Effects of Foaming Temperature and Carbon Black Content on the Cure Characteristics and Mechanical Properties of Natural Rubber Foams

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Abstract: The influences of the foaming temperature and carbon black content on the cure behavior and mechanical properties of the NR (natural rubber) foams were investigated at various temperatures and different feeding ratios of the carbon black. The physical properties of the foamed NRs were then measured as a function of the foaming temperature and carbon black content. The optimal temperature for vulcanization and foaming of NRs in this study was 155 °C; where the density of the foamed NRs was lower than those at 145 and 150 °C. The cure rate index of the NRs foamed at 145 °C was smaller than those at 150 and 155 °C. The results of the expansion ratio and micrographs of the foamed NRs supported the density characteristics. The tensile properties of the foamed NRs, such as tensile strength, tear strength, and modulus, gradually increased upon increasing the carbon black content, while the elongation at break decreased. The increase of the foaming temperature led to different results relative to those from the increase of the carbon black content.

Keywords: vulcanization temperature, cure behavior, foaming, cure rate index

Introduction

Cellular polymers may be prepared using a variety of methods. The most important process, by far, consists of expanding a fluid polymer phase to a low-density cellular state and then preserving this state. This approach has been termed a foaming or expanding process. Other methods of producing the cellular state include leaching out solid materials that have been dispersed in a polymer, sintering small particles together, and dispersing small cellular particles in a polymer. The latter processes, however, are of minor importance, and are relatively straightforward processing techniques [1-3].

The expansion process may be divided into three steps: creating small discontinuities or cells in a fluid or plastic phase, causing these cells to grow to a desired volume, and stabilizing this cellular structure by physical or chemical means.

Cellular polymers have been commercially accepted in a wide variety of applications since the 1940s because of their advantages of light weight, buoyancy, cushioning performance, thermal and acoustic insulation, impact damping, and cost reduction. The high strength-to-weight ratio of wood, good insulating properties of cork and balsa, and cushioning properties of cork have contributed to the incentive, as well as to the background knowledge necessary, for the development of the broad range of cellular synthetic polymers in use today.

Most uses of rubber foam have been derived from the desired combination of low density and some other physical properties. Although foamed rubber is widely manufactured and is in service all over the world, articles concerning their electrical, mechanical, and physio-mechanical properties are few in number. In fact, the search for new materials with specific physical properties has been mainly empirical, because no exact theory is currently known that relates the macroscopic properties of multiphase composites to their microscopic structures. The correlation between experimental data in both reinforced rubber and foamed rubber will be attractive from experimental and theoretical points of view [4,5].
Table 1. Formulations of NR Compounds

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Sampleb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NF-1</td>
</tr>
<tr>
<td>SMR-L 100</td>
<td></td>
</tr>
<tr>
<td>St. acid 2.5</td>
<td></td>
</tr>
<tr>
<td>ZnO 5.0</td>
<td></td>
</tr>
<tr>
<td>Carbon black</td>
<td>15</td>
</tr>
<tr>
<td>P. oil 27.5</td>
<td></td>
</tr>
<tr>
<td>MBTS 1.2</td>
<td></td>
</tr>
<tr>
<td>MBT 0.1</td>
<td></td>
</tr>
<tr>
<td>Sulfur 2.0</td>
<td></td>
</tr>
<tr>
<td>DPT 10.4</td>
<td></td>
</tr>
<tr>
<td>Cellex-A 4.2</td>
<td></td>
</tr>
</tbody>
</table>

a Parts per hundred rubber
b NF-1, 2, 3, and 4 refer to NR, F foam, and 1-4 filler content (15, 30, 50, and 70, respectively).

Foams can be reinforced by adding rigid fillers or short glass fibers to the polymer before it is foamed. The effects of reinforcing fillers, such as carbon black, carbon fiber, and silicate, on the physical properties of rubber composites have been studied extensively on experimental and theoretical scales. The compounding technique and also the vulcanization conditions were found to affect the final foam density. Foams are characterized by their density, cell size, shape, and modulus of the base polymer [6].

To obtain optimal foam expansion and good physical properties of the foams, optimal crosslinking is the most critical requirement. In this study, the NR foams were prepared at various temperatures (145, 150, and 155 °C) and different feeding ratios of the filler (10, 30, 50, and 70 phr). The influences of the foaming temperature and reinforcing filler content on the cure behavior and mechanical properties of the foams were studied. Furthermore, the physical properties of the foams, in terms of tensile strength, elongation at break, tear strength, and modulus, were investigated as a function of the foaming temperature and reinforcing filler content. The densities and expansion ratios of the foamed NRs were also studied and a microscope was used to investigate the effects of the foaming temperature and filler content on the morphologies of the foamed NRs.

