Effect of Palm Oil Fatty Acid on Curing Characteristics and Mechanical Properties of CaCO₃ Filled Natural Rubber Compounds

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ABSTRACT

The effect of palm oil fatty acid on curing characteristics and mechanical properties of calcium carbonate filled natural rubber compounds has been studied. Results show that the scorch time and $t_{90}$ increase with increasing concentration of palm oil fatty acid, while the $M_{HR} - M_L$ (maximum torque—minimum torque) passes through a maximum value and decreases with acid concentration. Mechanical properties viz. tensile modulus, hardness, tensile strength and tear strength also follow the similar trend as $M_{HR} - M_L$. Reversion studies indicate that incorporation of palm oil fatty acid improves the resistance to reversion of the natural rubber compounds.

Key Words: palm oil fatty acid, curing characteristics, mechanical properties, reversion, calcium carbonate

INTRODUCTION

In rubber compounding, organic acids are normally used in combination with metal oxides to assist the action of accelerators. They are generally high molecular weight monobasic acids or mixtures of the stearic, oleic, lauric, palmitic, and myristic acids and hydrogenated oils from palm, castor, fish, and linseed oils [1]. The usage of each particular type depends on the accelerator used and the amounts of other compounding ingredients present. Normally from 1 to 3 phr are used. These acids, when incorporated into a compound as part of the activation system for the accelerator acts in conjunction with the zinc oxide and at least partially forms a zinc salt e.g., zinc stearate, which then acts as a zinc ion donor activating the curing system.

Studies on the concentration effect of stearic acid on natural rubber was reported by Coran [2, 3]. He found that the specific rate of vulcanization is decreased if the concentration of stearic acid is increased.

Barton and Hart [4] reported that modulus values improve as the lauric acid content increases but remain constant above a critical concentration of lauric acid. Adding lauric acid, therefore, also brings about an improvement in the physical properties of the vulcanizate. Poh and Tang [5] studied the concentration effect of stearic acid on scorch behaviour of epoxidized natural rubber (ENR). They found that scorch time increases with stearic acid content for all the rubbers investigated,
Effect of Palm Oil Fatty Acid on Curing Characteristics

The rate of increase being fastest in ENR 50, followed by ENR 25 and SMR L.

Palm oil is predominantly made up of triglycerides. It is sold in the world markets on the basis of a 5% premium/penalty limit for free fatty acids. During the refining, free fatty acids must be removed. Fatty acids obtained from palm oil processing consist of a mixture of myristic, palmitic, stearic, oleic, linoleic acids, etc. These acids are long stearic chain compounds containing an even number of carbon atoms C_{10} to C_{18}.

It is felt that these fatty acids may be used in rubber industry in the same role as the commercial stearic acid. With regard to palm oil fatty acids, there is no report on the use of these fatty acids on the curing characteristics and mechanical properties of natural and synthetic rubber compounds. It is thus the aim of this article to describe some of our findings in this area of interest. In the present study, the effect of palm oil fatty acids on the curing characteristics and mechanical properties of natural rubber compounds is investigated. The effect of these acids on reversion behaviour will also be reported.

EXPERIMENTAL

Materials
Table 1 shows the materials, their manufacturers,

<table>
<thead>
<tr>
<th>Materials</th>
<th>Manufacturer</th>
<th>phr</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMR 10</td>
<td>RRIM</td>
<td>100</td>
</tr>
<tr>
<td>Calcium carbonate*</td>
<td>Bayer (M) Ltd</td>
<td>variable</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>Sulphur</td>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>MBT*</td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>Factor H*</td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Palm oil fatty acid</td>
<td>Acidchem (M) Ltd</td>
<td>0.1,3.5,7</td>
</tr>
</tbody>
</table>

* Used at 30 and 50 phr.
* 2-Mercaptobenzothiazole
* Poly-1,2-dihydro-2,2,4-trimethylquinoline

and loadings used in this study. Palm oil fatty acid, Palmac 770 specification, is shown in Table 2 [6].

All materials were used as supplied and conventional sulphur vulcanization system (CV) was employed.

Sample Preparation
Mixing was carried out on a laboratory size (160 mm×320 mm) two roll mixing mill (Model XK-160) in accordance to the method described by the American Society for Testing and Materials (ASTM), designation D 3184-80. The respective cure times at 150 °C as measured by t_{90} were then determined using a Monsanto Rheometer, model MDR 2000. The scorch times, torque, elastic modulus etc., can also be determined from the rheograph.

Measurement of Tensile, Tear Strength and Hardness
The tensile properties and tear strength of the vulcanizates were measured on an Instron Universal Testing Machine, model 1114, according to BS 903: Part A3, respectively. The cross-head speed for the tensile and crescent tear tests (Method A)
was set at 500 mm/min. The test for hardness was carried out by using the Shore A Durometer according to ASTM 2240. All tests were performed at room temperature (25 °C).

