

A MICROSTRUCTURAL INSIGHT OF MODIFIED BITUMEN USING EPI-FLUORESCENCE MICROSCOPY

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ABSTRACT

The widespread usage of polymer modified binders (PMBs) is due to the growing perception that they offer increased resistance to pavement distresses. The availability of inherently different modifiers has expanded the range of PMBs to select from when designing asphalt pavements. Correct blending of the polymer in bitumen remains an important requirement for optimal performance of PMBs. It is difficult to determine the polymer morphology by just measuring the physical properties of the PMB. This paper presents a microscopic technique that allows the use of high energy light (e.g. ultraviolet light or high-energy visible light) to excite and consequently cause the polymer-rich phase to fluoresce at a wavelength that can be detected by the eye. Epi-fluorescence microscopy can be used to differentiate between the bitumen phase (which does not fluoresce) and the polymer phase to show the polymer distribution/dispersion in the base bitumen. This is an important tool to characterise the *in situ* structural and chemistry effect of modifiers within bitumen in order to determine their influence on the modified binder performance. This paper shows that a sufficient degree of compatibility between polymer and bitumen is necessary in order to avoid separation during handling for the PMB to achieve the expected pavement layer performance.

1. INTRODUCTION

Empirical tests cannot effectively characterize polymer modified binders (PMBs), and this has resulted in a need to establish fundamental engineering properties capable of accurately predicting the performance of bituminous seals and asphalt mixes. Furthermore, there is the growing need to understand why PMBs perform the way they do. This has prompted research that links performance with the morphology of PMBs, in order to get a better understanding of the interaction between components of PMBs for formulating binders of consistent behaviour.

The availability and extensive experience in the use of inherently different modifiers has expanded the range of PMBs to select from when designing pavements. In the production of PMBs through a blending process, correct blending of the polymer in bitumen remains an important requirement for achieving optimal performance of PMBs. The term polymer morphology herein refers to the way in which the polymer-rich phase is distributed in the base bitumen through blending. It is difficult to visualize the polymer morphology by just measuring the physical properties of the PMB. There is however, a technique that allows the polymer within bitumen to be viewed directly using a microscope. The microscope uses high energy light (e.g. ultraviolet light or high-energy visible light) to excite and cause the polymer-rich phase, not the bitumen, to fluoresce at a wavelength that can be detected by the eye (Figure 1). As a result, the bitumen-rich phase appears dark, while the polymer-rich phase appears bright and often greenish yellow in colour when viewed through the microscope eyepiece (Hunter *et al.*, 2015).

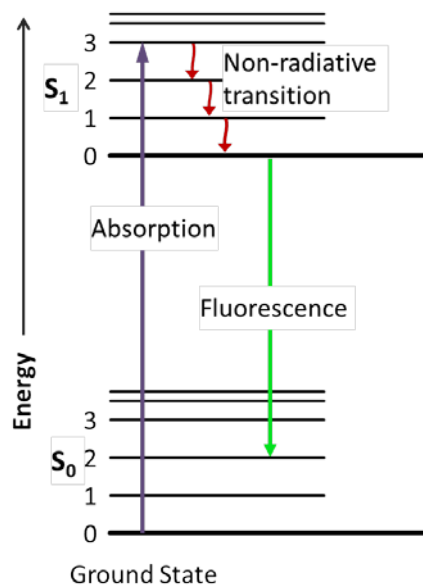


Figure 1: Electron absorption of a high energy photon results in excitation, and eventually fluorescence at a longer wavelength of lower energy when the system relaxes (Morajkar, 2012).

Fluorescent microscopy has been frequently used to differentiate between the bitumen phase from the polymer dispersion (Brion and Brûlé, 1986), in order to determine whether the PMB blend is homogeneous and stable with storage (Olard and Simard, 2015) and/or ageing. Brûlé *et al.* (1988) conducted one of the earliest investigations towards the influence of blending conditions, polymer content and chemical composition of the base binder on the morphology of Styrene-Butadiene-Styrene (SBS) modified bituminous blends. It has been generally accepted that an appropriate extent of compatibility between the polymer and bitumen phase is necessary in order to avoid separation during storage and handling.

Fluorescent microscopy has also been used for microstructural analysis of polymer modified binders in bituminous mixtures. Given the many disadvantages associated with the use of extraction solvents in bituminous laboratories, this can be viewed as an important alternative. Such solvents include benzene, which is a known carcinogen. Alternative solvents used in South Africa tend to also require compliance to intensive health and safety requirements depending on their degree of toxicity. This makes microscopy an ideal and safer option to give insight into the state of the *in situ* binder within the asphalt or seal layer.

