Optimizing Co-blends of Crumb Rubber and Ethylene Vinyl Acetate in 70/100 Bitumen

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ABSTRACT

Formulation of modified bitumen co-blends presents challenges associated with contributions of individual and interaction effects to thermo-rheological properties. Crumb rubber and ethylene vinyl acetate were used to study the optimization of co-blends in 70/100 bitumen and compared to industrial standards. A laboratory mixer fitted with a dual helical impeller was used to perform the mixing after which dynamic shear rheometer was utilized to characterize the bituminous binders. The results showed that phase angle decreases with co-blend proportions, whereas the rutting parameter and complex shear modulus increase. Response surface methodology can be used to optimize formulations for modification of 70/100 bitumen.

KEYWORDS: 70/100 bitumen, Co-blend, Crumb rubber, Ethylene vinyl acetate, Response surface methodology.

INTRODUCTION

The use of polymers in modifying thermo-rheological properties of bitumen for road paving applications has been widely reported (Costa et al., 2010; Ait-kadi, Brahim and Bousmina, 1996; Jin et al., 2002; Socal et al., 2004). High-temperature rutting associated with plastic or viscous behavior of bitumen can be reduced by the hardening effect of plastomeric polymers and crumb rubber. Ethylene vinyl acetate (EVA) or crumb rubber (CR) in bitumen increases rutting resistance (Ameri, Mansourian and Sheikhmotevali, 2013; Singh, Kumar and Maurya, 2014; Cong et al., 2013; Ali Hassan, Mashaan and Karim, 2013; Kebrich, Moafimadani and Goli, 2015).

Saboo and Kumar (2016) studied the rheological properties of EVA-modified bitumen and reported increases in complex modulus due to stiffening effect and further improvement in temperature susceptibility. Polacco et al. (2004) studied the efficacy of rheology in determining the formation of crosslinked networks. Extended network in bitumen disappears upon heating to enable easy processing and rigid network reappears after annealing, with polyethylene moieties swelling in the aromatic phase of bitumen.

Polymer co-blending in bitumen modification has gained popularity in road pavement applications (McNally, 2011). It enables further improvement and tailoring for binder-specific properties. To date, an incremental EVA/CR loading approach to optimizing co-blends has been used (Fang et al., 2016; Keymanesh

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et al., 2017; Yu et al., 2017). Co-blend choice is dependent on the properties of the resultant product, which is very often a trade-off of properties of the individual polymers. CR in bitumen exhibits good high-temperature stability, good low-temperature crack resistance, good fatigue resistance and elastic recovery, but poor storage stability (Xiang, Cheng and Que, 2009). On the contrary, EVA in bitumen has good storage stability, excellent digestion in bitumen with shortcomings in low-temperature crack resistance and elastic recovery (Ait-kadi, Brahimi and Bousmina, 1996; Jin et al., 2002; Socal et al., 2004; Ameri, Mansourian and Sheikhmotevali, 2013; Yuliestyan et al., 2016). Therefore, for optimum performance of polymer-modified bitumen, CR can be co-blended with EVA (Sawant and Kulkarni, 2014).

Predictable relationship between input and output variables in optimizing any blend formulation is paramount. Munera and Ossa (2014) reported on the use of Ashy’s material selection methodology amongst many other methodologies applied in mixture design. However, these are time-consuming and costly. Proper assessment of defined properties for particular application remains critical. Response surface methodology has been used previously by other authors to mainly obtain processing information, such as optimum screw speed and optimal processing parameters (Balasubramanian, 2009; Shi et al., 2014).

In this study, the proportions of components (Bitumen, CR and EVA) are optimized with a minimum number of experiments, using experimental mixture design methodology, which enabled mapping of the response surface over the region of interest based on industrial standards. Optimizing co-blends of CR and EVA in 70/100 bitumen using response surface methodology was the primary objective of this study. High-temperature properties in phase angle, complex shear modulus and rutting parameter were measured.

