Performance of treated distillate aromatic extract oil-coated petroleum-based sulfur on properties of natural rubber/acrylonitrile butadiene rubber blends

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Abstract

Petroleum-based sulfur is one of the sulfur types used in rubber vulcanization. The use of such sulfur still faces poor dispersion in the rubber matrix especially in acrylonitrile butadiene rubber (NBR) and its blends. The use of oil as a dispersing agent acts as a key factor to improve the dispersibility of the sulfur. The effects of treated distillate aromatic extract (TDAE) oil-coated petroleum-based sulfur on the properties of natural rubber/acrylonitrile butadiene rubber (NR/NBR) blends were studied. In this work, sulfur was coated with 20 wt% TDAE oil and then the effects on the properties of NR/NBR blends were investigated. The results revealed that the TDAE oil-coated sulfur offered a significant improvement in sulfur dispersion without significant changes in cure behaviors which led to an enhancement of mechanical properties.

Keywords: petroleum based sulfur, TDAE oil, NR/NBR blends, mechanical property, rubber vulcanization

1. Introduction

Rubber blends are being used increasingly in the rubber industry. When properly adjusted, the blends combine the best features of the individual blend components and the desired properties are obtained. Natural rubber (NR) is widely recognized to have good mechanical properties, i.e. high tensile and tear strengths, because it is able to crystallize upon stretching which is also known as strain-induced crystallization. Moreover, NR has excellent elasticity and dynamic properties. However, due to the existence of numerous reactive double bonds on its molecular backbone, NR is highly vulnerable to degradation by thermal aging and ozone attack. In addition, oil resistance of NR is relatively poor due to its non-polarity resulting in limited use in some applications. In order to tackle this problem, blending NR with polar synthetic rubbers such as acrylonitrile butadiene or nitrile rubber (NBR) is preferred.

NBR is a copolymer of acrylonitrile and butadiene. The polar group from the acrylonitrile makes NBR oil-resistant. A higher proportion of acrylonitrile imparts a greater resistance to oil. The blending of NR and NBR is intended to produce a vulcanizate with the best properties from each component, i.e. high oil resistance of NBR and good strength of NR. In practice, however, the result is often disappointing in terms of properties and service life due to the large difference in their polarity. In addition to rubber incompatibility, the poor properties of the final products might also arise from the maldistribution of crosslinks, i.e. one phase is over-crosslinked, whereas another is poorly crosslinked. For blends of two rubbers differing in polarity such as NR and NBR, maldistribution of crosslinks can arise through the

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preferential solubility of the curatives and vulcanization intermediates.

The curing system of the NR/NBR blend generally includes sulfur and thiourea derivatives with the addition of other conventional accelerators (Hoffmann, 1989). Apart from the curing system, the discrepancy in the polarity of the blend partners could also bring about high interfacial tension which is detrimental to the mechanical properties of the blend (Tinker, 1998). The addition of a suitable compatibilizer is therefore essential. Typically, there are 2 main systems of vulcanization used in the rubber industry: sulfur and peroxide (Hoffmann, 1989). Thanks to its low investment cost, adjustable cure behaviors, and superior mechanical properties, sulfur vulcanization is preferably used in the rubber industry. Generally, the sulfur used in the rubber industry includes sulfur and oil-coated sulfur (Akiba & Hashim, 1977; Nebb & Vydra, 2000; Struktol Company of America, 2004). The former has been used since the vulcanization process was discovered, whereas the latter was developed recently and introduced as a vulcanizing agent to alleviate some problems.

Sulfur coated with oil offers a dust-free alternative and it has a low electrostatic force, which can provide safety, suspendibility, and it has a lo...  