In South Africa, microscopy can also be an important tool to characterise the *in situ* structural and chemistry effect of modifiers within bitumen, in order to determine their influence on modified binder performance. It has been argued that separation due to insufficient blending or incompatibility between the polymer and bitumen observed with PMB blends does render the modification ineffective and without any benefit in an asphalt mix (Wegan and Nielsen, 2001). As a non-destructive tool, microscopy will enable the industry to relate microscopic images of PMB blends to their behaviour at the macro-level through performance evaluation. In this investigation, epi-fluorescence microscopy is presented as a quality control tool to assist the pavement industry in assessing the integrity of PMBs during production to their performance in asphalt or seal layers. As a result, special attention is paid to current challenges facing the industry that includes the use of different modifiers, ageing, poor compatibility and blending challenges.

2. EXPERIMENTAL

The morphology of modified PMBs strongly depends on sample preparation and sample conditioning. Therefore, it is important to create a precise preparation protocol in which the temperature, shearing and cooling are well defined and controlled (Soenen *et al.*, 2008). In literature, different methods have been suggested to study the morphology of PMBs by epi-fluorescence microscopy (DIN EN 13632, 2010; Pasquier *et al.*, 1997; Wegan and Nielsen, 2001). Given the morphology of PMBs depend on the preparation temperature and cooling history (Soenen *et al.*, 2008); it can be concluded from literature that the resulting morphology after fast cooling is likely not simulative of the eventual morphology in the asphalt mix (Lu *et al.*, 2010). In asphalt pavement construction, the *in situ* binder is subjected to high temperature mixing and transportation before naturally cooling down during placement. This matter should be considered important during performance testing of PMBs, especially when the test specimen is small e.g. for Dynamic Shear Rheometer (DSR) tests (Soenen *et al.*, 2008) – where rheological properties have been found to strongly relate to morphology (Lu *et al.*, 2010).

2.1. Sample preparation

PMBs were prepared and tested as per technical guideline requirements (TG1, 2015). Selected polymer samples were added to a tin of bitumen pre-heated in an oven to the appropriate temperature. The bitumen was maintained at the recommended temperature on a hotplate during polymer addition, and the blend was stirred using a high shear

(Silverson) mixer or paddle stirrer for the recommended time. In order to allow polymer swelling to reach an equilibrium condition, the PMBs were allowed to cool to room temperature and stand overnight after mixing (AP-T197-12, 2012).

Typically, 70/100pen grade binders are used as base binders for modification in South Africa. However, there has been a growing trend of using 50/70pen grade base binders for modification recently. It is envisaged that compatibility challenges would increase with 50/70pen grade base binders compared to the 70/100pen grade base binders. Consequently, a 50/70pen grade base binder was predominantly used in this investigation. The 50/70pen grade base binder (Much Asphalt sample no.: B0097/14; CSIR sample no.: 14015) investigated in this project was sourced from Much Asphalt Eikenhof (18/09/2014) and originated from the Natref refinery.

The test results of some of the PMBs investigated have been included as part of Table 1. The greater effect on the softening point and elastic recovery of the branched block SBS copolymer (Kraton® D1184) over the linear triblock SBS copolymer (Vector® 2518) is observed. Similarly, the difference in behaviour of non-elastomers (e.g. the plastomer Evatane® 20-20) compared to elastomers in affecting the elastic recovery and softening point is evident.

Table 1: Test results of the laboratory prepared PMB samples

Property	Polymer Modified Binders							Test Methods (TG1, 2015)
	3% SBS (Vector® 2518)	3% SBS (Kraton® D1184)	3% SBR (Lipaton® SB 2540)	3% EVA (Evatane® 20-20)	2% AC 3427 (Elvaloy®)	2% RET AM (Elvaloy®)	3% F-T Wax (Sasobit®)	
Softening Point (°C)	59.6	63.0	57.2	62.8	59.0	65.0	81.0	TG1 MB-17
Elastic Recovery @15°C (%)	68	73	57	Failed	Failed	Failed	Failed	TG1 MB-4
Dynamic Viscosity @165°C (Pa.s)	0.284	0.348	0.255	0.373	0.270	0.411	0.136	TG1 MB-18
Storage Stability @160°C (°C)	25.2	18.6	7.6	3.2	5.0	0.4	2.0	TG1 MB-6
After RTFOT-ageing								TG1 MB-3
Diff in Softening Point (°C)	+3.4	+1.4	+3.4	+3.8	+4.4	+3.0	+4.6	TG1 MB-17
Elastic Recovery @15°C (%)	63	70	50	Failed	Failed	Failed	Failed	TG1 MB-4

2.2. Epi-fluorescence microscopy

An epi-fluorescence microscope is one where the illuminating light travels through the objective lens to illuminate the sample, and subsequently the emitted light from the sample travels back through the same objective to the eye or camera (Thermofischer, 2016).