![Figure (1): TLC/FID (Iatroscan) SARA analysis according to IP 469 of 70/100 bitumen](image-url)
EXPERIMENTAL

Materials

EVA used was a commercial random copolymer of ethylene and vinyl acetate with 19-21 %wt. vinyl acetate content, melt flow index of about 17-23 g/10min and specific gravity of 0.95g/cm³. CR used was ambiently ground to 40 mesh (0.425 mm). 70/100 bitumen used was commercial grade crumb rubber-modified bitumen (AR1) and EVA-modified (AP1). All the materials were used as received from the suppliers. There was no further modification or preparation needed.

Fig. 1 shows the results for the SARA analysis and the greatest to least amount of 70/100 bitumen constituents are: resins, aromatics, saturates and asphaltenes, respectively. Bitumen in this study consists of an aromatic-resin rich phase, with minimal amounts of asphaltenes and saturates. The results of thermal analyses of crumb rubber and EVA are depicted in Fig. 2. Waste crumb rubber is a composite material (Fig. 2A). Thermogram (Fig. 2B) shows the thermal stability of the moieties in EVA. These are related to the participation of the moieties at different thermal stages and can be correlated to the depolymerization of the plastomer in its interaction with bitumen.

Figure (2): Thermograms of (A) waste tyre rubber crumb 40 mesh and (B) ethylene vinyl acetate used in the EVA/CR-modified bitumen formulations
Figure (3): The experimental runs for the three-component mixture design with upper and lower constraints for EVA, CR and bitumen

Simplex-centroid Mixture Design

After a series of experiments using response surface methodology, the optimum mixtures of the three components were determined. Fig. 3 depicts the experimental runs for the three-component mixture design with both lower and upper constraints. The bold dashed lines represent the design space for the study. The seventeen black circles represent EVA/CR/bitumen mixtures that were performed to obtain an appropriate response with binary mixtures on the edges and ternary mixtures inside the triangle. The values given in Table 1 are the EVA/CR/bitumen mixtures defined by DESIGN EXPERT™.

Table 1. Mixture design experimental runs for response surface methodology approach

<table>
<thead>
<tr>
<th>Mix Number</th>
<th>% EVA</th>
<th>% CR</th>
<th>% Bitumen</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.5</td>
<td>8.75</td>
<td>83.75</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>2.5</td>
<td>18.75</td>
<td>78.75</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>23.75</td>
<td>71.25</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>7.5</td>
<td>16.25</td>
<td>76.25</td>
</tr>
<tr>
<td>7</td>
<td>2.5</td>
<td>13.75</td>
<td>83.75</td>
</tr>
<tr>
<td>8</td>
<td>5</td>
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<td>65</td>
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<tr>
<td>9</td>
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<td>0</td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>0</td>
<td>90</td>
</tr>
<tr>
<td>12</td>
<td>5</td>
<td>17.5</td>
<td>77.5</td>
</tr>
<tr>
<td>13</td>
<td>7.5</td>
<td>23.75</td>
<td>68.75</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
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<td>10</td>
<td>15</td>
<td>75</td>
</tr>
<tr>
<td>17</td>
<td>2.5</td>
<td>23.75</td>
<td>73.75</td>
</tr>
</tbody>
</table>
Table 2. Rheological parameters at T\text{max} of 64 °C and failure temperatures associated with optimized mixtures relative to industrial standards and neat 70/100 bitumen

<table>
<thead>
<tr>
<th>Mix</th>
<th>G*(kPa)</th>
<th>δ (°)</th>
<th>G*/sinδ (kPa)</th>
<th>Failure temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat</td>
<td>1.4</td>
<td>88.3</td>
<td>1.38</td>
<td>66.8</td>
</tr>
<tr>
<td>AP-1</td>
<td>5.4</td>
<td>74.5</td>
<td>5.6</td>
<td>86.5</td>
</tr>
<tr>
<td>AR-1</td>
<td>3.4</td>
<td>71.4</td>
<td>6.51</td>
<td>89.3</td>
</tr>
<tr>
<td>1</td>
<td>5.4</td>
<td>73.6</td>
<td>5.66</td>
<td>89.0</td>
</tr>
<tr>
<td>6</td>
<td>9.9</td>
<td>51.2</td>
<td>12.68</td>
<td>90.8</td>
</tr>
<tr>
<td>7</td>
<td>7.6</td>
<td>78.5</td>
<td>7.71</td>
<td>86.7</td>
</tr>
<tr>
<td>11</td>
<td>4.3</td>
<td>74.5</td>
<td>4.48</td>
<td>86.2</td>
</tr>
<tr>
<td>15</td>
<td>7.5</td>
<td>76.6</td>
<td>7.72</td>
<td>88.3</td>
</tr>
</tbody>
</table>

