The Foaming Characteristics and Physical Properties of Natural Rubber Foams: Effects of Carbon Black Content and Foaming Pressure

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Abstract: Natural rubber (NR) was foamed at different feeding ratios of carbon black and different foaming pressures. The cure characteristics were studied with respect to the carbon black content, and the effects of the foaming pressure and filler loading on the mechanical properties and morphologies of the foams were also investigated. With an increase of the filler loading, ML increased together with MH as a consequence of the initial rising viscosity and reinforcement resulting from carbon black. The values of t₃₂ and t₇₀, however, increased with increasing carbon black content. The thickness of each of the struts formed inside the rubber matrix and the hardness both increased with increasing foaming pressure and carbon black content. The expansion ratio and micrographs of the foamed NRs supported the density characteristics. The tensile properties of the foamed NRs, such as their tensile strength, tear strength, and hardness, gradually increased with increased foaming pressure and carbon black content, while the elongation at break decreased.

Keywords: foaming pressure, cure characteristics, struts, expansion ratio

Introduction

Cellular polymers can be prepared using a variety of methods. The most important process, by far, consists of expanding a fluid polymer phase into a low-density cellular state and then preserving this state. This method has been termed a foaming or expanding process. Other methods of producing the cellular state include the leaching out of 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, but 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 using physical or chemical means. Cellular polymers have been used commercially in a wide variety of applications since the 1940s because of their light weight, buoyancy, cushioning performance, thermal and acoustic insulation, impact damping, and cost reduction. The high strength-to-weight ratio of wood, the good insulating properties of cork and balsa, and the cushioning properties of cork have acted as incentives 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 desire to combine its low density with some other physical properties. Although foamed rubber is widely manufactured and is in service all over the world, articles concerning its electrical, mechanical, and physico- 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 structure. The correlation between experimental data in both reinforced rubber and foamed rubber will be attractive from both experimental and theoretical points of view [4,5].

Foams can be reinforced by adding rigid fillers or short...
### Table 1. Formulations of NR Compounds

<table>
<thead>
<tr>
<th>Ingredient (phr)</th>
<th>Sample</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR-L</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>St. acid</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Carbon black</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>P. oil</td>
<td>27.5</td>
<td></td>
</tr>
<tr>
<td>MBTS</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>MBT</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>DPT</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td>Cellex-A</td>
<td>4.2</td>
<td></td>
</tr>
</tbody>
</table>

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

Sponge Rubber Preparation and Formulation

NR compounds were prepared in four different combinations. NR was compounded using a two-roll mill according to the recipe shown in Table 1. The ingredients were added in the same order as presented in Table 1. The compounded blend was then passed endwise ten times through the mill at the 1 mm opening, after which time it was sheeted off at 2 mm thick. The specifications of the mill are 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 foaming. To investigate the effects of the foaming pressure and filler content on the physical properties and morphology of NR foam, the foaming was performed at four different foaming pressures (15, 25, 35, 45 kgf/cm²). The compounded NRs were compression molded along the mill grain direction using an electrically heated hydraulic press at 150 °C to determine their optimum cure time $t_{90}$ with different foaming pressures. After removal of the pressure, expansion occurred immediately; the foamed samples were shelf-aged for at least 48 h before testing. An efficient blowing agent (DPT) and blowing activator (Cellex-A) were carefully selected through TGA analysis.

Cure Characteristics and Mechanical Properties

Cure characteristics were studied with different carbon black contents (15, 30, 50, 70 phr) using a rheometer (MDR 2000 E, 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 by a buoyancy method using a densimeter (SD-200 L, MIRAQE). A 2×2 cm sample was cut from a foam and its thickness $t_1$ (cm) and weight $W_2$ (g) were measured; the expansion ratio was calculated from the following equation [7]:

$$\text{Expansion ratio} = \left(\frac{2 \times 2 \times t_1}{W_2}\right)$$

where $t_1$ is the thickness and $W_2$ is the weight of the sample.

The tensile properties of the samples, such as tensile strength, elongation at break, and tear strength, were measured using an Instron Universal Testing Machine (4444-C10283) at a cross-head speed of 50 mm/min at 25±2 °C. The experimental conditions for the tear measurements were the same as those applied for the tensile testing. The morphology of the NR foams was analyzed using a microscope (Hi Scope Advanced KH-3000). A thin slice, cut vertically from the foamed NR, was magnified under the microscope and its picture taken.