Different types of microscopes were used for this investigation, but generally they followed the schematic diagram shown in Figure 2. The microscopes were upright with objectives above the sample stage, instead of inverted. High energy light (e.g. ultraviolet light or high-energy visible light) from a light source (a mercury or xenon lamp) passes through the excitation filter which restricts the light transmission to a certain wavelength range. This light is directed onto the sample surface, which when it fluoresces; emits light of a different wavelength (longer) from the incident light. The emitted light then passes through filters (beam splitter filter and barrier filter) that permit/transmit light of a particular range of wavelengths before they reach the eye or camera. The microscopic system is normally equipped with a special fluorescent camera to record the images. The microscopes used in this investigation include a Leica DM 2500P microscope, a Nikon eclipse Ci microscope, an Olympus BX51M microscope and an Agilent Cary 620 FTIR microscope.

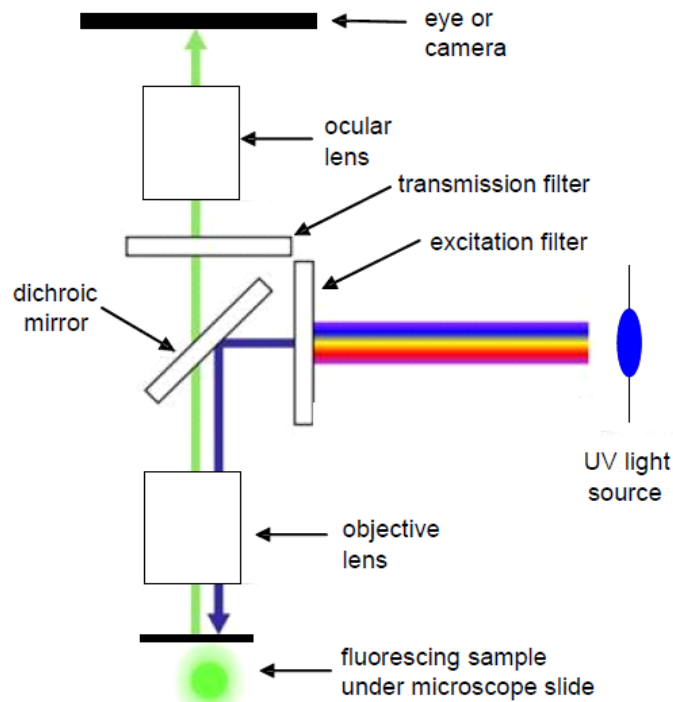


Figure 2: Epi-fluorescence microscope (AP-T197-12, 2012).

2.3. Methodology

Different types of sample preparation methods for epi-fluorescence analysis were investigated. But a method based on ASTM D36 (2006) sample preparation procedure was found ideal. During microscopic analysis, the exposed surface started to flow with UV exposure. The heat from the lens heats up the sample, which in turn flows. In order to prevent the sample from flowing and prevent bitumen-air interaction, which has been shown to affect PMB morphology (Soenen *et al.*, 2008), two glass slides were used to sandwich the sample (see Figure 3).



Figure 3: Bitumen inside a brass ring.

Like the European standardised freeze fracture method (DIN EN 13632, 2010), this method was considered repeatable. However, it resulted in a slightly different morphology of the tested blend given the difference in cooling. It was still preferred over the others for PMB morphology investigations due to the following reasons:

- It is in line with the current national sample preparation method for PMBs (TG1 MB-2 followed by empirical tests such as the softening point test).
- It is in line with the current national storage stability method for PMBs (TG1 MB-6 followed by softening point tests).
- It is in line with the current national ageing practice for PMBs (TG1 MB-3 followed by empirical tests such as the softening point test).
- It does not involve fast cooling. Please note:
 - Fast cooling is not simulative of actual *in situ* cooling of binder films in seals or asphalt pavement layers.
 - Fast cooling is useful for isothermal annealing investigations but does not take into account that some polymer domains re-associate on cooling to restore the strength and elasticity of PMBs. Wax crystallization also takes place during cooling of wax-modified bitumen. The cooling rate may therefore affect the way the polymer re-associates as well as the size of the emerging wax crystals.
 - A different cooling rate to that followed with current testing practices will prevent the development of any meaningful correlation studies with physical properties.

