Physical and rheological properties of epoxidized natural rubber modified bitumens

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HIGHLIGHTS

- Adding ENR to bitumen decreased bitumen temperature susceptibility.
- ENR modified bitumen increased in the complex modulus and decreased in the phase angle.
- ENR modified bitumen decreased the rutting for the binder and improved the fatigue behavior at low temperatures.

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ABSTRACT

The use of polymers as bitumen modifiers in pavements has been growing rapidly in the last decades because of the distresses on asphalt pavements. However, using polymers as a modifier mostly changes the properties of the asphalt pavement to be more stable and stiffer at high temperatures and more flexible at low temperatures. Therefore, this study was conducted to investigate the empirical and rheological properties of bitumen modified with epoxidized natural rubber (ENR). Four percentages (3%, 6%, 9% and 12%) of epoxidized natural rubber were used as modifiers. The effects of the modifier on the conventional properties, storage stability and rheological properties were investigated. Requirement tests (e.g., penetration, softening point, ductility and viscosity) and rheological analysis (e.g., isochronal plot, master curves, Black diagram and SHRP parameters) using a dynamic shear rheometer (DSR) were conducted to characterize the ENR-modified bitumen. The fundamental parameters were used to describe significant benefits of ENR as a modifier. The results indicated that the storage stability of epoxidized natural rubber modified bitumens (ENRMBs) depended mainly on the ENR content. Based on the results obtained from the DSR test, ENR reduces the temperature susceptibility and facilitated polymeric modification using a highly elastic network within the bitumen. This elastic network increases the viscosity, stiffness and elastic behavior of the ENRMBs. ENR improves rutting resistance and fatigue behavior at high temperatures and low temperatures respectively. The best results were recorded for polymer-modified bitumen containing 6% of ENR.

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1. Introduction

Over the past decades, research on polymer-modified bitumens (PMBs) and its benefits has dramatically increased and has been reported in many studies [1–3]. The use of PMBs can improve the performance of asphalt mixtures and substantially increase the service life of highway surfaces. However, the addition of polymers significantly improves various bitumen properties, such as elasticity, cohesion, stiffness and adhesion, thus resulting in an overall performance improvement of asphalt pavements, which become more stable and stiffer at high temperatures and more flexible at low temperatures. In addition to rutting resistance, a good polymer can supply a degree of flexibility or elasticity to an asphalt mixture, thereby improving the fatigue and thermal cracking properties of the asphalt mixture [4–6].

One of the most well-known, widely used category of polymers is thermoplastic elastomers (TE). Thermoplastic elastomers (TE) are polymers with thermoplastic and elastomeric properties [7]. TE polymers derive their strength and elasticity from a physical
of an oscillatory type testing of dynamic mechanical analysis (DMA), generally conducted within the region of linear viscoelastic response. DMA allows the viscoelastic nature of bitumen to be determined over a wide range of temperatures and loading times (or frequencies) [27–32].

2. Experimental works

2.1. Materials

The bitumen used in this study is 80/100 penetration grade, supplied by the bitumen factory at Port Klang, Malaysia. The ENR was obtained from the Malaysian Rubber Board under the trade name of ENR 50, with 53% epoxidation and passed through 2.36 mm mesh sieve (before shearing). The physical properties of the bitumen and the ENR used are shown in Table 1.

2.2. Preparation of binders

Five ENRMBs were produced by mixing ENR-50 (0%, 3%, 6%, 9% and 12% content by weight of bitumen) with base bitumen. All ENRMBs were prepared using a Silverson high shear mixer at 160 °C (±1 °C) under 4000 rpm of speed for one hour. ENR was added to the bitumen after the temperature stabilized at 160 °C. The different ENRMBs were coded as ENR (polymer), MB (modified bitumen) and (ENR content), e.g., ENR3B corresponds to the bitumen modified with 3% epoxidized natural rubber content (by weight).

