Impact of Fischer-Tropsch Wax on Ethylene Vinyl Acetate/Waste Crumb Rubber Modified Bitumen: An Energy-Sustainability Nexus

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Abstract—In an energy-intensive world, minimizing energy consumption is paramount to cost saving and reducing the carbon footprint. Improving mixture procedures utilizing warm mix additive Fischer-Tropsch (FT) wax in ethylene vinyl acetate (EVA) and modified bitumen highlights a greener and sustainable approach to modified bitumen. In this study, the impact of FT wax on optimized EVA/waste crumb rubber modified bitumen is assayed with a maximum loading of 2.5%. The rationale of the FT wax loading is to maintain the original maximum loading of EVA in the optimized mixture. The phase change abilities of FT wax enable EVA co-crystallization with the support of the elastomeric backbone of crumb rubber. Less than 1% loading of FT wax worked in the EVA/crumb rubber modified bitumen energy-sustainability nexus. Response surface methodology approach to the mixture design is implemented amongst the different loadings of FT wax, EVA for a consistent amount of crumb rubber and bitumen. Rheological parameters (complex shear modulus, phase angle and rutting parameter) were the factors used as performance indicators of the different optimized mixtures. The low temperature chemistry of the optimized mixtures is analyzed using elementary beam theory and the elastic-viscoelastic correspondence principle. Master curves and black space diagrams are developed and used to predict age-induced cracking of the different long term aged mixtures. Modified binder rheology reveals that the strain response is not linear and that there is substantial re-arrangement of polymer chains as stress is increased, this is based on the age state of the mixture and the FT wax and EVA loadings. Dominance of individual effects is evident over effects of synergy in co-interaction of EVA and FT wax. All-inclusive FT wax and EVA formulations were best optimized in mixture 4 with mixture 7 reflecting increase in ease of workability. Findings show that interaction chemistry of bitumen, crumb rubber EVA, and FT wax is first and second order in all cases involving individual contributions and co-interaction amongst the components of the mixture.

Keywords—Bitumen, crumb rubber, ethylene vinyl acetate, FT wax.

I. INTRODUCTION

MANY countries, such as South Africa, have an energy-intensive road industry which is affected directly by rising energy prices over the years attributed to increased demand and strain on fossil fuel reserves principally crude oil which serves as the main source of energy [1]-[3]. As a result, energy efficacy and minimization are considered paramount in growing economies, and thus, sustainable energy developments are being highly encouraged. Roads are the backbone of the economy playing a pivotal role in mobility for people and freight.

There are different types of asphalt mixtures generally adopted by industry, namely hot mix (150 °C and above), warm mix (100 – 140 °C), half warm mix (60 – 100 °C) and cold mix [4]. Warm mix technology is preferred because of its substantial safety and environmental benefits. Abdullah et al. [5] reported that warm mix technology curbs relatively higher energy costs and minimises the generation of greenhouse gases. They also observed that warm mixes increase paving seasons and hauling distances that result in earlier traffic opening, reduced binder aging and cracking and minimized oxidative hardening due to favourable correlation between the mixtures and operating temperatures. Rubberized bitumen is considered superior to any road binder, but its drawback is that it requires extremely high temperatures for manufacturing and application; which significantly compromises its shelf-life. Strides have been made towards improving the crumb rubber technology to improve rut resistance and enable the handling of material at lower temperatures [6], [7]. Although temperatures can be reduced with conventional rubberized bitumen, the drawback is that the material cannot be pumped because it becomes too viscous and therefore too difficult to handle. Warm mix technology, however, can reduce the viscosity of the binder. Therefore, a combination of warm mix and crumb rubber technology can enable handling of material at fairly lower temperatures and still allow pumping and mixing. It has been reported that the reduction of temperature can be by as much as 30 °C lower than conventional and modified bitumen mixes [7]. Application of this technology implies major cost benefits in shelf-life extension, reduction of requirement to have an established team on-site. Thus, manufacturing could take place at fixed operation depots and then transfer the material in a tanker at reduced temperatures, transport it to site, heat it up to the required temperature and apply; thus, reduction in
establishment and labor costs, and minimized risks and a need for extensive quality control [7].