3. RESULTS AND DISCUSSION

3.1. Classifying PMBs microstructurally

When microscopically studying low levels of polymer content ($\leq 3\%$, w/w) in bitumen, the bitumen rich phase appears dark and continuous in the background, while the polymer-rich phase appears as bright discrete units, see Figures 4-10. The exception was the Elvaloy® AM where the polymer dispersion was not observed under the microscope. This has also been found by other researchers studying reactive elastomeric terpolymers (Topal, 2010). Unlike SBS polymers that form physical 3-D networks in bitumen at room temperature (due to aggregating styrene end blocks) that dissociate at high temperatures (enabling handling); Elvaloy® AM is a reactive random terpolymer comprising of ethylene, n-butylacrylate and glycidyl methacrylate (GMA). It is proposed that the GMA molecule reacts with bitumen components to form stable bonds even at the high processing temperatures (Becker *et al.*, 2001), that may facilitate the relatively finer degree of distribution in bitumen and/or prevents polymer units from coalescing.

It has been argued that the increased concentration of aromatics with a high content of fluorescent benzene rings in the polymer-rich domains results in the greenish yellow appearance in fluorescent images (Lesueur, 2009). This is not easy to prove given there is no sign of fluorescence of these aromatics in pure bitumen samples. In addition, when you shine UV light directly onto certain pure modifiers, they also give off a greenish yellow

colour (Mturi *et al.*, 2016). However, given the fact that these polymer rich domains also fluoresce with high energy visible light in bitumen, whereas the pure polymers hardly show any absorbance at these wavelengths (Mturi *et al.*, 2016), does support the argument.



Figure 4: Fluorescent images of pure bitumen (using different microscopes).

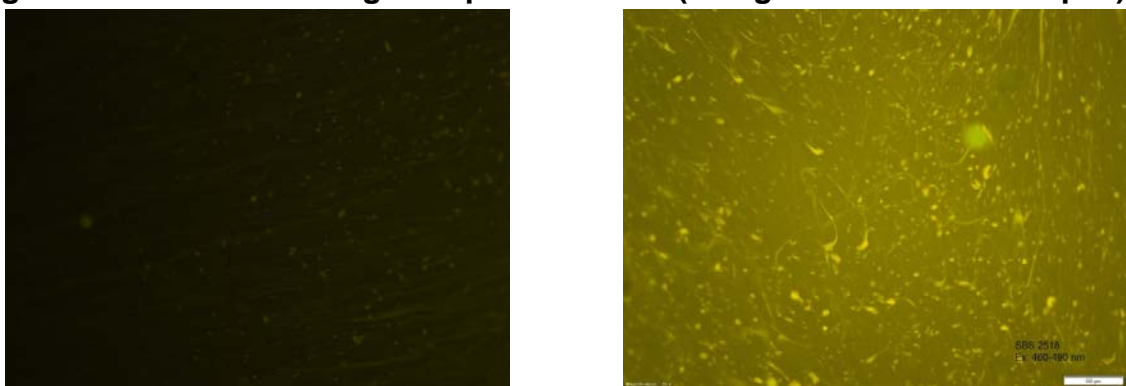


Figure 5: Fluorescent images of SBS (Vector® 2518) in bitumen.

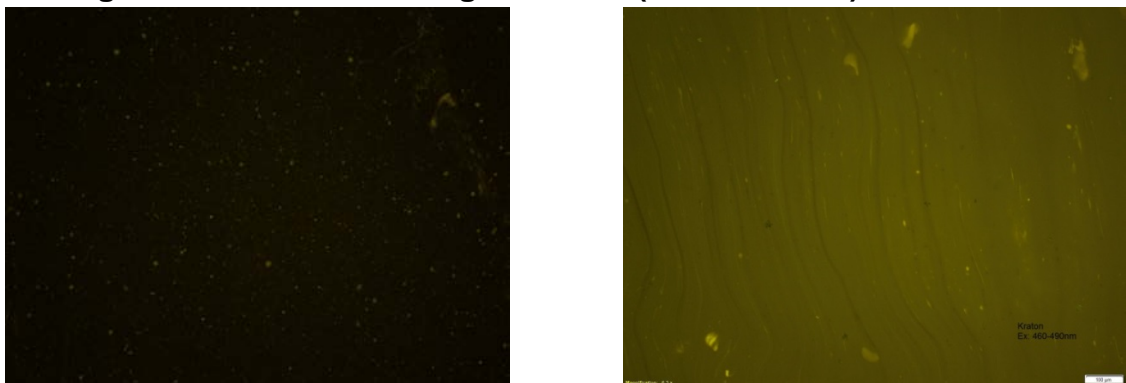


Figure 6: Fluorescent images of SBS (Kraton® D1184 ASM) in bitumen.