2.3. Conventional binder tests

According to ASTM standards, many conventional tests were conducted on the base bitumen and the modified bitumen, such as penetration, softening point, ductility, viscosity (using the Brookfield Model DV-II) and storage stability test [33–36]. The penetration test is used as a measure of consistency. Higher values of penetration indicate softer consistency. The sample is melted and then cooled to 25 ± 0.5 °C. The penetration is measured with a penetrometer by means of which a standard needle is applied to the sample at a temperature of 25 ± 0.5 °C [33]. In the softening point test, two horizontal disks of bitumen, cast in shouldered brass rings, are heated at a controlled rate in a liquid bath while each supports a steel ball. The softening point is reported as the mean temperatures at which the two disks soften sufficiently to allow each ball, enveloped in bitumen, to fall 25 mm [34]. Ductility testing provides one measure of tensile properties of bituminous materials. In a ductility test, bitumen is stretched in a water bath lower than 10 °C and at a stretching velocity of 5 cm/min. Ductility length is measured after the sample is cut [36].

2.4. Temperature susceptibility

Changing the temperature susceptibility with ENR was investigated with a calculating penetration index (PI) and a penetration viscosity number (PVN). The higher the PI and PVN values of bitumen, the lower is its temperature susceptibility. For PI, the temperature susceptibility for the binders is measured by calculating the PI using the penetration at 25 °C and softening point results.

Penetration index is calculated using an equation, shown as follows [11]:

\[
P_I = \frac{1952 - 500 \log \text{Pen} - 205P}{50 \log \text{Pen} - 5P - 120} \tag{1}
\]

where Pen is the penetration test at 25 °C and S.P is the softening point.

The penetration viscosity number (PVN) is calculated based on penetration at 25 °C and viscosity at 135 °C, such that

\[
\text{PVN} = \frac{\log L - \log X}{\log L - \log M} \times 1.5 \tag{2}
\]

where PVN is the penetration viscosity number, L is the logarithm of viscosity at 135 °C for PVN of 0.0, X is the logarithm of viscosity at 135 °C, and M is the logarithm of viscosity at 135 °C for a PVN of –1.5.

The viscosity values of L and M can be determined using the following equations. The equation for the line representing a PVN of 0.0 is:

\[
L = 4.25800 - 0.79670 \log \text{Pen} \tag{3}
\]
The equation for the line representing a PVP of $-1.5$ is:

$$M = 3.46289 - 0.61094 \log \text{Pen}$$

where Pen is the penetration at 25°C.

2.5. Storage stability

In storage stability testing, the binder is poured into an aluminum foil tube, 30 cm in height and 3 cm in diameter. The binder is kept vertically in an oven at 163 ± 5°C for 48 h without disturbance. Then, the binder is allowed to cool, after which it is cut horizontally into three pieces. The top and the bottom parts are placed separately into beakers and tested for their softening point. If the softening point difference is less than 2.5°C, then the binder can be considered a storage stable blend [37].

2.6. Dynamic shear viscoelastic properties

The dynamic shear rheometer (DSR) used in this study is the Rheometer HAAKE RheoStress 600 from Thermo Electron Corporation and was used to determine the binder properties. Frequency sweep was applied between 0.1 and 10 Hz. Temperature sweep ranged from 10 to 80°C. Two plates were used in DSR, namely an 8 mm diameter spindle with a gap of 2 mm and a 25 mm diameter spindle with a gap of 1 mm. The 8 mm spindle was used for temperatures in the range 10–30°C, and the 25 mm spindle was used for temperatures in the range 20–80°C. The lower plate must be warmed to establish a good bond with the binder, and the gap must be 50 μm longer than the targeted gap [29]. The final step after trimming is adjusting the target gap. The chosen strain should as small as possible to ensure that the measurement is in the linear area, and it must be large enough to obtain sufficient torque readings at low frequencies and high temperatures and sufficient strain at high frequencies and low temperatures.

