Introduction

Acrylonitrile butadiene rubber (NBR) is widely used in the automotive, aerospace, and oil-well industries because of its high oil-resistance. However, a disadvantage of this material is its aging behavior, which is caused by oxidation of the residual double bonds in the butadiene segments, which could deteriorate the properties of the polymer [1,2]. Saturation of the residual double bonds, through hydrogenation, is commonly used to overcome this deficiency. Removal of double bonds in the backbone of the polymer through catalytic hydrogenation results in improved UV and ozone resistance. Conventional hydrogenation of NBR is undertaken in polymer solution, using pressured hydrogen, rhodium, and palladium complex catalysts [3-5]. In addition to the high resistance to hot air, hot oils, oxidative and ozone degradation, sulfur-containing oils, even hydrogen sulfide, sulfur, nitrogen-containing oil additives, and industrial chemicals, the fully saturated H-NBRs possess excellent tensile strength, good low-temperature flexibility, and very good abrasion resistance.

Rubber materials consist mainly of a large amount of long polymer chains, distributed and oriented in space [6,7]. In the uncured state, shown in Figure 1(a), these chains are not connected together through cross-links and movement between them is possible. On a macroscopic basis, this situation can be observed as inelastic (plastic) behavior that is used intentionally during the molding process of rubber products. Nevertheless, physical links and entanglements between the molecules and links between rubber and filler particles cause some viscous and elastic effects. Therefore, it is reasonable to describe such materials as exhibiting a viscous fluid. Once the rubber materials undergo prevulcanization (also termed the precuring and scorch time), their flow properties decrease suddenly, although they depend on the conditions that can cause prevulcanization. Prevulcanization is the time during which tight curing (thickening) is observed; during that period, a rubber compound still flows uninhibited, as, for example, in compression molding. It may, however, be fatal to calendering and extruding processes. In general, prevulcanization is considered to
result in gelation, which is the phenomenon of the formation of unvulcanized rubber portion insoluble in a chosen solvent [8]. After vulcanization, in the cured state, additional chemical cross-links between the chains prevent them from undergoing extended relative movement and, thus, the ability to undergo plastic deformation vanishes; see Figure 1(b) for an illustration. A completely cured rubber material will instead show a clear elastic behavior that can be explained by molecular network models, e.g., the Treloar (1975) and Mark (1994) models. When considering carbon black-filled rubber compounds, a strong viscous behavior is superposed on the purely elastic response, which can be explained by reorganization effects between the rubber molecules and the filler particles.

The gel content in freshly prepared natural rubber from trees in regular tapping is low, usually about 5 to 10 %. However, the gel content of natural rubber increases upon storage, and may reach 50 % or more after prolonged storage. The increase in the gel content is mainly due to the storage hardening. Variation in gel content may give rise to differences in the processibility behavior [9-13]. Variation of the original viscosity of rubber compounds before vulcanization causes poor flow, scorch, and flow marks, which could be negative factors for processibility.

In actuality, it was observed that there was no constant increase in the temperature and time applied to the mold for air tanks. At the same time, it took a long time to reach the vulcanization, resulting in low tear and adhesive properties because of the poor flow behavior.

In this study, to further understand the effects that the temperature and time applied to the real manufacturing of air tanks have on the cure characteristics and mechanical properties, temperature and time, which are considered to affect the rubber flow, were checked and divided into eight regions. The tensile green strength of each of them was measured to study the relationship between gelation and optimal crosslinking. The thermally deformed H-NBRs were also investigated for their cure characteristics close to those processibility and physical properties, such as tensile properties, hardness, and swelling resistance.