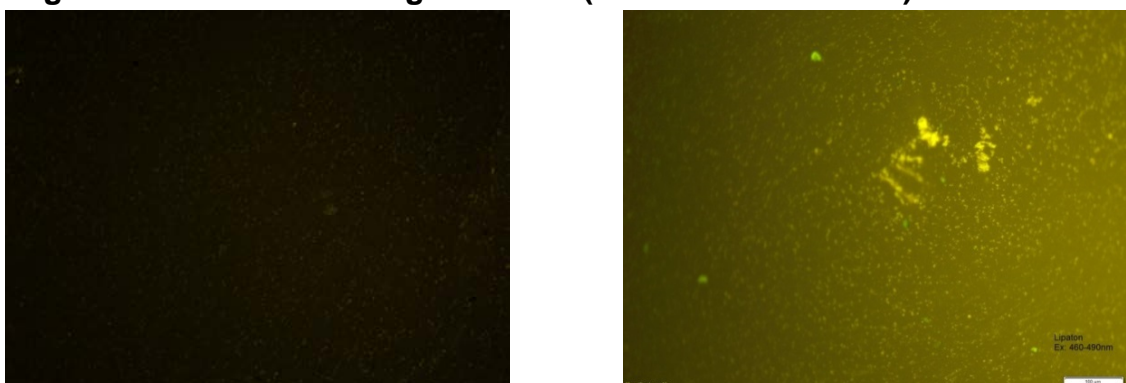


Figure 7: Fluorescent images of SBR (Lipaton® SB 2540) in bitumen.

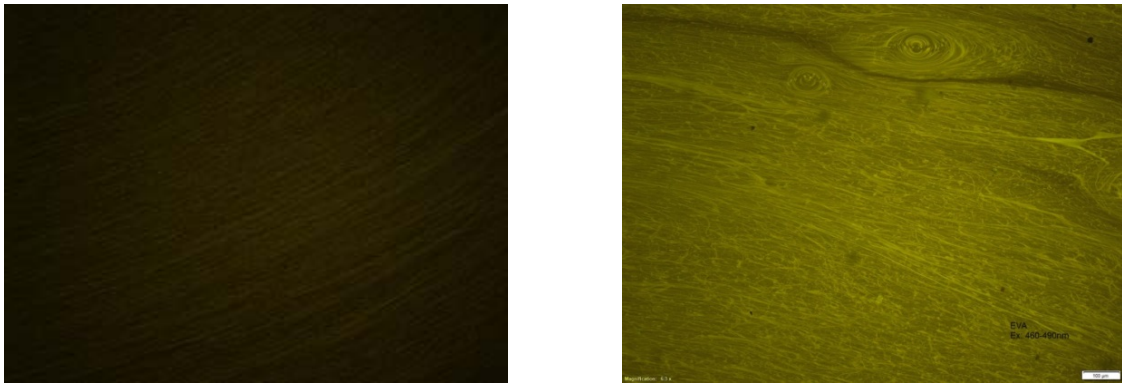


Figure 8: Fluorescent images of EVA (Arkema Evatane® 20-20) in bitumen.

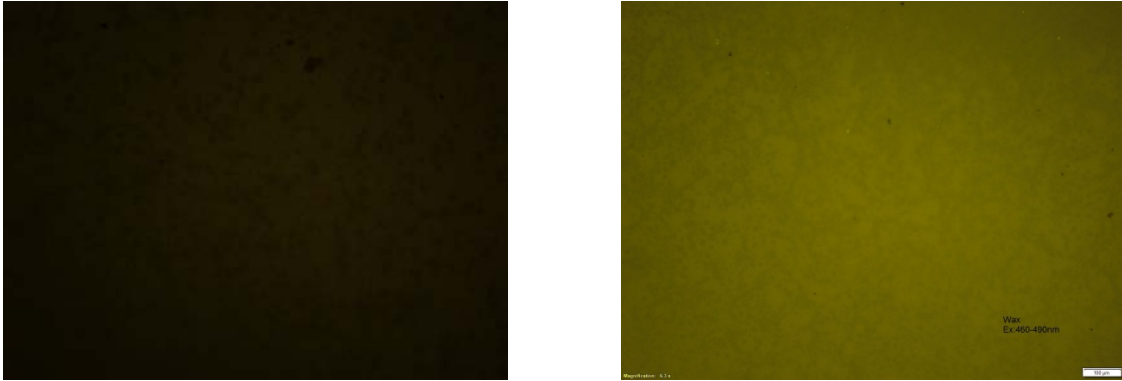


Figure 9: Fluorescent images of Wax (Sasobit® F-T Wax) in bitumen.