Sample Preparation and Rheological Testing

A laboratory mixer (RYOBI, 1/3 h.p. 5 speed) fitted with a dual helical impeller was used for mixing at the temperature of 180˚C and the maximum speed was set to 2500 r.p.m. CR was added to bitumen over a period of 30 minutes, followed by the addition of EVA. Although a longer mixing time may improve the properties of the product, it is not recommended due to the substantial increase in production costs.

Rutting parameter, complex shear modulus and phase angle were determined using a dynamic shear rheometer. All the rheological parameters were obtained according to ASTM D7175; the gap of 3mm was employed to accommodate the heterogeneities of the mixtures using plate-plate geometry and this was to reduce testing variability. Gap setting is usually 5-10 times larger than the largest dimension of the polymer, which in our case is the CR with a particle size of about 0.425mm (Mezger, 2014). The average values of the rheological parameters were calculated using at least 3 samples from the same container.

The theoretical basis of the Superpave specification \(G*/\sin\delta\) reflects the deformation of asphalt at high temperatures. Work partially recovered by the elastic component of the strain and partially dissipated by the viscous flow component of the strain and any associated generated heat (Hajikarimi, Rahi and Nejad, 2015).

The phase shift angle, \(\delta\) between the preset and resulting sine curves is the lag between the time-dependent stress and strain curves. The phase shift angle always occurs between 0° and 90°. For ideal elastic behaviour, \(\delta = 0°\), for ideal viscous behaviour \(\delta = 90°\) and for viscoelastic behaviour \(0° \leq \delta \leq 90°\) (Mezger, 2014).

RESULTS AND DISCUSSION

On the basis of the rheological parameters; phase angle, complex shear modulus and rutting parameter, a model for three components; bitumen, waste crumb rubber and ethylene vinyl acetate, was chosen to fit the experimental data with the best regression.

Failure Temperature

As a screening process, the impact of co-blend proportions on the failure temperature of EVA/CR mixtures relative to industry grade binders was used. The start temperature was 64˚C, with 6˚C increments up until samples failed. Failure temperature was gauged by the rutting parameter of 1.00kPa (Original Binder). Fig. 4 shows the failure temperature of 70/100 penetration grade bitumen, two industrial EVA (AP-1) and crumb rubber (AR-1) -modified bitumen samples and seventeen laboratory mixtures (see Fig. 3) tested according to ASTM D7175. The result of failure temperature, which shows the temperature at which the rutting parameter is less than its lower limit of 1 kPa, is depicted in Fig. 4 showing an improvement in failure temperature upon addition of polymers relative to 70/100 and 50/70 bitumen.

Mixtures 1, 6, 7, 11 and 15 were considered to be the promising formulations based on failure temperature
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relative to AR-1 and AP-1. Therefore, it is feasible to co-blend EVA/CR with bitumen and achieve failure temperatures similar to AR-1 and AP-1. An incentive for our formulations is the co-blend synopsis of incorporating both EVA and CR. A summary of failure temperatures as well as rheological properties of optimized mixtures are shown in Table 2.