Dynamic viscoelastic properties analysis, using a dynamic (oscillatory) type test, has been used as a fundamental rheological testing method for bitumen. In this study, sinusoidal shear strains were imposed on binder samples. Binder samples were placed between two parallel plates under a dynamic shear rheometer instrument and applied various frequencies under several temperatures [28]. Sinusoidally varying shear strain is expressed as

$$\gamma(t) = \gamma_0 \sin \omega t,$$

with resulting stress

$$\tau(t) = \tau_0 \sin(\omega t + \delta)$$

where peak stress, peak strain, $\omega$ is radian frequency, $t$ is time, and $\delta$ is phase angle.

After the phase change, the sinusoidally varying strain and the stress can be expressed as complex quantities with the following equation:

$$\frac{\tau}{\tau_0} = \gamma_0 e^{i \delta}$$

and

$$\tau = \tau_0 e^{i (\omega t + \delta)}$$

The complex shear modulus is then given by the following equation:

$$G^* = G' + iG'' = \frac{\tau}{\gamma_0} = \frac{\tau_0}{\gamma_0} (\cos \delta + i \sin \delta)$$

The final equation can be written as:

$$|G^*| = \frac{\tau_0}{\gamma_0} \sqrt{G'^2 + G''^2}$$

$$G' = |G^*| \cos \delta$$

$$G'' = |G^*| \sin \delta$$

where $G'$ is the complex shear modulus, $G''$ is the storage modulus, and $G^*$ is the loss modulus. Phase angle is the phase difference between the stress and the strain in the oscillatory test; it is a term to describe a material’s viscoelastic behavior. If $\delta = 90°$, then the bitumen behaves as purely viscous, whereas if, then the bitumen behaves as purely elastic. If, then the bitumen will exhibit a combination of viscous and elastic behaviors [27].

2.6.1. Isochronal plot

Iscrochronal plots are a curve on a graph representing a system's behavior at a constant frequency or loading time. In a DSR test, curves of the complex modulus $G^*$ versus temperature at constant frequencies constitute an isochronal plot [27].

2.6.2. Rheological master curve

In a master curve of dynamic mechanical data, the complex shear modulus ($G^*$) and the phase angle are plotted against frequency for various temperatures on a log-log scale. Master curves are valid for the reference temperature, which is 30°C in this study. Time temperature superposition principle (TTSP) must be applied to calculate the rheological properties at other temperatures. The temperature dependency of the viscoelastic behavior of bitumen is indicated by means of shift factors and expressed using the Williams, Landel and Ferry (WLF) equation [38]:

$$\log a(T) = \frac{C_1 (T - T_r)}{C_2 + (T - T_r)}$$

where $a(T)$ is the shift factor at temperature $T$, $T_r$ is the reference temperature and $C_1$ and $C_2$ are empirically determined coefficients that were chosen between 7 and 17 for $C_1$ and between 46 and 133 for $C_2$, depending on ENR content [38].

2.6.3. Block diagram

Black diagram is a graph of the magnitude of the complex modulus $G^*$ versus the phase angle $\delta$ obtained from a dynamic test. The frequency and the temperature are therefore eliminated from the plot, thus allowing all the dynamic data to be presented in one plot without performing TTSP manipulations of raw data. A smooth curve in a black diagram is a useful indicator of time-temperature equivalency, while a disjointed curve indicates the breakdown of the TTSP and the presence of a high wax content bitumen, a high asphaltene structured bitumen or a highly polymer-modified bitumen [39].

2.6.4. SHRP rutting and fatigue parameters

The specification criterion for rutting is calculated as the complex modulus divided by the sine of the phase angle, $G'/\sin\delta$, whereas that for fatigue is calculated as the complex modulus divided by the sine of the phase angle, $G'/\cos\delta$ [40].

