Cure Characteristics and Dynamic Mechanical Properties of Acrylic Rubber and Epoxidized Natural Rubber Blend

Chan Young Park

Division of Chemical Engineering, Pukyong National University, Pusan 608-739, Korea

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Abstract: With employment of ACM (acrylic rubber) and ENR (epoxidized natural rubber), the rubber and chemical additives were compounded by mechanical method using a Banbury mixer and an open 2 roll mill. Then rubber vulcanizates were prepared by compression mold, and cure characteristics (cure behavior, scorch time, and optimum cure time), maximum torque value, Mooney viscosity, and dynamic mechanical properties of the test specimens were measured. The torque value of rubber mix was obtained with a maximum at ACM/ENR (=25/75) blend. Results determined from a Rheovibron showed two glass transitions ($T_g$) for ACM/ENR (=75/25) indicative of the immiscible nature of the blend. However, in ACM/ENR (=25/75) blend, a single $T_g$ indicating miscibility was obtained.

Keywords: epoxidized natural rubber, Banbury mixer, Mooney viscosity, scorch time, Rheovibron

Introduction

The term polymer blend refers to intimate mixture of two or more polymers. The individual components could be melt-mixed, solution-blended, and coprecipitated or latices could be blended and coagulated before final processing [1-3]. Ultimately, the blend is converted to a final article by extrusion or moulding. The blend is homogeneous or heterogeneous on a microscopic scale, but should not exhibit any obvious inhomogeneity on a macroscopic scale. Also the blend could be tailored to meet the requirements of specific applications [4,5]. They could be developed much more quickly than new polymers and require much less capital investment. The ability to produce blends that have a better combination of properties than that of the individual components depends on the compatibility of the system.

The rubber industry has long practiced blending to achieve the balance of properties required for tires. A typical tire may be comprised of several rubbers, including butadiene, styrene-butadiene, natural rubber, and ethylene propylene diene terpolymer (EPDM), in which each component contributes to the overall property profile. Also the use of blends of rubbers is widespread normally to obtain a balance of properties which one elastomer alone cannot supply [6,7]. Natural rubber may be added to a synthetic rubber compound to improve building properties, resilience, tear strength, or, under some circumstances, fatigue resistance. Conversely, a basically natural rubber compound may have an admixture of synthetic rubber to improve wear or cracking resistance under particular circumstances, or merely to reduce the cost of the compound while retaining adequate properties. Such properties as cost, processing properties, strength properties, resilience properties, and aging properties are affected by blending a synthetic rubber with natural rubber.

ENR (epoxidized natural rubber) is derived from the partial epoxidation of the natural rubber molecule resulting in randomly distributed epoxy groups along with the natural rubber backbone. The incorporation of epoxy group in NR makes substantial changes [8]. ENR of 50 mole% epoxidation (ENR-50) has similar oil resistance to medium nitrile rubber [9] and the gas permeation property of ENR-50 is equivalent to that of butyl rubber [10,11]. A linear relationship is obtained between the degree of epoxidation and glass transition temperature, i. e., with every 1 mole% epoxidation approximately 1°C rise in $T_g$ occurs. As the degree of epoxidation increases the oil resistance increases and gas permeability decreases [12].
The cure characteristics including cure behavior, scorch time and optimum cure time together with maximum torque value, Mooney viscosity, and dynamic mechanical properties of the ACM/ENR blends were measured in this paper.

**Experimental**

**Materials**
ENR obtained from Kumpulan Guthrie Berhard, Malaysia under the trade name of Epoxyprene-50 containing 50 mol% epoxidation was used in the present experiment. The ACM (Acron AR-825) was obtained from Toa Co., Ltd., Japan, and Santogard PVI, used as the retarder, was purchased from Monsanto Corp., USA. Nonserl SK-1 employed as the vulcanizing agent was purchased by courtesy of Nippon Oil & Fat Co., Ltd., Japan. The technical grades of other ingredients, as footnoted in Table 1, were used without further treatment.