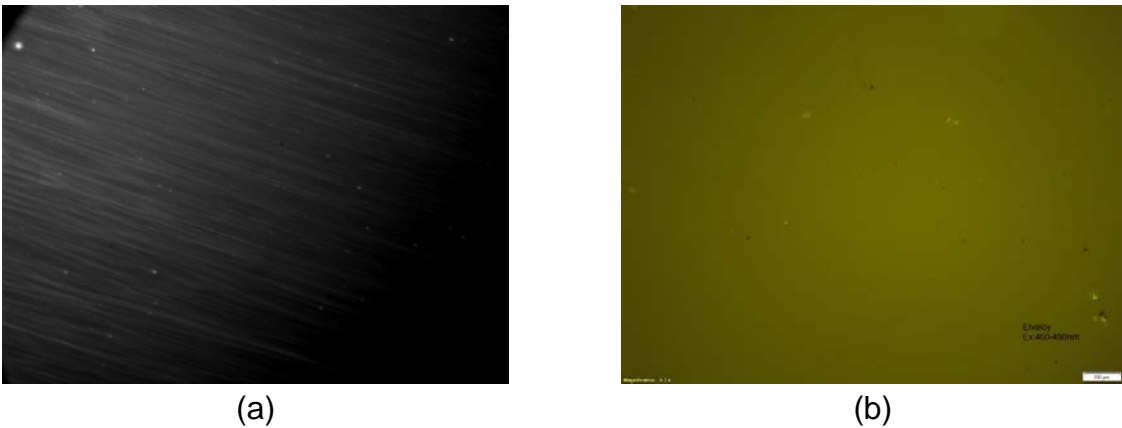


Figure 10: Fluorescent images of (a) Elvaloy® AC 3427 in bitumen, and (b) Elvaloy® AM in bitumen using different microscopes.

3.2. Blending Method

The bitumen and the polymer are often dissimilar in molecular weight, viscosity, polarity, density, and solubility. Hence, the manufacturing process must meet certain thermodynamic requirements to create a uniform stable dispersion.

The most important steps in the process of manufacturing PMBs include the dispersion of the polymer in bitumen and interaction between the polymer and bitumen, and this is what determines the morphology of the PMB. A number of factors influence the efficiency of the dispersion/interaction process, a few of these factors were investigated using a locally used SBS polymer (Kumho KTR KTR-401) and bitumen, as shown in Figures 11-15, and can be summarised as follows:

- Figure 11 shows the effect of shear during mixing. Typically high shear stirring results in better dispersions. However, in this case, the stirrer had minimal effect on the PMB morphology.
- Figure 12 shows the effect of bitumen chemistry. Typically, a base binder with higher maltenes content gives a better PMB morphology. As observed, a 70/100pen grade base binder shows a better PMB dispersion than a 50/70pen grade base binder does.
- Figure 13 shows the effect of cross-linking agents. Typically, cross-linking agents create a more stable polymer network. As observed, this resulted in a finer dispersion.
- Figure 14 shows the effect of processing temperature. Typically, the higher the temperature, the more the interaction between the bitumen and the polymer. As can be observed, this had the biggest impact in the eventual morphology of the PMB.
- Figure 15 shows the logic behind the current modification practice in South Africa. It is done with the aim of increasing PMB stiffness (going from right to left in the plotted bar chart). However, an increase in stiffness is not necessarily accompanied by an increase in elastic response, as observed when the base binder was changed.

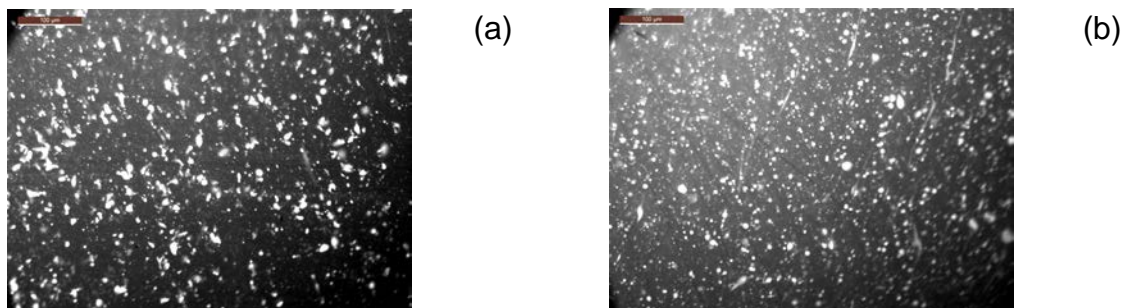


Figure 11: Fluorescent images of SBS (Kumho KTR KTR-401) blended at 180°C in a 70/100pen grade bitumen with (a) a high shear stirrer, and (b) a pedal stirrer.