3. Results and discussion

3.1. Conventional physical properties

The penetrations and softening points for the binders, i.e., ENRMBs, are shown in Table 2. All ENRMBs exhibit decreased penetration with increasing ENR content. The increase in binder hardness can be attributed to a hardening effect caused by the addition of ENR to the base bitumens. The softening points, shown in Table 2, increased after polymer modification, thus indicating an identical increase in hardness or stiffness or in ENRMB stiffness, as observed in the penetrations. Relying on the results from these two conventional tests, the mechanism of modification of ENRMBs would seem to correspond only to a stiffening of the base bitumen.

Table 2 shows that the ductility values decreased for ENRMB3 and then increased again, thus indicating that increasing the ENR content in turn increased ductility. This increase moreover indicates a performance improvement at low temperatures. Consequently, the compatibility between ENR and bitumen is reinforced because of increasing ductility at low temperatures. The addition of ENR increased the viscosity of the base bitumen, implying a good rutting resistance as cited in previous studies [11]. Fig. 2 shows that viscosity increased with the addition of more ENR, a variation that became more evident at lower temperatures. The same consistent increasing in viscosity was recorded with SBS modified bitumen in a previous study [8]. The viscosities of both the base and the modified bitumen decreased as temperatures rose because of the Newtonian properties. The viscosity of
ENRMB12 decreased more than did that of ENRMB9, likely because of the segregation between the base bitumen and the ENR. Viscosities and modification indices at 100, 135 and 160 °C for the base bitumen and modified binders are shown in Table 3. However, the modification indices at 100 and 135 °C are approximately similar for each bitumen group.

3.2. Temperature susceptibility

Penetration index (PI) and penetration viscosity number (PVN) are frequently used to approximate the expected temperature susceptibility for bitumen. The PI value for base penetration bitumens normally ranges from approximately −3 (for high temperature susceptible bitumens) to approximately +7 for highly blown (low temperature susceptible) bitumens [11]. In this study, the highest values (0.55) were obtained with the addition of ENR, and PVN increased subsequently. Therefore, ENR decreases the base bitumen’s temperature susceptibility.

3.3. Storage stability

The isolation test was conducted for the modified bitumen to evaluate its storage stability at high temperatures. Table 2 shows that the softening point differences between the ENRMB3 and ENRMB6 binders are less than 2.5 °C, thus indicating these binders can remain stable if stored at high temperatures. However, this equilibrium between bitumen and polymers can be reached with a medium–high percentage of polymer, around 5–6% by weight, which create a three-dimensional polymer network that completely changes the properties of bitumen; with lower percentage (<3–4%) a continuous bitumen phase with a dispersed polymer is obtained, with higher amount (6–7%) instead is the bitumen that is dispersed in a continuous polymer phase [41].

3.4. Rheological properties of the ENRMB’s

3.4.1. Isochronal plot

Isochronal plots of complex modulus ($G'$) versus temperature at 0.1 Hz and 1 Hz of frequency are shown in Figs. 3 and 4. The

![Fig. 3. Isochronal plots of complex modulus at 0.1 Hz for the ENRMB binders.](image)

![Fig. 2. Rotational viscosities of ENRMBs.](image)

![Fig. 4. Isochronal plots of complex modulus at 10 Hz for the ENRMB binders.](image)

Table 2

Conventional properties for the base bitumen and modified binders.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Penetration @ 25 °C (dmm)</th>
<th>Softening point (°C)</th>
<th>Penetration index (PI)</th>
<th>Penetration viscosity number (PVN)</th>
<th>Ductility @ 10 °C (cm)</th>
<th>Temperature difference in isolation test (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENRMB0</td>
<td>82</td>
<td>45.7</td>
<td>−1.16</td>
<td>−1.180</td>
<td>19.50</td>
<td>−</td>
</tr>
<tr>
<td>ENRMB3</td>
<td>73</td>
<td>50.6</td>
<td>−0.11</td>
<td>−0.342</td>
<td>4.00</td>
<td>1.00</td>
</tr>
<tr>
<td>ENRMB6</td>
<td>64</td>
<td>53.8</td>
<td>0.32</td>
<td>−0.118</td>
<td>9.70</td>
<td>1.25</td>
</tr>
<tr>
<td>ENRMB9</td>
<td>52</td>
<td>58.6</td>
<td>0.46</td>
<td>0.017</td>
<td>12.50</td>
<td>&gt;2.50</td>
</tr>
<tr>
<td>ENRMB12</td>
<td>53</td>
<td>57.0</td>
<td>0.55</td>
<td>−0.136</td>
<td>21.50</td>
<td>&gt;2.50</td>
</tr>
</tbody>
</table>