Polymers, such as EVA, are also commonly used to modify various properties of bitumen and improve the manufacturing process (time, temperature and rate of malaxation) [8], [9]. They are usually provided in the form of pellets or powder which can subsequently be diluted to the required polymer content by blending with base bitumen using low to high shear mixer, resulting in a special polymer concentration suitable for different applications [10]. There are two main methods of adding polymers to the asphalt mixtures, particularly by addition of polymer directly to bitumen prior mixing with the aggregate (wet process) and by addition of solid polymers at the same time bitumen is blended with the aggregates (dry process) [11], [12]. The digestion time or immersion time of rubber particle into bitumen is a critical parameter in the quality of mixtures, with best quality mixtures obtained at longer immersion times [13].

The use of petroleum and synthetic waxes in bitumen mixes has also been studied [14]-[17]. Introduction of wax in bitumen makes it relatively more resistant to deformation under high loads and improve its fuel resistance [18]. A petroleum FT wax (Sasobit®) was deemed suitable for this study because it is one of the commonly used waxes in road pavement applications in South Africa. This wax is microcrystalline in nature and has a wide range of chain length (40 – 150 carbon atoms) [19].

The wide range of chain lengths extends the plastic limits and increases the melting temperatures of asphalt binders. Longer chain lengths keep the wax in solution reducing energy costs and environmental pollution by decreasing viscosity and consequently mixing and compaction temperatures of asphalt cement by 20-30 °C. FT process for production of FT wax maintains control over chain length, avoids branching, with absence of double bonds on the molecular chain backbone alleviating oxidative chain scission [20]-[22]. Optional additions from 0.8-4% by weight bitumen have been reported [19]. FT wax provides structural stability as they crystallize in layers that consist of molecules having zigzag conformations below its melting temperatures of approximately 100 °C owing to a lattice structure and has a considerable effect on high temperature properties as its melting point lowers in bitumen and is much more thermally stable than bitumen [16], [17].

Sasobit® in crumb rubber modified bitumen improves the rutting resistance [23], offering better resistance to permanent deformation due to high failure temperatures [24], whereas the crumb rubber component enhances cracking resistance of the mixture [25]. At 2 and 4 % Sasobit® loading with 15 % crumb rubber, the mixtures showed a decrease in viscosity beyond 100 °C [26]. Crumb rubber technology involving FT wax provides a 25-30% reduction in mixing temperature and extends shelf-life up to about seven days relative to conventional bitumen rubber [27], [28]. However, Gonzalez et al. [29] reported that crumb rubber sedimentation at high temperatures still prevails and suggested that crumb rubber amount, mesh size, FT wax content and bitumen source affects the change in rheological properties of the modified binder.

Jamshidi et al. [30] highlight viscosity depressant characteristics of FT wax that led to 10 °C decrease in dispersion temperature of styrene-butadiene-styrene (SBS) with precise amount of modified asphalt binder properties and the required performance obtained based on the SBS-FT wax ratio which determines miscibility in the crystalline phase. Polymer compatibility with FT wax leads to a phase change material owing to FT wax’s high latent heat of fusion with the ability to store or liberate energy from its polymeric surroundings. Crystallization or melting occurs without phase segregation and decrease in latent heat of fusion. Blends of low density polyethylene and FT wax lead to co-crystallization upon cooling even though the wax loading is critical to the reinforcement of the low density polyethylene matrix. FT wax is usually the dispersed phase in a network structure of the polymer, hence the polymer keeps the FT wax in a compact shape to prevent leakage [31].

There is, however, paucity in findings considering the role of FT wax in EVA/crumb rubber modified bitumen and the design of experiment of FT wax/EVA/crumb rubber loadings in the bitumen. Response surface methodology proposed in this study offers an improved and optimal experimental design using minimal experimental effort [32]. A user defined mixture design for response surface methodology was adopted to allow for first order interaction amongst the factors and provide second order polynomials which can be used to optimize mixtures. The response variables in this study will be failure temperature (ft), complex shear modulus (cm), phase angle (pa) and rutting parameter (rp).