2 Preparation of oil-coated petroleum based sulfur

The TDAE oil-coated sulfur was prepared by the dry blending technique using a high speed mixer (Labtech Engineering Co., Ltd., Samutprakarn, Thailand). The physical characteristics of the TDAE oil used (Chartreenuwat, 2013) in this work are tabulated in Table 1. The TDAE oil content and blending time were kept constant at 20 wt% and 3 min, respectively.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Test method</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density/g.cm³ at 15 °C</td>
<td>ASTM D4052</td>
<td>0.96</td>
</tr>
<tr>
<td>Viscosity/ m².s⁻¹</td>
<td>ASTM D445</td>
<td>759.5</td>
</tr>
<tr>
<td>40 °C</td>
<td></td>
<td>26.6</td>
</tr>
<tr>
<td>Total acid number</td>
<td>ASTM D664</td>
<td>0.03</td>
</tr>
<tr>
<td>Carbon type/°wt</td>
<td>ASTM D2140</td>
<td></td>
</tr>
<tr>
<td>Cₐ*</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Cₜ*</td>
<td></td>
<td>41</td>
</tr>
<tr>
<td>Cₑ*</td>
<td></td>
<td>29</td>
</tr>
<tr>
<td>Viscosity-Gravity-Constant (VGC)</td>
<td>ASTM D2501</td>
<td>0.882</td>
</tr>
<tr>
<td>Aniline point °C</td>
<td>ASTM D611</td>
<td>73.7</td>
</tr>
<tr>
<td>Sulfur/°wt</td>
<td>ASTM D2662</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Cₐ*=Aromatic carbon; Cₜ*=Napthenic carbon; Cₑ*=Paraffinic carbon

2.2 Preparation of the NR/NBR blends

The NR/ NBR blends were prepared using a lab-scale internal mixer (Haake Rheocord 90, Essen, Germany) with a fill factor, rotor speed, mixing time, and mixing temperature of 0.8, 40 rpm, 8 min, and 50 °C, respectively. Table 2 shows the compound formulations used in this work. The amount of sulfur used in this work excluded the oil content and thus the actual weight of oil-coated sulfur used during mixing was calculated in order to keep the content of active sulfur constant.

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Amount, phr*</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>NR</td>
<td>100, 75, 50, 25, 0</td>
<td>Raw rubber</td>
</tr>
<tr>
<td>NBR</td>
<td>0, 25, 50, 75, 100</td>
<td>Raw rubber</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3</td>
<td>Activators</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>1</td>
<td>Activators</td>
</tr>
<tr>
<td>CBS</td>
<td>1</td>
<td>Cure accelerator</td>
</tr>
<tr>
<td>Sulfur (all types)</td>
<td>2</td>
<td>Curing agent</td>
</tr>
</tbody>
</table>

*phr=parts per hundred of rubber
NR=natural rubber; NBR=acrylonitrile butadiene rubber; CBS=N-cyclohexyl-2-benzothiazolesulfenamide.
2.3 Property investigation of the rubber vulcanizates

The cure behaviors of the blends, e.g., scorch time (t<sub>92</sub>) and optimum cure time (t<sub>90</sub>) including minimum torque (ML) and maximum torque (MH) were determined using a moving die rheometer (MDR TechPro MD<sup>+</sup>, Mesa, AZ, USA) at 150 °C according to ISO 6502. Afterwards, the blends were compression molded using a hydraulic hot press at 150 °C based on the cure time as pre-determined by the MDRs.

Mechanical properties of the rubber vulcanizates were measured by the Instron 5566 universal testing machine (Norwood, MA, USA) in accordance with ISO 37 (die type 2) at a load cell and a crosshead speed of 1 kN and 500 mm.min<sup>-1</sup>, respectively. Hardness of the vulcanizates was determined by Shore A hardness tester (Cogenix Wallace, Burlington, UK) as per ISO 48. Moreover, photographs of the blends were also recorded.