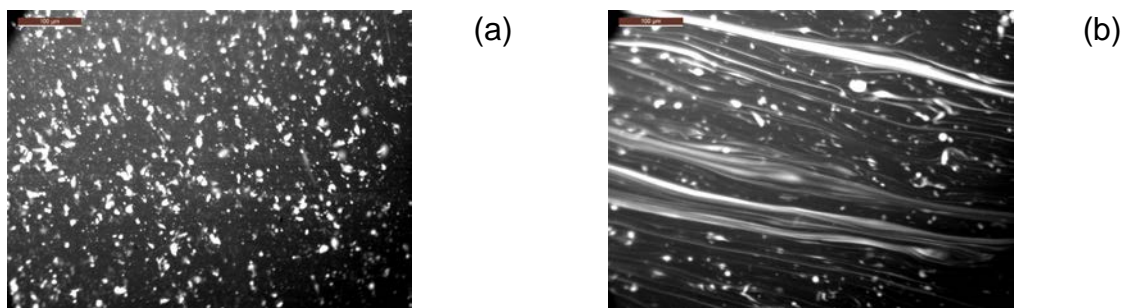


Figure 12: Fluorescent images of SBS (Kumho KTR KTR-401) blended at 180°C with a high shear stirrer in (a) a 70/100pen grade bitumen and (b) a 50/70pen grade bitumen.

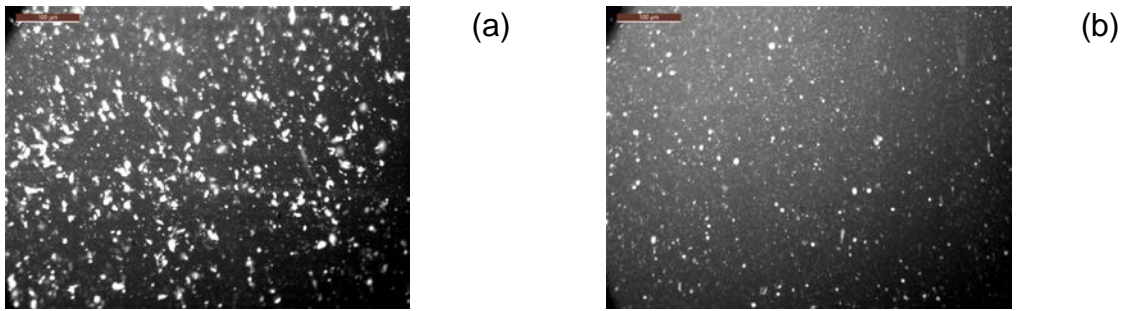


Figure 13: Fluorescent images of SBS (Kumho KTR KTR-401) blended in a 70/100pen grade bitumen with a high shear stirrer at 180°C (a) without a cross-linking agent and (b) with a cross-linking agent.

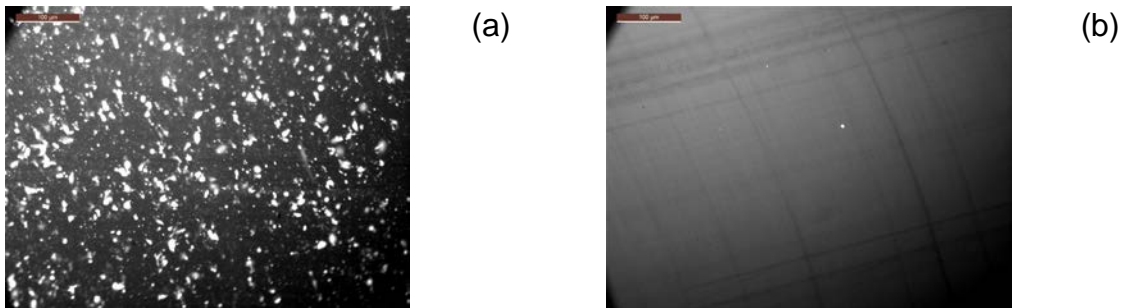


Figure 14: Fluorescent images of SBS (Kumho KTR KTR-401) blended in a 70/100pen grade bitumen with a high shear stirrer at (a) 180°C and (b) 200°C.