Table 3

Rotational viscosities of ENRMBs.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Viscosity @ 100 °C (mPa s)</th>
<th>Viscosity @ 135 °C (mPa s)</th>
<th>Viscosity @ 160 °C (mPa s)</th>
<th>$\eta_{ENRMB}/\eta_{Bitumen}$ @ 100 °C</th>
<th>$\eta_{ENRMB}/\eta_{Bitumen}$ @ 135 °C</th>
<th>$\eta_{ENRMB}/\eta_{Bitumen}$ @ 160 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ENRMB0</td>
<td>2381.5</td>
<td>244.0</td>
<td>52.0</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td>ENRMB3</td>
<td>4690.0</td>
<td>469.0</td>
<td>119.0</td>
<td>1.96</td>
<td>1.92</td>
<td>2.29</td>
</tr>
<tr>
<td>ENRMB6</td>
<td>5619.0</td>
<td>606.5</td>
<td>175.5</td>
<td>2.36</td>
<td>2.49</td>
<td>3.38</td>
</tr>
<tr>
<td>ENRMB9</td>
<td>7806.5</td>
<td>787.5</td>
<td>237.5</td>
<td>3.28</td>
<td>3.23</td>
<td>4.57</td>
</tr>
<tr>
<td>ENRMB12</td>
<td>7238.0</td>
<td>694.0</td>
<td>212.5</td>
<td>3.04</td>
<td>2.84</td>
<td>4.09</td>
</tr>
</tbody>
</table>
increase in $G'$ for all binders is similar except ENRMB12 which shows an extreme increase in $G'$ at high temperature, greater than 50 °C, indicating a different compatibility between base bitumen and ENR comparing with the other binders. This behavior was also recorded for another elastomer modifier, natural rubber and SBS [8,10]. In addition, ENRMB6 shows a more pronounced increase in $G'$ and an improved temperature susceptibility.

In a previous study, isochronal plots for SBS modified bitumen show same minor increasing in $G'$ at low frequency, 0.02 Hz, and low temperatures, less than 20 °C. Another study was done with using natural rubber latex (NR) and shows same minor increasing in $G'$ for high frequency which indicating improvement in term of temperature susceptibility [8,42].

3.4.2. Rheological master curve

The frequency dependence of $G'$ and $\delta$ for the ENRMBs was assessed in Figs. 5 and 6 by producing rheological master curves at a reference temperature of 30 °C using the time–temperature superposition principle (TTSP) and shift factors determined for the $G'$ master curves [7]. ENRMB3 and ENRMB6 show similar increases in the complex modulus with increasing polymer content, whereas ENRMB9 and ENRMB12 behaved differently. However, SBS as modifier showed a similar increase in $G'$ with increasing modifier content for 3%, 5% and 7% [8]. The effect in the latter cases is not as marked as for ENRMB3 and ENRMB6. The differences in rheological behavior can be attributed to variances in compatibility of the different bitumen–polymer blends. This different behavior for ENRMB9 and ENRMB12 was observed in the storage stability and rotational viscosity results. The same results have been noted in other research that used a hard bitumen with a polymer [43].