The Mooney-Rivlin equation was conducted to determine the degree of crosslinking (crosslink density) of the rubber vulcanizates. Equations 1 and 2 are based on the phenomenological theory of rubber elasticity (Campbell et al., 1992; Meissner, 2000).

\[ F = 2A_0(\lambda - \lambda^{-2})(C_1 + C_2\lambda^{-1}) \]  
\[ \frac{\sigma}{(\lambda - \lambda^{-2})} = 2C_1 + 2C_2 \lambda \]  
where \( F \) is the force required to stretch the rubber specimen, \( A_0 \) is the cross-sectional area of the un-stretched specimen, \( \sigma \) is equal to \( F/A_0 \), \( \lambda \) is the extension ratio, and \( C_1 \) and \( C_2 \) are material constants.

By plotting \( \sigma/(\lambda - \lambda^{-2}) \) against \( 1/\lambda \) obtained from equation 2, both \( C_1 \) and \( C_2 \) can be determined. Then, the physically manifested crosslink density (\( n_{poly} \)) or the overall crosslink density can be finally assessed according to equation 3.

\[ n_{poly} = \frac{C_1}{RT} \]  
where \( R \) is the gas constant (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>) and \( T \) is the absolute temperature.

3. Results and Discussion

Cure characteristics of the NR/NBR blends with uncoated and TDAE oil-coated sulfurs are listed in Table 3. The results revealed no profound discrepancy in cure behaviors with an increasing NR/NBR blend ratio. At a given blend ratio, there were slight differences in cure behaviors. The TDAE oil-coated sulfur system offered slightly shorter scorch time and cure time than the uncoated sulfur system. This was possibly due to two reasons: (1) the enhanced degree of sulfur dispersion brought about by the TDAE oil having good compatibility and solubility with NBR matrix (Dasgupta et al., 2007; Dick, 2009; Guo et al., 2008) and (2) the increase in sulfur content from the existing sulfur in the TDAE oil (Table 1). The torque difference of the blends is shown in Figure 1. Our results showed that neat NBR had the highest magnitude of torque difference due to the presence of the acrylonitrile group in its chemical structure leading to high polarity which, in turn, tends to hold the structure together. Moreover, the polar acrylonitrile group makes NBR become stiffer than NR (Hoffmann, 1989; Dick, 2009). In addition, the magnitude of the torque difference decreased with increasing NR ratio in the blend. This might be due to the dilution effect. The oil-coated sulfur system provided a higher magnitude of torque difference than the uncoated sulfur system. This is attributed to the enhanced degree of sulfur dispersion brought about by the good compatibility and solubility of the TDAE oil with rubber matrix. In other words, the TDAE oil is capable of acting as an effective dispersing agent for sulfur. Better dispersion of sulfur leads to more homogeneous crosslinking and, hence, possibly an increase in effective crosslinks.

Figures 2 and 3 illustrate hardness and tensile modulus (M100) results of the blends. Both systems showed similarity in hardness and M100 trends. The lower hardness and M100 values were observed at the higher NR ratio. When the NR ratio changed, the trend of hardness and M100 results was similar to that of the torque difference. As discussed earlier, the polarity of the petroleum-based sulfur leads to better solubility and compatibility with NBR than NR. With higher NR in the blend, the solubility and compatibility are thus reduced which, in turn, decreases the hardness and M100 of the blend. It could be seen that the oil-coated sulfur system provided higher magnitudes of hardness and M100 than the uncoated sulfur system due to the improved dispersibility of sulfur in the NBR phase.

Table 3. Cure characteristics of the NR/NBR blends.

<table>
<thead>
<tr>
<th>NR/NBR ratio</th>
<th>T-0&lt;sup&gt;0°&lt;/sup&gt;</th>
<th>T-20&lt;sup&gt;0°&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>t&lt;sub&gt;2&lt;/sub&gt;, min</td>
<td>t&lt;sub&gt;90&lt;/sub&gt;, min</td>
</tr>
<tr>
<td>0/100</td>
<td>4.52</td>
<td>10.06</td>
</tr>
<tr>
<td>25/75</td>
<td>5.34</td>
<td>9.39</td>
</tr>
<tr>
<td>50/50</td>
<td>5.08</td>
<td>8.04</td>
</tr>
<tr>
<td>75/25</td>
<td>4.41</td>
<td>6.52</td>
</tr>
<tr>
<td>100/0</td>
<td>7.36</td>
<td>10.09</td>
</tr>
</tbody>
</table>

<sup>a</sup> the uncoated blend
<sup>b</sup> the blend with 20 wt% treated distillate aromatic extract oil coated sulfur
NR=natural rubber; NBR=acrylonitrile butadiene rubber.