Experimental

Materials

The NR used was SMR, obtained from Malaysia. All other rubber ingredients, such as sulfur, zinc oxide, stearic acid, paraffin oil, 2-mercaptobenzothiazole (MBT), and dibenzothiazyl disulfide (MBTS), were of commercial grade. As a blowing agent and blowing activator, respectively, $N,N'$-dinitroso pentamethylene tetramine (DPT) and Cellex-A were used as received from Kumyang, Korea.
The results obtained in this study are discussed with respect to the cure properties, foaming characteristics, and mechanical properties of the natural rubber foams.

Blowing Promoter and Cure Properties

Figure 1 shows the variation of the decomposition temperature of DPT upon the addition of the blowing promoter, Cellex-A. DPT-A refers to a mixture of DPT and Cellex-A. The decomposition temperature changed from 206 °C to 138 °C upon the addition of Cellex-A.

The cure characteristics of the NRs foamed at 150 °C with different carbon black contents are presented in Figure 2. The scorch time or time to incipient cure is a measure of the time at which premature vulcanization of the material occurs. 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 filler loading. This observation may be attributed to the viscosity increase upon increasing the carbon black content. Therefore, a shorter time is required to initiate the vulcanization process for the NR foam compounds. A decreasing trend of the cure time is also observed upon increasing 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, ML, increases with increasing carbon black content because of the viscosity increase and decrease of the relative amount of process oil upon increasing the carbon black content. The maximum torque, MH, 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. The MH increases with the addition of filler into an NR matrix. The initial increase in torque is due to the further addition of the filler into the rubber matrix. The torque also increases as a result of the formation of crosslinks between the macromolecular chains and the relative decrease of the oil content.

The effect of the feeding content of carbon black on the viscous torque ($S''$ at ML and MH) is shown in Figure 3. It can be seen that $S''$ at ML and MH increased with the carbon black content. $S''$ at ML increased with increasing carbon black content. Because the viscous torque ($S''$ at MH) is related to the damping characteristics or loss modulus [8], this result indicates that it is important to control the carbon black content to less than 50 phr due to the rapid increase of the viscous torque, which causes the bigger loss modulus.

Figure 4 shows the effect of the carbon black content on the cure rate index of the foamed NRs. The cure rate
Figure 4. Variation of the cure rate index of the foamed NR as a function of the carbon black content.

Figure 5. Variation of the density of the foamed NR as a function of the foaming pressure and carbon black content.

Figure 6. Variation of the expansion ratio of the foamed NR as a function of the foaming pressure and carbon black content.

Figure 7. Flexible natural rubber foam at 100 magnification.

Foaming Characteristics

The effects of the carbon black content and the foaming pressure on the foaming characteristics were studied by investigating the apparent densities and expansion ratios of the NRs foamed at 15, 25, 35, and 45 kgf/cm² with different filler content. As shown in Figure 5, the density of the foamed NR increases with increasing carbon black content and foaming pressure, and the foaming efficiency decreases. This finding was supported by the results of expansion ratios (Figure 6). We explain such behavior in the following way. It is common that the density increases with increasing filler content because of the higher density of filler. There is, however, no significant increase of the density with increased foaming pressure.

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

$$\phi_c^0 = \frac{V_c}{V} = \frac{m_c}{\rho_c} \cdot \frac{\rho_f}{m_f}$$

(1)
where \( V, m_c, \) and \( \rho_c \) and \( V_t, m_t, \) and \( \rho_t \) are the volume, mass, and density for the carbon and the rubber matrix, respectively. For example, by substituting the following NF-1 values = 15 g (variables 15, 30, 50, and 70 g for NF-1, NF-2, NF-3, and NF-4, respectively), \( \rho_c = 1.8 \text{ g/cm}^3, m_t = 140.4 \text{ g} \) (variables 125.4, 105.4, and 85.4 g for NF-1, NF-2, NF-3, and NF-4, respectively), \( \rho_t = 0.93 \text{ g/cm}^3, \) we obtain \( \phi_c \approx 0.06, 0.1, 0.15, \) and 0.19 for NF-1, NF-2, NF-3, and NF-4, respectively.

The relationship between the volume fractions of carbon black for foamed NNRs (\( \phi_c \)) and unfoamed NNRs (\( \phi_0 \)), can be expressed as

\[
\phi_c = \frac{\rho_f}{\rho_t} \phi_0
\]  
(2)

where \( \rho_f \) is the measured apparent density of the foamed sample. We obtained \( \phi_0 \approx 0.036, 0.060, 0.105, \) and 0.145 for NF-1, NF-2, NF-3, and NF-4 foamed at 150 °C, respectively. The volume fraction of carbon black in the unfoamed sample as well as in the foamed sample increased with the increasing filler loading, while the volume fraction of carbon black in the foamed sample was smaller than that of carbon black in the unfoamed sample as a result of the foaming process.
Foams are three-dimensional agglomerations of gas bubbles, separated from each other by thin sections of polymer. For a finished flexible NR foam, like that shown in Figure 7, the void areas as “cells” are artifacts of gas bubbles that were introduced into the reacting mixture early in its existence. The thin, geometrical structures separating the void areas are made up of the polymer formed from the various reactions.