Reversion

A Monsanto Rheometer, model MDR 2000 was used to test the rubber compound since the rheometer torque is found to be suitable as an indicator of reversion behaviour [7].

Percentage reversion (R) is defined as:

\[ R = \frac{(T_{\text{max}} - T_t)}{T_{\text{max}} - T_{\text{min}}} \times 100 \]

where \( T_{\text{max}} \): maximum torque, \( T_t \): torque at t min, and \( T_{\text{min}} \): minimum torque on the rheometer.

Determination of Cross-link Density

Cure test pieces of dimension 30 mm x 5 mm x 2 mm were weighed using an electrical balance and each test piece was immersed in a glass vessel containing toluene (30 mL) at 25 °C. The vessels were kept in the dark to prevent oxidation. The samples were then removed from glass vessels and excess toluene was removed by lens blotting paper. The samples were then placed in a closed vessel, to prevent toluene evaporation and the weights of the swollen samples were determined. The sample was then reimmersed in the toluene and the process was repeated until a constant swollen weight could be obtained. The sample was de-swollen in a vacuum at room temperature to a constant weight in order to find the volume fraction of toluene adsorbed in the rubber. Cross-link density of samples was determined by using Flory-Rehner equation [8] (Eqn 1). Physical cross-link density \((2M_c)^{-1}\) was related to volume fraction of rubber in swollen gel by solvent at equilibrium \((V_r)\).

\[-\ln(1 - V_r) - V_r - XV_r^2 = 2P_{RN}V_r(2M_c)^{-1}V_r^{1/3}\]

where \( V_r \): volume fraction of swollen rubber at equilibrium.

\( X \): interaction constant characteristic between rubber sample and toluene (0.39).

\( P_{RN} \): rubber network density = 0.932 at 35 °C.

Table 3. Concentration effect of palm oil fatty acid on curing characteristics of 30 phr of CaCO_3 filled natural rubber compounds.

<table>
<thead>
<tr>
<th>Palm oil fatty acid (phr)</th>
<th>0</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max torque (lb.in)</td>
<td>6.22</td>
<td>6.49</td>
<td>6.55</td>
<td>6.88</td>
<td>6.43</td>
</tr>
<tr>
<td>Scorch time (min)</td>
<td>1.14</td>
<td>1.35</td>
<td>2.10</td>
<td>2.40</td>
<td>2.42</td>
</tr>
<tr>
<td>( t_{90} ) (min)</td>
<td>4.59</td>
<td>5.24</td>
<td>5.40</td>
<td>7.17</td>
<td>7.20</td>
</tr>
</tbody>
</table>

\( V_r \): molar volume of the toluene = 108.05 at 35 °C.

By using Flory-Rehner equation, \((2M_c)^{-1}\) value was obtained.

RESULTS AND DISCUSSION

Curing Characteristics

Concentration effect of palm oil fatty acid at 30 and 50 phr of calcium carbonate (CaCO_3) filled natural rubber compounds on curing characteristics is shown in Tables 3 and 4, respectively. It can be seen that the \( t_{90} \) and scorch time increase with increasing concentration of palm oil fatty acid. This shows that palm oil fatty acid like other well-known retarders i.e., benzoic acid retard the onset of vulcanization [9]. Coran [2, 3] carried out studies on the concentration effect of stearic acid on natural rubber. He found that the specific rate of vulcanization is decreased if the concentration of stearic acid is increased. This is attributed to the complex formation of chelates between zinc ions (brought into solution by stearic acid) and the

Table 4. Concentration effect of palm oil fatty acid on curing characteristics of 50 phr of CaCO_3 filled natural rubber compounds.

<table>
<thead>
<tr>
<th>Palm oil fatty acid (phr)</th>
<th>0</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max torque (lb.in)</td>
<td>6.58</td>
<td>7.13</td>
<td>7.47</td>
<td>8.15</td>
<td>8.13</td>
</tr>
<tr>
<td>Scorch time (min)</td>
<td>1.27</td>
<td>1.38</td>
<td>2.03</td>
<td>2.26</td>
<td>2.30</td>
</tr>
<tr>
<td>( t_{90} ) (min)</td>
<td>4.55</td>
<td>5.19</td>
<td>5.50</td>
<td>6.54</td>
<td>7.39</td>
</tr>
</tbody>
</table>
Effect of Palm Oil Fatty Acid on Curing Characteristics

The effect of acid concentration on max. torque—min. torque in CaCO\textsubscript{3} filled natural rubber compounds.

accelerator, intermediate reaction products, or cross-link precursors.