Figure 1. Torque difference of the uncoated NR/NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20).
Tensile strength and elongation at break of the vulcanizates cured with uncoated and oil-coated sulfurs are exhibited in Figures 4 and 5, respectively. The magnitude of tensile strength increased with an increasing NR ratio in the blends resulting from the strain-induced crystallization of NR (Campbell et al., 1992; Dick, 2009; Hoffmann, 1989; Toki, 2006). At a given blend ratio, the vulcanizates cured with oil-coated sulfur provided higher tensile strength than those cured with uncoated sulfur. This is attributed to the improvement of sulfur dispersion in the rubber matrix along with the increment of crosslink density. The result of elongation at break also agreed well with the tensile strength results. Similarly, the magnitude of elongation at break increased with the increasing NR ratio. In addition, the higher elongation at break was observed in the blends cured by oil-coated sulfur. This was attributed to the good sulfur distribution in the blends as evident in Figure 6. In this study, the tensile strength and elongation at break of neat NR in the uncoated sulfur system were unexpectedly low, possibly due to the poor sulfur dispersion and, thus, uneven crosslink distribution leading to the ineffective stress transfer capability (Sae-Oui et al., 2007; Zaimova et al., 2012). Therefore, poor tensile strength and elongation at break were observed.

Figure 6 shows photographs of the NR/NBR blends cured by uncoated and oil-coated sulfurs. A number of dark spots observed in the blends cured by uncoated sulfur resulted from the poor sulfur distribution in the blends as evident in Figure 6. In this study, the tensile strength and elongation at break of neat NR in the uncoated sulfur system were unexpectedly low, possibly due to the poor sulfur dispersion and, thus, uneven crosslink distribution leading to the ineffective stress transfer capability (Sae-Oui et al., 2007; Zaimova et al., 2012). Therefore, poor tensile strength and elongation at break were observed.

Figure 6. Photographs of the uncoated NR/NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20). Scale = centimeter.
from poor sulfur dispersion. As can be well seen, in the case of oil-coated sulfur, no dark spots were observed. This result clearly confirmed that the oil coating plays an important role in the improvement of sulfur dispersion in the blend, leading to the enhancement in mechanical properties.

The crosslink density was calculated from the Mooney-Rivlin equation and the results are exhibited in Figure 7. The results revealed that the crosslink density tended to increase as the NR content increased. The increasing crosslink density observed with the increasing ratio of NR was not in accordance with the results of our other experiments which showed that NBR had better solubility with petroleum-based sulfur. This unexpected result might have something to do with the limitations of this method which was not suitable for measurement of a blend of more than one type of polymer. The oil-coated sulfur system showed higher crosslink density than the uncoated sulfur system. This result agreed well with previous results in which the oil-coated sulfur caused better sulfur dispersion than the uncoated sulfur (Figure 6).

![Figure 7. Mooney-Rivlin crosslink density of the uncoated NR/NBR blends (T-0) and 20 wt% treated distillate aromatic extract oil-coated sulfur (T-20).](image)

### 4. Conclusions

Compared with the uncoated petroleum-based sulfur, the TDAE oil-coated sulfur offered greater dispersibility in the NR/NBR blends which led to an improvement of cure behaviors and enhancement of the mechanical properties. As a consequence, the coating of sulfur with TDAE oil can be considered as an efficient method to improve sulfur dispersion in rubber.

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### References