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-NBR</td>
<td>100.0</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1.0</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5.0</td>
</tr>
<tr>
<td>Semi-reinforcing furnace (SRF)</td>
<td>29.4</td>
</tr>
<tr>
<td>Fast-extrusion furnace (FEF)</td>
<td>44.1</td>
</tr>
<tr>
<td>Dioctyl phthalate (DOP)</td>
<td>22.1</td>
</tr>
<tr>
<td>N-Cyclohexyl-2-benzothiazole sulfenamide (CZ)</td>
<td>1.5</td>
</tr>
<tr>
<td>Tetramethyl thiuram disulfide (TMTD)</td>
<td>0.9</td>
</tr>
<tr>
<td>Tetraethyl thiuram disulfide (TETD)</td>
<td>0.9</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.4</td>
</tr>
</tbody>
</table>

<sup>a</sup> Parts per hundred rubber
Experimental

Materials and Formulations
The H-NBR (THERBAN® C 3446 grade; acrylonitrile content: 34 wt%; specific gravity: 0.95 g/cm³) was supplied by Bayer. All other ingredients, sulfur, stearic acid, and zinc oxide, the semi-reinforcing furnace (SRF), the fast-extrusion furnace (FEF), dioctyl phthalate (DOP), antioxidant, N-cyclohexyl-2-benzothiazole sulfonamide (CZ), tetramethyl thiuram disulfide (TMTD), and tetraethyl thiuram disulfide (TETD) were of commercial grade. The formulations are given in Table 1. The samples are designated as H-NBR a-b; a and b refer to the temperature and time applied, respectively.

Cure Characteristics and Vulcanization Process
Cure characteristics were studied using a rheometer (MDR 2000E, Alpha Technologies) according to ASTM D 2240-93. Samples (5.5 g) of the respective compounds were tested at the vulcanization temperature (160 °C). In this study, the H-NBR compounds were exposed to different temperatures and times to determine the cure characteristics and physical properties. The rubber sheets (3 mm thick) were then compression-molded at 160 °C with a force of 10 MPa using a hot press according to the respective cure times, t₉₀, determined using MDR 2000E.

Mechanical Properties
Dumbbell-shaped samples were cut from the molded sheets according to ASTM D 412. The tensile green strength sample was measured according to ASTM D 6746-03. Tensile testing of the samples was performed using an Instron Universal Testing Machine (4444-C10283) at a cross-head speed of 50 mm/min and at 25 ±2 °C. The tear test was conducted as per ASTM D-624, using 90° angle test pieces. The experimental conditions for the tear measurements were the same as those used for the tensile testing. The hardness of the samples was measured as per ASTM D-2240, using a Mitutoyo Shore A meter. For hardness measurements, sheets having an effective thickness of 6 mm were used.

Gel Content Measurement
NBR samples were weighed and inserted in labeled steel nets, which were then heated under reflux in xylene for 24 h. Thereafter, the steel nets were removed from the remaining solvent, washed with xylene, and immersed in methanol for 3 h. Subsequently, the samples were dried at 50 °C in a vacuum oven and weighed. The gel content was calculated from the ratio of the weight after extraction to the original weight.

Swelling Study
Swelling was studied in tetrahydrodichloropentadiene according to ASTM D471-79. Cured test pieces of the compounds (dimensions: 30×5×2 mm) were weighed using an electrical balance; these values were taken to be the initial weights.

Results and Discussion

Cure Characteristics
The variations of the torque of the H-NBR compounds, which were observed on the rheocurves, depend on the difference between the eight temperature and time zones and can be discussed in terms of cure characteristics. The torque-versus-time curves are divided into three regions, giving the following information about the processing: (a) H-NBR plasticization; (b) mixing, homogenization, and reaction among the components; (c) equilibrium of the reaction. The appearance of stage (a) is expected for curing behavior. For stage (b), we suggest three possibilities to explain the torque increase: (i) dispersion of components into the H-NBR matrix, (ii) physical entanglement with H-NBR. There is also an increase in the temperature during stage (c), which indicates the presence of an exothermic reaction that can be related to the curing processing.