Tables 3 and 4 also show that compared to control compound (without palm oil fatty acid), all natural rubber compounds have higher maximum torque with increasing concentration of acid. The maximum torque value passes through a maximum value and decreases slightly with increasing concentration of acid. This result shows that palm oil fatty acid acts as a plasticizer when used in excess. At similar concentration of palm oil fatty acid, compounds with 50 phr of calcium carbonate show higher maximum torque. The increment in the torque with filler loading is due to the presence of more fillers which impart more restriction to the deformation and consequently increase the compound stiffness [10]. The relationship between $M_{HR}-M_{L}$ (max. torque—min. torque) and palm oil fatty acid concentration is shown in Figure 1. It can be seen that $M_{HR}-M_{L}$ increases up to certain concentration of acid and then decreases slightly. This shows that palm oil fatty acid has an activating effect to cause more efficient use of sulphur for higher degree of cross-linking. Results from swelling test (Figure 2) show the similar trend.

Other researchers [4, 11] reported that there was an increment in cross-link density with increasing fatty in natural rubber compounds by using MBT accelerated system. Higher concentration of soluble zinc stearate complex in hydrocarbon cause faster desulphuration of cross-linking and most of the cross-linking formed were mono and disulphidic [4]. According to Loo [12] the reduction of maximum torque and the differences between maximum torque and minimum torque ($M_{HR}-M_{L}$) might be due to plasticizing effect of excess zinc stearate and complex (actual accelerator) formed during vulcanization. At high testing temperature (i.e., 150 °C) zinc stearate and its complex would be softened and resulted in lower torque values.

Mechanical Properties
The concentration effect of palm oil fatty acid on mechanical properties is shown in Figures 3—6. It can be seen from Figure 3 that tensile modulus (modulus at 300% elongation) at two calcium carbonate loading increased up to 3 phr and then decreased with further addition of acid concentration. This indicates that palm oil fatty acid has softening effect when used in excess of 3 phr. It can be seen from Table 2 that palm oil fatty acid contains various acids such as oleic acid, palmitic acid, linoleic acid, lauric acid, etc. When more than 3 phr used, some of these acids would act as internal plasticizer. However, the tensile modulus enhancement up to 3 phr may be due to increasing in the degree of cross-linking. Results obtained from swelling measurement and torque values (Figures 1 and 2) support this argument. According to Sloan et al. [13] stiffness property (modulus) and hardness are dependent only on the degree of

![Figure 1. The effect of acid concentration on max. torque—min. torque in CaCO\textsubscript{3} filled natural rubber compounds.](image)

![Figure 2. The effect of acid concentration on cross-link density in CaCO\textsubscript{3} filled natural rubber compounds.](image)
cross-linking. Hardness and stiffness of rubber compound increased with increasing the degree of cross-linking. Figure 4 shows that hardness of the natural rubber compounds follows the similar trend as tensile modulus. However, with equal palm oil loading, compounds of 50 phr of calcium carbonate

![Figure 3. Relationship between modulus at 300% elongation (M300) and acid concentration in CaCO3 filled natural rubber compounds.](image)

![Figure 4. The effect of acid concentration on hardness in CaCO3 filled natural rubber compounds.](image)

![Figure 5. Relationship between tensile strength and acid concentration in CaCO3 filled natural rubber compounds.](image)
have higher hardness and tensile modulus due to the mobility reduction of the macromolecular rubber chains in the compound.

The concentration effect of palm oil fatty acid on tensile strength is shown in Figure 5. It can be seen that tensile strength increased with acid concentration up to optimum value and then decreased.

Morrison and Porter [14] found that increment in the degree of cross-linking may be one of the factors contributing to enhancement in tensile strength. Actually increment in cross-link density resulted in higher tensile strength at the beginning and then decreased. As explained before, after optimum level, plasticizing effect of acid become dominant compared to cross-linking effect and resulted in reduction of tensile strength. Tear strength results in Figure 6 also show the similar trend. According to Hamed [15], fracture properties such as tear strength, pass through a maximum as cross-linking is increased.

Reversion
Figure 7 shows the variation of percentage reversion (30 min after maximum torque) with concentration of palm oil fatty acid in calcium carbonate filled natural rubber compound. It can be seen that incorporation of palm oil fatty acid improved the resistance to reversion indicating the formation of more stable cross-link i.e., less polysulphidic type. Bristow [16], reported that higher amount of stearic acid in rubber formulation improved the resistance to reversion. Sloan et al. [13] obtained the similar result i.e., the reduction of reversion with increasing concentration of stearic acid. This shows that more stable mono-and disulphidic cross-links formed as the concentration of acid increased compared polysulphidic cross-link.
Desulphuration process decreased due to less polysulphidic cross-link and lead to reduction of reversion.

**CONCLUSION**

From this study, the following important conclusions can be drawn:
- Maximum torque increases with palm oil fatty acid concentration for both calcium carbonate loadings used. Natural rubber compounds with 50 phr of calcium carbonate show higher torque.
- Scorch time and t<sub>90</sub> increase with increasing palm oil fatty acid concentration which indicate that palm oil fatty acid has retardation effect on vulcanization.
- Mechanical properties viz tensile modulus, hardness, tensile strength and tear strength pass through a maximum value and decrease with increasing concentration of acid.
- Incorporation of palm oil fatty acid improves the reversion behaviour of natural rubber compounds.

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**REFERENCES**