**Compounding Procedure**
Table 1 represents the basic formulations of the rubber mix. In the rubber compounding process, the first step included mastication or breakdown of the polymer. Some synthetic rubbers require a certain degree of softening in order to improve compounding and processing. Mixing is the process called for obtaining a thorough and uniform dispersion in the rubber stocks required by the formulation. With mixing operation which is employing an open roll mill, an internal mixer, or a batch mixer/ extruder combination, each batch should involve definite time, temperature, and order of addition procedure. In the present experiment, the mastication and mixing were carried out on a 2 roll mill following the polymer blend method [13]. Then, after mixing the ENR-50 and ACM, the other ingredients were added. The mixing operation was carried out on a laboratory open mill (150 × 330 mm) at 50 ± 5 °C, with cold water circulation, at a friction ratio of 1:1.25 and nip gaps of 1.5 mm. Vulcanized sheets were then produced in an electrically heated press at 165 °C. The blends were prepared as follows. First rubber stocks, stearic acid, FEF, ZnO, and Naugard #445 were mixed. In order to avoid scorching, sulfur, CZ, and TT, were added during the last stage of mixing. The master batch compounds were then fed into an open mill with crosslinking agents. Rubber mixes require heat to convert them into final products. As such, vulcanization was performed using several methods, depending on the compounds involved in the process, size, shape, and overall structure of the finished products.

**Table 1. Formulation of ACM/ENR Rubber Compound**

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<tr>
<th>Item</th>
<th>Kind</th>
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<th>C</th>
<th>D</th>
<th>E</th>
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<td>75</td>
<td>100</td>
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<tr>
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<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>FEF</td>
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<td>75</td>
<td>75</td>
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<td>0.3</td>
<td>0.3</td>
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<td>Powdered sulfur</td>
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<tr>
<td>Nonserl SK-1</td>
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<tr>
<td>NS Soap</td>
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<tr>
<td>CZ</td>
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<tr>
<td>TT</td>
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* *Functions and Suppliers:
ACM: Toa Acron AR-825 (Acryl rubber).
Naugard #445: antioxidant, diphenylamine derivatives, Uniroyal Corp., USA.
FEF: carbon black (fast extrusion furnace).
Santogard PVI: retarder, N-cyclohexylthiophthalamide, Monsanto Corp., USA.
Nonserl SK-1: vulcanizing agent, sodium stearate, Nippon Oil & Fat Co., Ltd., Japan.
NS soap: vulcanizing agent, potassium stearate, Nippon Oil & Fat Co., Ltd., Japan.
CZ: tetramethylthiuram disulfide.
TT: N-cyclohexyl-2,2-benzothiazyl sulfenamide.*

**Measurement of Cure Characteristics and Dynamic Mechanical Properties**
The rheometer is employed to measure cure characteristics in compound development or production control. The effect of rubber mix variations on the viscosity and scorch characteristics can be measured from the initial part of the cure curve, whereas the effect on the rate of cure and the modulus can be examined from the latter one. The optimum cure time at 165 °C, defined as the time to reach 90% of the maximum torque, was determined from a Rheometer (Monsanto R-100) according to a standard method [14]. The specimens for testing were prepared by compression molding at 165 °C, 150 kg/cm². Mooney viscometer is used for detection of the shearing viscosity in rubber stocks. In the Mooney viscosity test, the sample is permitted to warm up for 1 minute after the platens are closed, and then the motor is started. A plot of the viscosity versus time curve indicates that a minimum viscosity value is reached after which the value rapidly increases. The oil resistance test of the blend was performed in ASTM #3 oil with different treatment time at 150 °C [15]. The dynamic mechanical properties of the rubber blend specimens were measured on a Rheovibron (Orientec DDV-25 FP) at 11 Hz, -100 to 100 °C, with liquid N₂ purging. The rate of temperature rise was 3 °C/min.
Results and Discussion