Experimental

Materials
The NR used was SMR (standardized Malaysian rubber) obtained from Malaysia. All other rubber ingredients, such as sulfur, zinc oxide, stearic acid, paraffin oil, 2-mercaptobenzothiazole (MBT), and mercaptobenzothiazyl disulfide (MBTS) were of commercial grade. As a blowing agent and blowing activator, respectively, N, N’-dinitroso pentamethylene tetramine (DPT) and Cellex-A were received from Kumyang, Korea.

Sponge Rubber Preparation and Formulation
NR compounds were prepared in four different combinations. Basic formulations of the NR compounds prepared in the experiments are given in Table 1. The ingredients were added in the same order as written in Table 1. The compounded blend was then passed endwise ten times through the mill at the 1 mm opening, after which it was sheeted off at 2 mm thick. The specifications of the mill were as follows: length, 0.45 m; radius, 0.10 m; speed of slow roll, 20 rev min⁻¹; gear ratio, 1.4. The compounded rubber was left for at least 24 h before vulcanization. The vulcanized samples were shelf-aged for at least 48 h before testing. To investigate the effects of the foaming temperature and filler content on the physical properties and morphologies of the NR foams, the foaming was performed at three different temperatures (145, 150, 155 °C). The compounded NRs were then compression-molded along the mill grain direction using an electrically heated hydraulic press at different temperatures under a pressure of 14 kgf/cm² for their optimum cure time t₉₀. The most efficient blowing agent (DPT) and blowing activator (Cellex-A) were carefully selected through TGA analysis.

Cure Characteristics and Mechanical Properties
Cure characteristics were studied at 145, 150, and 155 °C using a rheometer (MDR 2000E, Alpha Technologies) according to ASTM D 2240-93. The scorch time, cure time, and cure rate index were calculated based on the rheometer curve or curing curve. The density of the foam was measured through a buoyancy method using a densimeter (SD-200L, MIRAQE). A 2 × 2 cm sample was cut from a foam; its thickness t₁ (cm) and weight W₂ (g) were measured and the expansion ratio was calculated from the following equation [7]:

Expansion ratio = [(2 × 2 × t₁)/W₂]

where t₁ is the thickness and W₂ is the weight of the sample.

The tensile properties of the samples, such as tensile strength, elongation at break, tear strength, and 50 and 100 % moduli, were determined using a Universal Testing Machine (4444, Instron, U.S.) at a cross-head speed of 50 mm/min and at 25 ± 2 °C. The experimental conditions for the tear measurements were the same as those used for the tensile testing. The morphologies of the NR foams were analyzed using a microscope (Hi Scope Advanced KH-3000). A thin slice cut vertically from the foamed NR was magnified with a microscope and its picture was taken.
Table 2. Cure Characteristics of the NRs Foamed at 145, 150, and 155 °C

<table>
<thead>
<tr>
<th>Sample code</th>
<th>$t_{90}$ (min)</th>
<th>Maximum torque (dNm)</th>
<th>Minimum torque (dNm)</th>
<th>$t_{42}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>145</td>
<td>150</td>
<td>155</td>
<td>145</td>
</tr>
<tr>
<td>NF-1</td>
<td>5.83</td>
<td>3.91</td>
<td>2.95</td>
<td>7.53</td>
</tr>
<tr>
<td>NF-2</td>
<td>5.61</td>
<td>3.86</td>
<td>2.82</td>
<td>10.18</td>
</tr>
<tr>
<td>NF-3</td>
<td>4.78</td>
<td>3.69</td>
<td>2.78</td>
<td>12.19</td>
</tr>
<tr>
<td>NF-4</td>
<td>4.45</td>
<td>3.58</td>
<td>3.56</td>
<td>14.70</td>
</tr>
</tbody>
</table>

Results and Discussion

Blowing Accelerator and Cure Characteristics

As shown in Figure 1, the decomposition temperature of a mixture of DPT and Cellex-A was lower than that of single DPT. DPT-A refers to a mixture of DPT and Cellex-A. The decomposition temperature changed from 206 to 138 °C after the addition of blowing accelerator (Cellex-A).