![Figure (4): Failure temperature of two penetration grade bitumens, two industrial EVA- and crumb rubber-modified bitumen samples and seventeen laboratory mixtures tested according to ASTM D7175 (ASTM D7175-15 2015)](image)

Optimized mixtures (1,6,7,11 and 15) according to industrial standards (AP-1 and AR-1) show a reduction in phase angle relative to neat bitumen. Mixture 6 shows the least phase angle, the most rutting parameter and complex shear modulus. The highest amount of crumb rubber (16.25%) and EVA (7.5%) in the failure temperature-screened mixtures (Table 2) could have contributed to the result, given that individual factors EVA and crumb rubber contribute to decrease the phase angle. AP-1 phase angle, complex shear modulus and rutting parameter were similar to those of mixture 1 and mixture 11, thus EVA and crumb rubber components match the industrial standard in terms of the rheological parameters. The closest match in terms of rheological parameters to AR-1 was for mixture 1.

Mixture 7 and 15 showed similar rheological parameters although the mixture components were different, hence mixture choice would be based on the use of lesser material to achieve the similar rheological properties. Preference would be for mixture 7 over mixture 15, since the former uses 50% of the amount of EVA and less phase inversion for just an 18% increase in the amount of waste crumb rubber; hence it is much more economical. Failure temperature was used as a baseline screening process, but industrial standard matching then allowed for particular screened mixtures to match the rheological properties of interest.

Other studies (Saboo and Kumar, 1997; Xu et al., 2015; Tayfur, Ozen and Aksoy, 2007; Shen et al., 2009; Lesueur, 2009) suggest swelling of the plastomer on absorption of maltenes from bitumen, resulting in stiffening of the binder which is present in the polymer/bitumen blend as extended polymers and often occurs as a single phase with the base bitumen. Polymer
content exceeding 6% may result in phase inversion with polymer as the dominant phase due to high fraction of swollen polymer, leading to strand connection and formation of a three-dimensional network. When EVA was used, the polar, non-crystallizable vinyl acetate moiety of EVA played a critical role in swelling as the non-polar, crystalline moiety ethylene has been suggested to participate less in the swelling process.

Introduction of waste crumb rubber into the co-blend system was an environmentally friendly polymer modification technology as an alternative to disposal of waste tyres. The composite nature of crumb rubber interactions might not be entirely based on swelling and depolymerization of the rubber component in the crumb rubber. For instance, the role played by carbon black in bitumen modification is not negligible and could be as important as the rubber component (Lopez-Moro et al., 2013). Truck tyres absorb more bitumen than passenger car tyres owing to the component of increased natural rubber relative to synthetic rubber (Shen et al., 2009; Lesueur, 2009). Thermal dissociation of sulphur-sulphur bonds in the partial devulcanization contributes to depression in viscosity of the crumb rubber bitumen system (Frantzis, 2004; Renshaw, 1984), but the EVA’s plastomeric nature contributes more to the increase in viscosity until a maximum viscosity point is reached. The maximum viscosity point coincides with the yield stress of the co-blend system, where deformation is more non-linear than linear (Dong et al., 2012; Navarro et al., 2004).

**Complex Shear Modulus**

Complex shear modulus of EVA/CR/bitumen mixtures revealed the stiffness of the polymer-modified binder on addition of different proportions of EVA and CR to the bitumen. Fig. 5 shows the results for the complex shear modulus for the 17 mixtures of EVA, CR and bitumen.

![Figure (5): The contour plot for the results of complex shear modulus for EVA/CR/bitumen mixtures](image)

As depicted in the right region of the design space diagram shown in Fig. 5, an increase in EVA content shows an increase in complex shear modulus. A specific equation relating complex shear modulus to polymer
addition was deduced as shown in Eq. 1:

\[
\text{Complex Shear modulus} = 13.5A + 3.2B + 0.11C - 0.12AB - 0.16AC - 0.04BC.
\]  
(1)

The contour lines within the design space exhibit curvature based on the quadratic model adopted for complex shear modulus for the interaction between A, B and C. In the interest of complex shear modulus, individually the factors A, B and C, which are EVA, CR and bitumen, respectively work to increase the complex shear modulus based on the positive equation sign. The interaction effects of AB, AC and BC work to decrease the complex shear modulus due to the negative signs. EVA (A) relative to the other factors individually contributes the greatest to complex shear modulus with the least contribution from the bitumen (C). The interaction effect of EVA and bitumen (AC) contributes the most to the decrease in complex shear modulus with the least contribution for crumb rubber and bitumen (BC). The co-blend synopsis based on EVA and crumb rubber (AB) shows intermediate contribution to the decrease in complex shear modulus.