The experimental results which show cure characteristics of ACM/ENR blends are given in Table 2. The data could be transformed into graphic mode when such method of presentation is required. The blends included ACM/ENR in the ratio of 100/0, 75/25, 50/50, 25/75 and 0/100 parts by weight. The cure behaviors of the blends were represented in Figure 1. The rubber mix was subjected to the shearing action of constant amplitude. As vulcanization proceeds, the torque required to shear the rubber mix increases. Cure curve representing a variation in torque versus cure time can be measured for the entire curing process. In the case of ACM/ENR (=100/0) and ACM/ENR (=75/25) blend system, it was generally seen that the torque value gradually increased as the curing time proceeded. On the other hand, the torque value of the blend was obtained with a maximum at ACM/ENR (=25/75) blend, the composition at which the highest Mooney viscosity was observed. For ACM/ENR (=50/50), ACM/ENR (=25/75) and ACM/ENR (=0/100), the torque value of cure curve was reached at peak and then decreased. This downward trend was representative of cure reversion after optimum cure.

Figure 2 shows the variation of the maximum torque values of ACM/ENR with blend composition. From the Figure, it is seen that the maximum torque increases as the ENR loading increases up to ENR 75 wt%, and then decreases. That is, the highest level of maximum torque was obtained at this composition (ACM/ENR=25/75). And also this should indicate the most extensive crosslink among the present blend ratios.

The variation of Mooney viscosities, ML_{1+4} (100 °C) with different blend ratio is shown in Figure 3. The Mooney viscometer is used for determining the shearing viscosity of rubber. The larger rotor is commonly employed for viscosity measurements less than 200 ML units, and the smaller one is available for higher viscosities more than 200 ML. As the Figure 3 show.

### Table 2. Cure Characteristics of the ACM/ENR Blends

<table>
<thead>
<tr>
<th>item</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<tr>
<td>$T_{on}$</td>
<td>4.81</td>
<td>6.85</td>
<td>6.92</td>
<td>6.34</td>
<td>3.94</td>
</tr>
<tr>
<td>$T_{on}$</td>
<td>11.81</td>
<td>22.30</td>
<td>24.86</td>
<td>27.99</td>
<td>25.91</td>
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<tr>
<td>$t_1$</td>
<td>9:27</td>
<td>1:12</td>
<td>1:08</td>
<td>1:03</td>
<td>0.52</td>
</tr>
<tr>
<td>$t_{90}$</td>
<td>21:16</td>
<td>11:10</td>
<td>2:30</td>
<td>1:41</td>
<td>1:24</td>
</tr>
<tr>
<td>ML_{1+4} (100 °C)</td>
<td>69.8</td>
<td>82.8</td>
<td>85.2</td>
<td>86.1</td>
<td>82</td>
</tr>
</tbody>
</table>

a) : minimum torque value (lb in)
b) : maximum torque value (lb in)
c) : scorch time (min:sec)
d) : optimum cure time (min:sec)
e) : Mooney viscosity (dN.m)

![Figure 1. Cure behaviors of ACM/ENR blends in different composition ratios.](image1)

A : ACM/ENR(=100/0), B : ACM/ENR(=75/25), C : ACM/ENR(=50/50), D : ACM/ENR(=25/75), E : ACM/ENR(=0/100)

![Figure 2. Maximum torque value of ACM/ENR blends.](image2)

![Figure 3. Mooney viscosities of ACM/ENR blends.](image3)
the graphic mode of Mooney viscosity with a wide range of blend composition indicates an arc type representing positive deviation from the simple additivity (dashed line). In blend system where strong interactions between the dispersed phases exist, positive deviation of viscosity is often obtained [16]. With ACM/ENR blend pair, ENR having higher viscosity than ACM would have stronger interparticle interactions each other.