II. MATERIALS AND METHODS

A. Materials

EVA a commercial random copolymer of ethylene and vinyl acetate (EVATANE®) with 19-21 wt.% vinyl acetate content (FTIR, Internal Method), melt flow index of about 17-23 g/10min (ASTM D1238, 230 °C, 2.16 kg) and specific gravity of 0.95 g/cm³ (ISO 1183) was supplied by Arkema Group, France. Crumb rubber ambiently ground to 40 mesh (0.425 mm) was supplied by Mathe Group, South Africa. 70/100 bitumen was supplied by Colas, Port Elizabeth, South Africa. FT wax (Sasobit®) a hard wax was supplied by SASOL, South Africa.

B. Production of Warm Mix FT Wax/EVA/CR Modified Bitumen

A laboratory mixer (RYOBI, 1/3 h.p. 5 speed) fitted with a dual helical impeller was used for preparation of FT wax/EVA/crumb rubber modified bitumen mixtures. 500 g of each binder sample was prepared. EVA and FT wax were varied from 0-2.5% with a consistent amount of 13.75% crumb rubber as shown in Table I. 70/100 bitumen was preheated in an oven to 150 °C, the warm mix additive (Sasobit®) was introduced and mixed for 15 minutes at 2500 rpm to integrate the additive into the binder. Crumb rubber and EVA were then added at a binder manufacturing temperature of 180 °C. Lastly, the mixture was blended at
2500 rpm for 45 minutes [26].

C. Experimental Design

To investigate the effect of FT wax (Sasobit®) on rheological parameters, response surface methodology was employed. A simplex-lattice mixture design used in process optimization studies was adopted to study two factors (Sasobit® and EVA) at four response variables (failure temperature, complex shear modulus, phase angle and rutting parameter) by the principle of response surface methodology seven experimental runs of Sasobit® added, hence seven mixtures in total. The simplex-lattice mixture design matrix employed included different levels of EVA and Sasobit® and consistent amounts of bitumen and crumb rubber with design constraints as shown in Table I.

Montgomery [33] proposed a quadratic polynomial regression model which in the study was chosen for predicting the response variable in terms of the four independent variables chosen as shown in (1).

$$Y = b_0 + \sum_{i=1}^{4} b_i X_i + \sum_{i=1}^{4} b_{ii} X_i^2 + \sum_{i=1}^{4} \sum_{j=i+1}^{4} b_{ij} X_i X_j$$

(1)

where Y is the response variable (i.e. failure temperature, complex shear modulus, phase angle, rutting parameter), b0, bi, bi, and bij are constant coefficients of intercept, linear, quadratic and interaction terms, respectively, and Xi and Xj represent the two independent variables (i.e. FT wax, EVA).

The experiments were conducted in a randomized order to avoid systematic bias. Analysis of variance (ANOVA) at 95% confidence intervals (α = 0.05) was used to evaluate the statistical significance of the developed model as well as the effect of factors (linear, quadratic and interactive terms).

D. Rheological Binder Tests

In this study, all FT wax/EVA/crumb rubber binder samples were tested with dynamic shear rheometer (DSR) according to AASHTO T315. Parallel plate geometry was employed with plate-plate gap of 3 mm to account for heterogeneity of the crumb rubber component because the plate gap should at least be 5-8 times the size of the largest particles of crumb rubber (0.425 mm) in the modified binder [34]. The DSR testing for high temperature properties was operated from 58˚C until warm mix binders. Phase angle represents the relative distribution of the total response between an in-phase component (elastic) related to energy storage and an out-of-phase component (viscous) related to energy loss; all per cycle in permanent flow. Phase angle can also be used as a measure of ductility, of which ductility of crumb rubber inclusive warm mixtures is more favourable at high temperatures with the ability to resist rutting and fatigue damage. The viscosity or elasticity distribution is on the composition of the material, loading time and is temperature dependent.