Microscopic studies were performed for the NRs foamed at different foaming pressures and carbon black contents. Micrographs of NF-1, NF-2, NF-3, and NF-4 samples at four pressures (15, 25, 35, and 45 kgf/cm²) are shown in Figures 8, 9, 10, and 11, respectively. The thickness of each of the struts formed inside the rubber matrix increased with increasing carbon black content and foaming pressure. With the increase of the carbon black content, rubber matrix did not have a sufficient volume fraction for foaming, resulting into the formation of thick struts. The increased foaming pressure, however, decreased the foaming efficiency, leading to thicker struts. It is clear from the micrographs that the NRs foamed at 15 kgf/cm², exhibited higher foaming efficiency, supporting the density and expansion ratio results shown in Figures 5 and 6.

**Mechanical Properties**

The effects of the foaming pressure and carbon black content on the tensile strength of the NRs foamed at 150 °C are shown in Figure 12. The tensile strengths increased steadily with an increased of the carbon black content, but there was little effect observed as the foaming pressure increased. The tensile strengths of the compounds increased with the increasing carbon black content because of the reinforcing effect of carbon black [10]. The tensile strengths of NRs foamed at 15 kgf/cm² are lower than those at 25, 35, and 45 kgf/cm² because of lower density, indicating better blowing efficiency; the NRs foamed at 45 kgf/cm², having the lowest blowing efficiency and highest density, exhibited better tensile properties. The density of gas cells inside the rubber matrix decreased upon increasing the carbon black content, whereas their volume was enlarged by the thermal expansion effect. This phenomenon will affect the volume fraction of carbon black as a reinforcing filler for the rubber matrix. It will also affect the mechanical properties. In other words, the volume fraction of carbon black will increase upon increasing the carbon black content, so the reinforcement of the rubber matrix will increase and, consequently, the sample will become stronger.

The change in the elongation at break of the foamed NRs is shown in Figure 13. The elongation at break decreases continuously upon increasing the carbon black.
content, while it increases with increasing foaming pressure. This trend may be attributed to the rigid carbon black-rubber interface formed upon increasing the carbon black content. This situation is a similar case as increasing the particulate filler in the rubber compounds. We found that the increment in the filler content resulted in reduction of the deformability of the rigid interface between the filler and the rubber matrix. Furthermore, in our study of the elongation at break, foams with high blowing efficiency were inferior to those having low blowing efficiency.

Tear strength results for the samples under the same conditions as used in tensile strength measurements are shown in Figure 14. Tear strength is the force per unit thickness used to initiate a rupture or tear of a material. The tear strengths of the samples increased continuously with increasing carbon black content and foaming pressure because of the reinforcing effect, which is similar to the results obtained for the tensile strength.

The hardness of the NR foams increases with increasing carbon black content and foaming pressure, as presented in Figure 15. This finding can be attributed to the hardness of carbon black and the lower foaming efficiency.

**Conclusion**

From this study, the following conclusions are drawn: The scorch time ($t_s$) and cure time ($t_90$) decrease with increasing carbon black content. For a fixed phr filler loading, the decreasing rate of the cure time is greater than that of the scorch time as a result of the increase of the carbon black content and cure rate index. In contrast, the maximum torque and delta torque increase with increasing carbon black content. Also, our results from viscous torque and loss modulus studies show that carbon black contents over 50 phr would cause an abrupt increase of $S''$ at MH, resulting in hysteresis and reduced resilience.

The density of the foamed NR increases with increasing carbon black content and foaming pressure, but the foaming efficiency decreases; these findings were supported by the results of measuring expansion ratios, which decrease with increasing carbon black and foaming pressure. The volume fraction of carbon black in the foamed sample is smaller than that of carbon black in the unfoamed sample as a result of the foaming process.

The tensile strength increases steadily with an increase in the carbon black content because of the reinforcing effect of carbon black, but there is a little effect as the foaming pressure increases. The elongation at break decreases continuously with increasing carbon black content, while it increases with increasing foaming pressure as a result of the more-rigid carbon black-rubber interface for the former and lower blowing efficiency for the latter. The tear strength results were similar to those of the tensile strength measurements. The hardness increases with increasing carbon black content and foaming pressure because of the hardness of carbon black and the lower foaming efficiency.

**References**