The scorch time and optimum cure time for the ACM/ENR blends are given in Figure 4. For Mooney viscometer, when the large rotor is used, scorch time (tₜₙ) is defined as the time at which the viscosity reached a value of 5 units above the minimum. The optimum cure time (tₒₜ) is the time required for an increase of 35 units above the minimum viscosity. Described to the cure behavior which was characterizing ACM, the optimum cure time (Tₒₜ) of ACM was much longer than that of ENR. With ACM/ENR blend system, optimum cure time represented a strong negative deviation from the simple additivity (dashed line), that is, Tₒₜ of the ENR-rich blends was fundamentally the same as that of ENR. The optimum cure time abruptly decreased with ENR up to 50 wt% ENR in the blend. However, the optimum cure time decreased slowly at 100 wt% ENR. Similar tendency was also given for the scorch time. It is probable that the rapidness of cure time in blends is related to increase of viscosity with respect to the simple additivity. In blends with ENR-rich regions, the reduction of optimum cure time to the level of ENR could in part be attributed to the higher viscosity of ENR compared to that of ACM. Since curative was distributed evenly over the entire rubber blend and the chemical association of curative with both ACM and ENR was similar, curative included in rubber whose viscosity was lower had a tendency to migrate into higher viscosity component. On the other hand, curative captured in higher viscosity component was relatively unpreferable to migrate into lower viscosity one [17].

Figure 5 represents the variation of specimen volume upon immersion in oil. The oil resistance of vulcanizate describes that it may be expected to retain its original physical properties without undue dimensional change, decomposition, or disintegration when immersed in oil for fixed periods. The procedures for determining the resistance of vulcanizates in specific oil and fuels are described in ASTM D-412 [15]. Oil resistance is measured from immersion in oil under prescribed time and temperature conditions. In addition the increase in weight per unit volume exposed is determined. A significant increase in oil resistance and reduction in gas permeability results from the epoxidation of natural rubber [12]. As the Figure 5 represents, oil resistance of ACM is comparable to that of ENR. Volume change in oil test is an indication of swelling in specimen. The volume variation with composition ratio for different treatment time is smooth. This relatively smooth tendency given in Figure 5 would suggest the similar interaction of ENR and ACM with oil/solvent [18]. It is probable that partial miscibility exerted by interfacial crosslinking would contribute to the smooth variation over the entire composition of ACM/ENR blend.

The experimental results of the dynamic mechanical properties of the blends determined using a Rheovibron are given in Figures 6 to 8. The amorphous nature of rubber blends clearly defines glass-rubber transition (Tₓ) with a significant drop in modulus. In rubber, Tₓ increases significantly with the increase of crosslinking density [12]. The glass transition temperatures (Tₓ’s) of each specimens determined from the position of the loss peak and tan δ are shown in Figures 7 and 8. For pure ACM, there is a sharp decrease in storage modulus (Figure 6) at the glass transition temperature which
corresponds to a peak in the loss modulus and tan δ curve (Figures 7 and 8). The Tg’s of pure ACM and ENR-50 are observed at around -21 °C and -7 °C, respectively determined from the position of the loss peak (Figure 7). In incompatible rubber blends, double Tg is generally observed [19,20]. On the other hand, ACM/ENR (=50/50) blend composition has two Tg’s corresponding to that of each rubber component (Figure 7). And at the ratio of ACM/ENR (=75/25), two Tg’s were also observed from the tan δ peak indicative of incompatibility (Figure 7). But ACM/ENR (=25/75) blend ratio gives a compatibility which is inferred from a single peak shown from both loss modulus and tan δ data (Figures 7 and 8).

Figure 6. Temperature dependence of storage modulus on ACM/ENR blends.

Figure 7. Temperature dependence of loss modulus on ACM/ENR blends.

Figure 8. Temperature dependence of tan δ on ACM/ENR blends.

Conclusion

After mixing of ACM and ENR-50 were carried out on a two-roll mill following the polymer blend method, other ingredients were added. Vulcanized sheets were prepared by compression press. Cure characteristics, Mooney viscosity, and dynamic mechanical properties of the blends were determined. The torque value progressively increased with time. The scorch and optimum cure time of ACM was much longer than ENR. The storage modulus (E'), loss modulus (E''), and tan δ for the blends are shown in the Figures 6 to 8, respectively. From Figure 8, ACM/ENR (=75/25) blend composition yields two Tg's indicative of incompatibility. However, at the ratio of ACM/ENR (=25/75), only a single peak showing a desirable compatibility determined from both E'' curve and tan δ peak was observed (Figures 7 and 8).

References