The phase angle master curves for the ENRMBs showed a reduction in phase angle with modification (Fig. 6); again, the difference between the binders occurred at low frequencies, when the nature of the polymer network depends on the properties of the base bitumen (maltenes composition) and the compatibility of the bitumen–polymer system. The differences in the plots of phase angle versus frequency can be related to differences in the molecular interaction (e.g., dispersion, swelling and compatibility) between the base bitumen and ENRs. The rheological properties of the ENRMBs are functions of the mutual effect of polymer and bitumen and consequently were influenced by bitumen composition and polymer nature and content.

3.4.3. Black diagram

The Black diagrams for ENRMBs are shown in Fig. 7. The relatively smooth Black diagram curves shift, with tiny plateau regions in the modified binders, toward lower phase angles with increasing ENR modification. A linear behavior is an indicator of low elasticity. However, the ENRMB12 curve exhibited a different behavior, specifically, a shift toward lower phase angles with increasing polymer content. In general, the elasticity of the modified binder increased
with the increasing of ENR content. In a previous study, 3% of SBS was modified bitumen, the effect of polymer modification appeared insignificant, and the behavior of the modified binders remained close to that of the base bitumens. After modification with a sufficiently high polymer content (≥6%), the binders changed fundamentally in their rheological behavior, as indicated by a substantial decrease in phase angle (a substantial increase in the elastic response) with decreasing complex modulus [44]. These differences showed that SBS may improve bitumen rheology over a wide temperature range, while ENR show its effect mainly with 12% of ENR content at high temperature.

3.4.4. SHRP rutting and fatigue parameters

The effect of temperature on the rutting parameter (\(G'\sin\delta\)) is shown in Fig. 8. The rutting parameter \(G'\sin\delta\) is defined as the stiffness indicator for evaluating the rutting resistance of both unmodified and polymer modified bitumen and as the permanent deformation of each layer of the pavement under repeated loads. It was observed that \(G'\sin\delta\) increased considerably, except for ENRMB12, probably because of the incompatibility between the bitumen and polymer. The same results were recorded in previous studies, increasing NR latex content as a modifier with bitumen resulted increasing in stiffness where indicating improvement in rutting resistance [42].

Fig. 9 shows the effect of temperature on fatigue parameter (\(G'\sin\delta\)). Fatigue damage is a complex phenomenon that can occur in asphalt pavements because of repeated bending loads and outcomes in microdamage in pavements. This damage is a competitive practice between microcracking and healing and results in decreased stiffness, thus declining the applied load capacity and capability to resist additional damage. The fatigue parameter decreased with increasing ENR content at less than 30 °C, thus indicating an improvement in fatigue behavior. Between 30 and 80 °C, the \(G'\sin\delta\) parameter increased with increasing ENR content, thus indicating that at high temperatures, ENR negatively affects binders in terms of fatigue behavior.

4. Conclusions

This study was conducted to investigate the effect of ENR on the conventional properties, temperature susceptibility, storage stability and rheological properties of bitumens. Based on penetration and softening point results, the mechanism of modification of ENRMs seemed to entail a stiffening of the base bitumen. The ductility decreased initially after adding ENR and then started increasing. This increase indicated a performance improvement at low temperatures. Furthermore, the PI and PVN results indicate that adding ENR to bitumen decreased bitumen temperature susceptibility. Moreover, Storage stability test results indicated that 6% or less of ENR content for binder was stable for use at high temperatures. On the other hand, isochronal plots showed that ENRMB6 more pronounced increase in the complex modulus and hence improved temperature susceptibility. Furthermore, ENRMs increased in the complex modulus (except 12% of ENR content at low frequencies) and decreased in the phase angle. However, based on master curves, ENR provides polymeric modification by means of a highly elastic network within the bitumen and this elastic network increases the viscosity, stiffness and elastic behavior of the ENRMs. In addition, based on the rutting and fatigue parameters, adding ENR decreased the rutting for the binder and improved the fatigue behavior at temperatures lower than 30 °C. As a result, the rheological properties indicated that 6% ENR content optimally modified bitumen.

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