Table 2 shows the cure characteristics of the com-

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Cure time t₉₀ (min)</th>
<th>Minimum torque (dNm)</th>
<th>Maximum torque (dNm)</th>
<th>Scorch time tₛ (min)</th>
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</thead>
<tbody>
<tr>
<td>H-NBR 30-20</td>
<td>6.76</td>
<td>1.28</td>
<td>28.01</td>
<td>2.00</td>
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<td>H-NBR 40-40</td>
<td>6.55</td>
<td>1.30</td>
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<td>2.00</td>
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<td>H-NBR 50-55</td>
<td>6.46</td>
<td>1.34</td>
<td>28.01</td>
<td>2.00</td>
</tr>
<tr>
<td>H-NBR 60-71</td>
<td>6.26</td>
<td>1.39</td>
<td>28.02</td>
<td>2.00</td>
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<tr>
<td>H-NBR 70-89</td>
<td>5.94</td>
<td>1.45</td>
<td>28.00</td>
<td>1.98</td>
</tr>
<tr>
<td>H-NBR 80-106</td>
<td>5.73</td>
<td>1.47</td>
<td>27.90</td>
<td>1.90</td>
</tr>
<tr>
<td>H-NBR 90-127</td>
<td>5.48</td>
<td>1.49</td>
<td>27.76</td>
<td>1.75</td>
</tr>
<tr>
<td>H-NBR 100-149</td>
<td>5.03</td>
<td>1.52</td>
<td>27.74</td>
<td>1.46</td>
</tr>
</tbody>
</table>

The temperature and time were maintained the same as those applied during the real manufacture of air tanks.
Cure Characteristics and Physical Properties of Hydrogenated Acrylonitrile Butadiene Rubber: Effects of Prevulcanization Temperature and Time

Figure 2. Variation of the cure rate index as a function of the temperature and time.

Figure 3. Variation of the tensile green strength and tensile strength as a function of the temperature and time.

pounds. The initial decrease in torque is due to softening of the matrix. The torque then increases due to the formation of crosslinks between the macromolecular chains. The cure time decreases upon increasing both the temperature and time. The scorch time, $t_{s2}$, is the time taken for the minimum torque value to increase by two units, which refers to the time to a two-point rise in scorch. It is a measure of the premature vulcanization of the material. It can be seen from Table 2 that with increasing temperature and time, the rheometric torque shows a different relationship between the ML (minimum torque) and the MH (maximum torque). In the case of the ML, upon increasing the temperature and time, the torque increases. This result is attributed to the gel formation by prevulcanization, thermal aging, which is accelerated with increasing temperature. This finding shows that the scorch safety of the compounds decreased with an increase in the temperature and time. The maximum torque, MH, which is a measure of the cross-link density, is also given in Table 2. MH generally correlates with the durometer hardness and/or modulus. We found that the MH decreased upon increasing the temperature and time. This phenomenon is due to the decreased crosslink density because the number of non-optimally crosslinked gels increases with increasing temperature and time although ML, which is attributed to premature vulcanization.

Figure 2 shows the cure rate index of the H-NBR vulcanizates at the various temperature and time zones. The cure rate index is a measure of the rate of vulcanization based on the difference between the optimum vulcanization and the incipient scorch time. The cure rate index is calculated as follows [14]:

$$
\text{Cure rate index} = \frac{100}{(\text{cure time, } t_{oo} - \text{scorch time, } t_{s2})}
$$

Only a constant increase in the rate of vulcanization was observed upon increasing the temperature and time. This finding can be ascribed to gel formation through prevulcanization, which accelerates the time to incipient cure, which is proportional to the increase in the temperature and time. This result shows that the increase in cure rate index, as well as in the scorch time, makes processibility worse because of the low flow properties. Therefore, the poor adhesion and tear properties of the manufactured air tank is attributed to the higher scorch time and cure rate index.