The cure characteristics of the NRs foamed at 145, 150, and 155 °C with different carbon black contents are presented at Table 2. The scorch time or time to incipient cure is a measure of the time required for the premature vulcanization of the material to occur. It is the time taken for the minimum torque value to increase by two units. It can be seen that the scorch time decreased with increasing foaming temperature and filler loading. This observation may be attributed to the viscosity increase upon increasing the carbon black content and prevulcanization along with the rising foaming temperature. Therefore, the shorter time is required to begin the vulcanization process for the NR foam compounds. A decreasing trend of the cure time was also observed upon increasing the foaming temperature and the carbon black content. The minimum torque is a measure of the stiffness of the unvulcanized test specimen taken at the lowest point of the cure curve. It can be seen that the minimum torque increases upon increasing the carbon black content, but decreases slightly upon increasing the foaming temperature. The former is due to the viscosity increase and the decrease of the relative amount of process oil upon the increasing carbon black content; the latter is due to the viscosity decrease through plastic deformation upon increasing the curing temperature. The maximum torque is a measure of the stiffness or shear modulus of the fully vulcanized test specimens at the vulcanization temperature. In other words, it is also a measure of the crosslink density. Both the maximum torque and the difference between the maximum and minimum torque increased after the addition of the filler into the NR matrix. The initial increase in torque was due to the further addition of the filler to the rubber matrix. Torque then also increases, due to the formation of crosslinks between the macromolecular chains and the relative decrease of the oil content.

Figure 2 shows the cure rate index of the foamed NRs with respect to various foaming temperatures and carbon black contents. The cure rate index is calculated as follows [8]:

\[
\text{Cure rate index} = \frac{100}{\text{cure time}, t_{90} - \text{scorch time}, t_{42}}
\]
Effects of Foaming Temperature and Carbon Black Content on the Cure Characteristics and Mechanical Properties of Natural Rubber Foams

Figure 3. Variation of the density and expansion ratio of the foamed NR as a function of the foaming temperature and filler content.

The cure rate index at 145 °C was smaller than those at 150 and 155 °C. The cure rate index is a measure of the rate of vulcanization based on the difference between the optimum vulcanization time, \( t_{90} \), and incipient scorch time, \( t_{s2} \). Vulcanization, as well as scorch, is very sensitive to the temperature conditions. As shown in Figure 2, the effects of the foaming temperature and the carbon black content on the cure rate index were different. Cure rate index gradually increases upon increasing the carbon black content, but there was no significant rise. Meanwhile, the increase of the foaming temperature accelerated the cure rate index. It is obvious that the cure rate index is more sensitive to the vulcanizing temperature than to filler content.

Foaming Characteristics

To investigate the effects of the foaming temperature and carbon black content on the foaming characteristics, the apparent densities and expansion ratios of the NRs foamed at 145, 150, and 155 °C with different filler contents were measured (Figure 3). The density of the foamed NR increases with increasing carbon black content, while it decreases with increasing foaming temperature. The NRs foamed at 145 and 150 °C show lower densities than those foamed at 155 °C.

We explain such behavior in the following way. It is common that the density increases with the increasing filler content because of the higher density of filler. There is, however, a different phenomenon exerted by the foaming temperature. The density of gas cells inside the rubber matrix increases upon increasing the foaming temperature, whereas their volume is enlarged by the thermal expansion effect. This phenomenon will affect the volume fraction of carbon black used as the reinforcing filler for the rubber matrix; it will also affect the mechanical properties. In other words, the dilution of carbon black will increase, so the reinforcement of the rubber matrix will be reduced, and, consequently, the sample will become weaker. This situation is also supported by the expansion ratios, which can be closely related with the time difference between the decomposition temperature of the blowing agent and curing temperature. It has been reported that the curing temperature should not be prior or not be too close to or too far from the decomposition temperature of the blowing agent. Therefore, control of the curing temperature is very important for foaming. As a result, in this study, the lowest foam density for the foamed NRs was achieved at 155 °C.

To obtain an empirical relation describing the dependence of the volume fraction of carbon black, \( \phi_c \), on the foaming, we suggest the following ideal and simple model.

Let us consider the volume fraction of carbon black in the unfoamed sample \( \phi_c^0 \) as

\[
\phi_c^0 = \frac{V_c}{V_f} = \frac{m_c}{\rho_c} = \frac{m_t}{\rho_t}
\]

where \( V_c, m_c, \rho_c \) and \( V_f, m_f, \rho_f \) are the volume, mass, and density for carbon and rubber matrix, respectively. For example, by substituting the following NF-1 values, \( m_c = 15 \text{ g}, \rho_c = 1.8 \text{ gcm}^{-3}, m_f = 140.4 \text{ g}, \rho_f = 0.93 \text{ gcm}^{-3} \), we obtain values of \( \phi_c^0 \sim 0.06, 0.1, 0.15, \) and 0.19 for NF-1, NF-2, NF-3, and NF-4, respectively.