Low temperature testing of seven FT wax/EVA/crumb rubber binders is done on the thermoelectric bending beam rheometer (BBR), after short-term aging and long-term aging in the rolling thin film oven and pressure aging vessel respectively. The Kelvin-Voigt viscoelastic model is applied of a constant load to the modified binder beam and measurement of centre deflection of the beam over the test time enable flexural-rut stiffness (S) and creep rate (m) to be calculated. Based on the elastic-viscoelastic correspondence principle shown in (2), S is calculated as:

$$S(t) = \frac{P L^2}{4 b h^3} \delta(t)$$

(2)

where S(t) is the time dependent creep stiffness, P is the constant applied load (N), L is the span length (102 mm), b is the beam width (12.7 mm), h is the beam thickness (6.35 mm), and $\delta(t)$ is the time dependent deflection of the beam at mid-span (mm) based on the elementary beam theory. Prediction of age-induced cracking using black space plots (log S vs m-value) and master curve development (log S vs log reduced time) followed based on time temperature superposition over a narrow strain amplitude.

III. RESULTS AND DISCUSSION

A. Failure Temperature

Failure temperature refers to the critical temperature when the rutting parameter equals 1.0 kPa for the unaged binder. It can be seen in Fig. 1 that mixtures 3, 4 and 6 (only EVA, 1:3 FT wax to EVA and only FT wax) had the highest failure temperatures of 97.9, 97.1 and 97.4˚C, respectively. Mixture 3 has the greatest of the three, meaning that EVA/waste crumb rubber modified bitumen shows the greatest resistance to high temperature susceptibility. The lowest failure temperature was observed for mixture 7, a 1:2 FT wax to EVA mixture hence at such wax: plastomer loadings the high temperature effects in the modified binder would have shown the least viscosity. Fig. 2 shows the two component (EVA and FT wax) results for the seven mixtures and the distribution over the quadratic model adopted for failure temperature. Equation (3) shows the relation of actual components for the individual and co-interaction effects of FT wax and EVA. Failure temperature is thus related to rutting resistance at high temperatures.

$$ft = 39.1 \text{ FT wax} + 39.4 \text{ EVA} - 4.6 \text{ FT wax. EVA}$$

(3)

The curvature of the 95% confidence interval bands, over
which the seven mixtures are distributed, shows the quadratic model adopted. Equation (3) shows that EVA individually contributes slightly more to the value of the failure temperature. FT wax also contributes positively to the failure temperature; hence both FT wax and EVA, given their plastomer nature, increase the high temperature resistance. Plastomers form a 3D network that is known to be rigid and confers with high failure temperatures [35]. FT wax is a hard wax, and at the test temperatures, its physical form is solid since it is below its melting point. The chemistry of FT wax allows it to be in solution, hence given the nature of EVA the vinyl acetate moieties would participate in destabilizing the balance of interaction as the FT wax and EVA interaction effects reduce the failure temperature of the material as shown by (3).

Overall, the individual effects of EVA and FT wax contribute the most to the value of failure temperature. The possible effect of the crumb rubber component, which is elastomeric in nature and consists of other components such as carbon black and other additives from the initial formulation of tires that could influence the behaviour of the FT wax and EVA in bitumen, was taken into consideration. The crude source clearly played a role as the finger print of the crude unique to the source would have affected the nature of the interaction chemistry amongst the mixture components. Refining technology as well could have played a role now based on the 70/100 bitumen used in the study as this would affect the finger print of the bitumen used in the study.

The participation of FT wax as a warm mix additive for purposes of energy and sustainability is deduced from its ability to reduce high failure temperature of mixtures 3 and 6 relative to mixture 7. At loadings used in mixture 7, FT wax would be optimal for warm mix FT wax/EVA/CR modified bitumen. It is possible that factors such as interaction time and temperature could have been pivotal in influencing the failure temperature of the mixtures [36]. Another possibility is that crumb rubber component in mixtures contributes to high temperature viscosity due to the porous surface of the ambient ground crumb rubber which can absorb the maltene fraction and thus increase failure temperature of the mixtures [36]-[38]. Considering costs and the energy-sustainability nexus, it would therefore be economical to use FT wax because there is not much difference in failure temperature relative to EVA/crumb rubber mixture as shown in Fig. 2.