Mechanical Properties

The tensile green strengths and tensile strengths of the samples are shown in Figure 3. The tensile green strength gradually increased upon increasing the temperature and time, while the tensile strength decreased. The former situation is due to non-optimally crosslinked gel formation caused by prevulcanization. The non-optimally crosslinked gel can be considered as a thermal aging point, which stiffens and changes from elasticity to rigidity, from the resultant relationship between the tensile green strength and later gel content. It can be seen that the samples obtained at low temperature and time exhibited tensile strengths higher than those of the samples obtained at high temperature and time. It is thought that the scorch occurs faster as the temperature and time increase, resulting in the formation of localized gelation where the applied stress concentrates. Therefore, the tensile strength of a sample prevulcanized at a higher temperature and for a longer time was shown to be lower than that of a sample obtained at lower temperature and shorter time. In particular, NBR 90-127 and NBR 100-149 show much lower tensile strengths because of the accelerated thermal aging. The elongation at break of the prevulcanized samples
decreased upon increasing the temperature and time, as shown in Figure 4. This result is similar to that of the tensile strength.

Figure 5 presents the variations of the 100 and 200% moduli with respect to the increasing temperature and time. The moduli decreased upon increasing the temperature and time because the crosslink density decreased upon increasing the temperature and time, as shown in Figure 6, where the variation in the swelling value increased steeply as the temperature and time approached 100-149. This situation is due to the sudden decrease in the crosslink density, in particular, in the neighborhood of 100 °C, which is mainly related to the scorch time, \( t_s \), being directly proportional to the crosslink density. The tear strength of the NBR series is presented in Figure 7. The tear strength is the force per unit thickness used to initiate a rupture or tear in a material. It can be seen that the dependence of the tear strength on the temperature and time is very similar to that of the tensile strength.

This observation is associated with the inability of the prematurely C-C bonds, and the formation of the non-optimally crosslinked gel by prevulcanization, to transfer the tearing force applied, and also, probably, because of the rigid interface between the gel and rubber phases.

The hardness of the vulcanizates is given in Figure 8. No considerable variation in hardness was noted when the temperature and time was varied. The rubber vulcanizates, however, became very slightly stiffer and harder as the prevulcanization temperature and time increased. This result was expected because as the degree of formation of the non-optimally crosslinked gel increases, the elasticity of the rubber chains is reduced, resulting in more-rigid vulcanizates.

The gel content increased upon increasing the temperature and time, as shown in Figure 9. It is obvious that there is a close relationship between the gel content and the crosslink density. The effect of non-optimally crosslinked gel formation by prevulcanization, however, on
Cure Characteristics and Physical Properties of Hydrogenated Acrylonitrile Butadiene Rubber: Effects of Prevulcanization Temperature and Time

the mechanical properties and oil resistant properties is somewhat different.

Swelling Behavior
It can be seen from Figure 6 that upon increasing the temperature and time the samples exhibited worse swelling resistance. Calculation of the change in mass for the swelling test of the vulcanizates was performed as follows [15]:

Swelling percentage = \[(M_2 - M_1)/M_1\] \times 100

where \(M_1\) is the initial mass of the specimen (g) and \(M_2\) is the mass of the specimen (g) after immersion. The reciprocal swelling value was used as the crosslink density. We expected that the penetration of tetrahydrodichloropentadiene into the H-NBR compound would increase with the prevulcanizing temperature, which decreases the crosslink density, resulting in an increase in the swelling value. On the contrary, the presence of crosslinked precursors and unreacted curative by prevulcanization might reduce the penetration of tetrahydrodichloropentadiene into the H-NBR compound. In this study, we believe that the swelling value was determined by the degree of crosslinking, but no significant change was observed. These results of tensile properties and swelling resistance allow us to understand that non-optimally crosslinked gel formation by prevulcanization may be more sensitive to the mechanical properties than to the swelling resistance.

Conclusion
The minimum torque of H-NBR compounds increases upon increasing the temperature and time, whereas the scorch time and cure time exhibit decreasing trends, which can be expected to be ineffective for processing. The tensile properties, such as tensile strength, elongation at break, and tear strength, decreased as a result of non-optimally crosslinked gel formation by prevulcanization. The hardness and gel content increased upon increasing the temperature and time, while the swelling resistance exhibited no significant variation, except for NBR 90-127 and NBR 100-149. We believe that the effect of non-optimally crosslinked gel formation generated by prevulcanization is greater on the mechanical properties than on the swelling properties in this study.

References