree of cure $\Delta\varepsilon=\Delta[RX]/[RX]_0$ instead of $\Delta[RX]$, the $\Delta\varepsilon$ values are 0.83, 0.77 and 0.30 for S=1, 3 and 5 percent, respectively.

The former two results can be almost the same each other, whereas the result for S=5 percent seems to be lower than the other two. As reviewed in the introduction, the sul-
fur curing process has not been completely analyzed and modeled\textsuperscript{9–12} and experimental verifications of the models have been restricted to the sulfur concentration up to 2 weight percent at most. In addition, previous works have been conducted using DSC or oscillating rheometer and no available data exists obtained in the temperature controlled mold with relatively large size. Therefore it is not possible to make conclusive comments to the experimental results of $\Delta \varepsilon$ for S=5 percent, but it might be caused by any complex behaviors of free sulfur and crosslink decomposition reactions, \textit{etc.}

**Conclusions**

Progress of curing process under the mold cooling stage has been studied using styrene-butadiene-rubber packed in a cylindrical mold with inner diameter of 74.6 mm. The mold was set to 414 K for 45 min., then it was cooled by natural convection to the surroundings up to 75 min. at an interval of 15 min. Sulfur concentration was set to 1, 3 and 5 weight percent and the effects of the concentration on the temperature history and crosslink density were measured. Following concluding remarks can be derived.

1. The reference experiment with continuous 180 min. mold heating at 414 K showed that the temperature history at the rubber center with sulfur concentration of 5
weight percent was maximum 15 K higher than the heating wall temperature. This was caused by the effect of heat of reaction.

2. The experimental results with mold cooling stage showed that the curing reaction progressed being closely connected with the temperature history. Especially, in the cooling stage, rubber temperature in the outer zone decreased whereas that in the inner zone increased and took a maximum then decreased gradually.

3. In the cooling stage, the crosslink density in the inner zone increased and the increase was larger for higher sulfur concentration condition. The increase in the degree of cure at the rubber center was found to be around 0.8 for the sulfur concentrations of 1 and 3 weight percent. It took 45 min. after the heater input was switched off.

References