### B. Complex Shear Modulus

Across all mixtures, complex shear modulus decreased on increment of test temperature from 58, 64 and 70 °C as can be seen in Fig. 3. The greatest contrast in material behaviour was observed in mixtures 6 and 7 for FT wax only and 1:2 FT wax to EVA mixture respectively. The complex shear modulus at 58 °C for mixture 7 is similar to mixture 6 at 70 °C. For a 12 °C difference in temperature, 2.5 % loading of FT wax in mixture 6 reflected a great degree of stiffness. As opposed to the interaction nature in FT wax/ EVA co-blend, the FT wax could have coated the rubber crumb as it interacted with the crumb rubber and hence increasing the rigidity of the final mixture. It has been reported that the vinyl acetate component of EVA provides the amorphous and rubbery properties to the bitumen relative to the polyethylene segments which are crystalline, hence the crystallinity is disrupted by the vinyl acetate component [35].
The interaction effects of the various components were also considered. Fig. 4 depicts a two-component mixture response for the complex shear modulus and the quadratic model adopted for the seven mixtures as reflected by the curvature where design points are distributed on the design space. Equation (4) shows the impact of the plastomer component of the mixtures individually and co-interaction at 64 °C.

\[ cm = 9.7 \text{ FT wax} + 7.7 \text{ EVA} - 6.7 \text{ FT wax. EVA} \]  

Individually, FT wax and EVA contributed to the increase in complex modulus though interaction effects of FT wax and EVA led to a decrease in complex modulus. The variation in loading of EVA and FT wax across all 7 mixtures showed that a combination of two plastomer components result in crumb rubber leading to a decrease in complex shear modulus. Overall FT wax is a good warm mix additive especially with crumb rubber [39].

\[ p a = 28.9 \text{ FT wax} + 29.9 \text{ EVA} + 2.6 \text{ FT wax. EVA} \]  

C. Phase Angle

Phase angle, as expected, increased with an increase in test temperature for all mixtures, with sample 7 being the most viscous as shown in Fig. 5, owing to the highest phase shift angle. Mixture 6 showed the greatest elasticity as reflected by the least phase angle at all test temperatures. This is in agreement with the greatest increase in rigidity noted for complex shear modulus in Fig. 3. The rheological behaviour as shown by the phase angle reflected the degree of elasticity or viscosity for either extreme. For individual EVA and FT wax loadings in mixtures 3 and 6 respectively, the former showed higher phase angle values depicting EVA’s contribution to viscous behaviour relative to FT wax which contributed more to elastic behaviour. In mixture 2, where 1:1 loading of FT wax to EVA was added, the behaviour was more inclined towards mixture 3. This increases expectation that the leading synergy towards viscous behaviour between FT wax and EVA will reflect in the overall equation of the response surface methodology.

Equation (5) shows the individual and co-interaction effects of FT wax and EVA. These interaction effects are seen to be positive, hence as suggested from the similarity in behaviour of mixture 2 to mixture 3, interaction effects led to an increase in phase angle. Equation (5) also shows that the individual contribution of EVA in increasing phase angle was greater than that of FT wax at the test temperature of 64 °C. Temperature profiles of phase shift angles are shown in Fig. 5. It can be seen that the synergy, as a result of the positive contribution of the quadratic interaction shown in (5), was unique to the contribution of FT wax and EVA to the phase angle.

![Fig. 5 Phase shift angle for the 7 mixtures measured at 58, 64 and 70°C](image-url)
harnessing two plastomers in terms of network rigidity but also optimizing for warm mix abilities owing to FT wax. The use of FT wax in crumb rubber improves mix workability at lower temperatures and decreases the viscosity of crumb rubber modified bitumen at high temperatures [30].