The relationship between the volume fraction of carbon black for foamed NRs (\( \phi_c \)) and unfoamed NRs (\( \phi_c^0 \)) can be expressed as

\[
\phi_c = \frac{\rho_f}{\rho_t} \phi_c^0
\]

where \( \rho_f \) is the measured apparent density of the foamed sample. We obtain values of \( \phi_c \sim 0.039, 0.044, 0.046, \) and 0.049 for NF-1, NF-2, NF-3, and NF-4 foamed at 145 °C, respectively. The volume fraction of carbon black in
Figure 5. Microscopy images of the NR samples foamed at 145 °C as a function of filler content: (a), (b), (c), and (d) refer to NF-1, NF-2, NF-3, and NF-4, respectively.

Figure 6. Microscopy images of the NR samples foamed at 150 °C as a function of filler content: (a), (b), (c), and (d) refer to NF-1, NF-2, NF-3, and NF-4, respectively.

Figure 7. Microscopy images of the NR samples foamed at 155 °C as a function of filler content: (a), (b), (c), and (d) refer to NF-1, NF-2, NF-3, and NF-4, respectively.

Mechanical Properties

The nature of the deformation of the NR foams under an applied load can be understood from the stress-strain curves. The stress-strain curves plotted as a function of the foaming temperature and the carbon black content are given in Figures 8, 9, and 10. NR foams can accommodate more stress, while exhibiting lower elongation, with increasing carbon black content. Meanwhile, as the foaming temperature increases, the stress decreases together with the elongation at break as a result of the thinner thickness of each of the struts formed inside the rubber matrix.
black content, but there was little effect observed as the foaming temperature increased. The tensile strength of the compounds increased with increasing carbon black content because of the reinforcing effect of carbon black. The tensile strengths of the NRs foamed at 155 °C were lower than those at 145 and 150 °C because of the lower density, indicating better blowing efficiency; the NRs foamed at 155 °C indicated the lowest blowing efficiency, highest density, and better tensile properties.

The change of elongation at break of the foamed NRs is shown in Figure 12. The elongation at break dropped continuously with increasing foaming temperature and carbon content. This trend may be attributed to the rigid carbon black-rubber interface formed upon increasing the content of carbon black. This case is similar to that observed upon increasing the particulate filler in the rubber compounds. It was found that the increment in the filler content resulted in reduction of the deformability of a rigid interface between the filler and the rubber matrix. Furthermore, in this study for elongation at break, foams with high blow-
The tear strength of the samples under the same conditions as those used to measure tensile strength are shown in Figure 13. Tear strength is the force per unit thickness used to initiate a rupture or tear of a material. The tear strengths of the samples increase continuously with carbon black content due to the reinforcing effect of carbon black, which is similar to the results we observed for the tensile strength. However, the tear strengths decreased with increasing foaming temperature.

Variations of the 50, 100, and 200 % moduli of the foamed NRs with respect to the foaming temperature and carbon black content are shown in Figures 14, 15, and 16, respectively. As in the cases of the tensile strength and tear strength, the modulus was maximized for the NRs foamed at 145 °C.
The hardness of the NR foams increases with increasing carbon black content, while decreases with increasing foaming temperature, as shown in Figure 17. This result can be attributed to the carbon black amount for the former and the greater foaming efficiency for the latter.

**Conclusion**

The cure rate indices of the NRs foamed at 150 and 155 °C with respect to the filler content and various curing temperatures are bigger than those at 145 °C, because the difference between the curing time and scorch time decreases with the increase of the foaming temperature and carbon black content. The optimal temperature of vulcanization and foaming of the NRs in this study was 155 °C. The densities of the NRs foamed at 155 °C are lower than those at 145 and 150 °C, supporting the foaming efficiency results. The tensile strength of the compounds increases with the increasing filler content because of the reinforcing effect of carbon black. For the foaming temperature, the tensile strength decreases in the order 145, 150, and 155 °C, which is closely related to the density and expansion ratio results. The elongation at break drops continuously with increasing foaming temperature and carbon black content. Like the tensile strength, the tear strength and modulus of the samples increase continuously with carbon black content, while decrease with increasing foaming temperature. As a result, we found that the foaming temperature was a clear main factor for determining the curing characteristics, while the mechanical properties are more closely related to the filler content than to the foaming temperature.

**References**