Cumulatively, complex shear modulus is deemed as a result of both effects. The rheological property complex shear modulus, was not enough in isolation to describe the nature of the laboratory mixtures; hence phase angle and rutting parameter were also considered and measured as additional parameters.

**Phase Angle**

Phase angle of EVA/CR/bitumen mixtures was used to supplement the findings from the complex shear modulus.

Phase angle is often used as an indication of viscosity and elasticity of binders (Xu et al., 2015). The results for the phase angle for the 17 mixtures are shown in Fig. 6. When moving on the base from right to left in Fig. 6, there is a marked increase in the phase angle from 45.6° to 83.4° with a decrease in EVA and CR content. Therefore, EVA and CR play a critical role of decreasing the phase angle. Linearity of the contour lines in Fig. 6 supports the linear model for phase angle, as shown by Eq. 2. The contribution of EVA and crumb rubber works to decrease the phase angle relative to bitumen which works to increase the phase angle. Owing to the viscous nature of neat bitumen, EVA and crumb rubber confer the degree of elasticity which is inherent to them thus decreasing the phase angle as predicted by the equation.

\[
\text{Phase angle} = -0.67A - 0.36B + 0.95C
\]  
(2)

**Rutting parameter**

Rutting parameter, which reflects the deformation of asphalt at high temperatures upon application of a load, was used to complement the findings pertinent to complex shear modulus and phase angle as a property to relate the rheological parameters to dissipated energy from viscous component of strain. Rutting is defined as the progressive accumulation of permanent deformation of each layer of the pavement structure under repetitive loading (Xiang, Cheng and Que, 2009). Universal to all the mixtures, there is a reduction in rutting parameter with an increase in temperature (Ameri, Mansourian and Sheikhmotevali, 2013). Hence, more rutting resistance is expected at higher temperatures in the case of polymer modification relative to neat bitumen (Ait-kadi, Brahim and Bousmina, 1996; Saboo and Kumar, 1997).

Fig. 7 depicts the results for the rutting parameter for the 17 mixtures of EVA, CR and bitumen. There was a variation in rutting parameter from 4.48 kPa to 63.57 kPa. The highest value of rutting parameter at maximum temperature was a result of the mix containing the greatest amount of polymers for both EVA and CR. An equation relating rutting parameter to polymer addition was deduced as follows (Eq. 3):

\[
\text{Rutting parameter} = 17.9A + 5.17B + 0.17C - 0.15AB - 0.21AC - 0.064BC;
\]  
(3)

with the trend in individual contributions and interaction effects similar to complex shear modulus behaviour of the mixtures.
Figure (6): The contour plot for the results of phase angle for EVA/CR/bitumen mixtures

Figure (7): The contour plot for the results of rutting parameter for EVA/CR/bitumen mixtures
CONCLUSION

This study revealed that both EVA and CR improve the rutting resistance at high in-service temperatures. Polymer modification has a significant effect on bitumen rheology by increasing its complex shear modulus and decreasing its phase angle. Co-blend modification increases binder stiffness at high service temperatures and low loading frequencies with the degree of modification being a function of bitumen-polymer compatibility and polymer concentration.

Individual effects of the factors only contributed to the phase angle, with crumb rubber and EVA decreasing the phase angle relative to the bitumen which increased the phase angle. Rutting parameter and complex shear modulus highlighted the effect of the co-blend synopsis as individual effects and interaction effect amongst the factors contributed to the value of the rheological parameters obtained. Quadratic equations were obtained for the complex shear modulus and the rutting parameter, which showed positive contribution of interaction effects of the factors to decreasing the rheological parameters, but negative contribution of the individual factors to decreasing the rheological parameters.

REFERENCES