Equation (7) shows the relationship between EVA and FT wax, where the rutting parameter has a component of both complex shear modulus and phase angle and hence sums up the rheological parameters used as response variables in the study.

\[
rp = 10.2\text{ FT wax} + 8.0\text{ EVA} - 7.1\text{ FT wax EVA}
\]  

(6)

According to (6), supported by Fig. 8, the FT wax component contributed the most to the rutting parameter at 64 °C. The magnitude of interaction effects of FT wax and EVA show a greater degree of antagonistic behaviour reducing the rutting parameter, hence rutting resistance. EVA and FT wax are both plastomers, and therefore, the plasticity increases the strain component owing to the inability of the material to recovery on application of stress. Fig. 8 shows the two-component mixture representation of the seven mixtures for the rutting parameter at 64 °C. Similar to failure temperature and complex modulus, the rutting parameter convex curvature on the 95% confidence interval (\(\alpha = 0.05\)) band (Fig. 8) resembles the same quadratic behaviour for the seven mixtures distributed over the design space. The convex nature of the curvature is associated with the reduction in failure temperature, complex modulus and rutting parameter because of the antagonistic interaction effects of FT wax and EVA. The concave nature of phase angle is associated with the interaction effects of FT wax and EVA as well as highlight synergistic materials properties.

Rheology of modified binders reveals the nature of rutting at different test temperatures as a reflection of accumulation of permanent strain which is a primary distress mechanism and a major design criterion at all stages of constructing the different courses of the asphalt pavement [40]. The modified binders...
consisting of multi-component systems such as in the case of FT wax/EVA/crumb rubber enable different properties of the constituents to participate in a ternary phase interaction with bitumen and co-interaction amongst each other. This creates enhanced rutting properties of the mixtures, thus reduction in deformation under load from the plastomer component and elastic properties from the crumb rubber component [41].

E. Black Space Plots and Master Curve Development

Black space plot is very useful method for understanding how materials change with aging. Fig. 9 shows the black space plots of the seven mixtures with varying mixture proportions of EVA and FT wax. The source of bitumen and effects of oxidation play a critical role in binder properties in black space. Mixtures 3 and 6 show the least resistance to age induced cracking, based on the loading of the most EVA and FT wax respectively. Interaction effects of the EVA and FT wax contribute to the resistance to age induced susceptibility to cracking with mixture 7 showing the best resistance to cracking and very close to mixture 4 as well. Understanding the contribution of both FT wax and EVA to reduction in aging is important as the elastomeric nature of crumb rubber contributes as well to rearrangement of polymer chains in EVA. Increase in EVA proportionally to FT wax enabled the blend composite to improve the failure and rheological properties. In essence at the given loadings of FT wax and EVA, it was important to strike the balance to achieve improved performance based on the criteria of choices which was addressing optimum performance. Short term and long term aging thus were evident in black space.

In approaching an aging and low temperature nexus master curves were developed as shown in Fig. 10. The broadness of the relaxation spectrum became more disperse and gradual in the transition from elastic to viscous behaviour. Modification of binders in black space seldom hence the master curve development in mixture 1 shows reduction in the relaxation spectrum and less gradual transition from elastic to steady flow state. This may be attributed to the dominant FT wax loading improving the binder’s ability to relax stress due to viscous flow. Rheological simplicity and complexity of systems is highlighted in the relaxation properties related to the distribution of loss, storage and complex modulus.

Master curves show high values of flexural creep stiffness at low reduced time and low values of flexural creep stiffness at high reduced time. Improvement in thermal resistance to cracking is achieved on addition of loadings of FT wax and EVA.

F. Model Fitting and Optimization of the Process Responses

The P value is the probability of obtaining a test statistic that is at least extreme as the one that was actually observed in statistical significance testing. The assumption being that the null hypothesis is true and P value determines the appropriateness of rejecting the null hypothesis. The smaller the P value, the smaller will be the probability that rejecting the null hypothesis is a mistake. In the study, the alpha level was 0.05; thus, in statistical testing, if the P value is less than the assumed alpha, the null hypothesis is rejected and P value is calculated from the observed sample. Table II lists the values of responses at each of the factorial levels generated by the principle of response surface methodology. The surface contour plots in Figs. 2, 4, 6 and 8 represent the mathematical fitted model and that the best settings were used for the model fitting. Contour plots represent the predictor factors as plotted on the x and y axes while the contour lines represent the response and connects points with the same response value.

Optimum settings of the control variables were obtained which resulted in a maximum or minimum response over the 0-2.5% range of EVA and FT wax loading with the consistent amount of crumb rubber and bitumen. Derived models in (3)-
REFERENCES