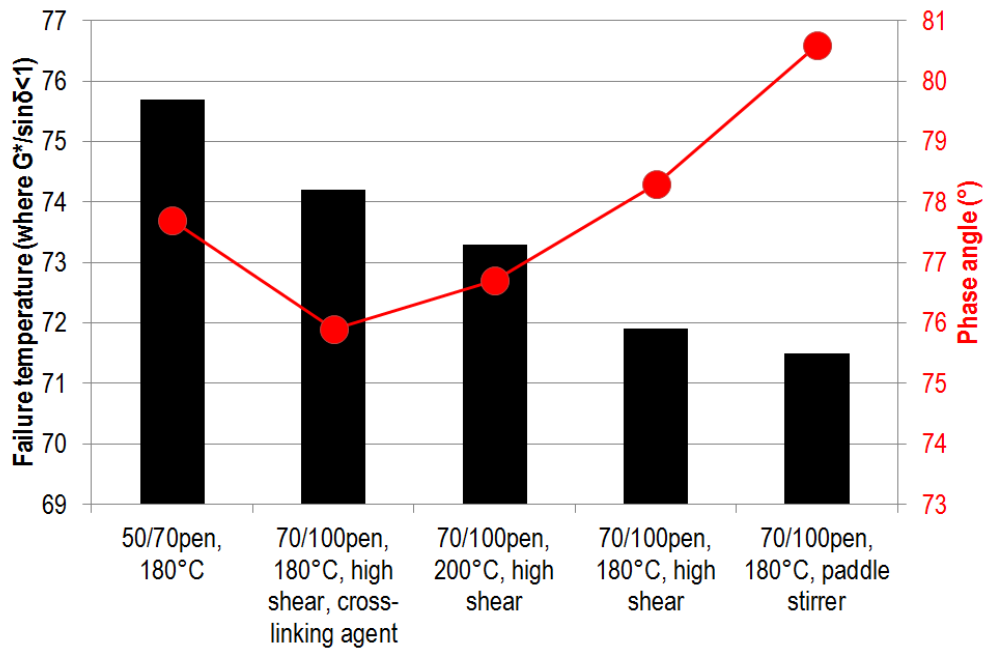


Figure 15: Failure temperature (where $G^*/\sin\delta < 1$) and phase angles at 10rad/s for the various SBS (Kumho KTR KTR-401) blends.

Based on the size of the discrete polymer units, it appears that most modifiers exist as agglomerates in bitumen. This begs the question as to what is the correct mechanism of PMB performance in relation to dosage and PMB dispersion? As a distinctly separated phase of agglomerates, it suggests that these PMBs are inherently not optimally distributed. This could be due to poor compatibility and questions whether the modifier grade(s) used in South Africa are ideal for the local bitumen types. For instance, the large radial SBS types historically used in South Africa are widely perceived to be more efficient

(in increasing stiffness and elasticity) but less compatible with bitumen. In addition, it questions the use of 50/70pen grade base binders that typically have insufficient maltenes than 70/100pen grade base binders to enable the polymer to swell (good compatibility). When examining the black space diagrams in Figure 16, the phase angle can be considered as a general assessment parameter to estimate the degree of modification and compatibility imparted by the polymer onto the bitumen. As can be observed from the shape of the SBS-curve for SBS modified binders, the better compatibility of the polymer with a 70/100pen grade base binder results in greatly reduced phase angles at higher temperatures compared to when a 50/70pen grade base binder is used. This issue of compatibility could explain the range in storage stability test results observed in the country (see Figure 17).

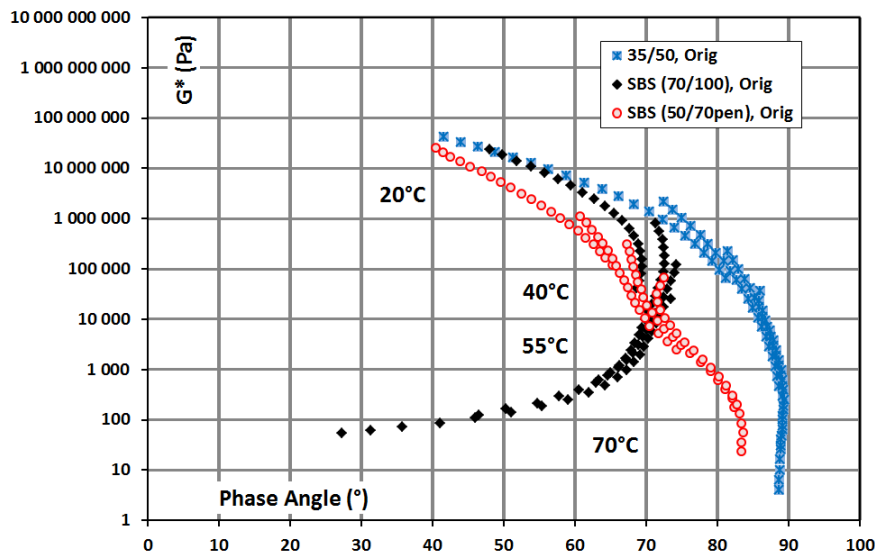


Figure 16: Black diagrams comparing a 35/50pen grade bitumen with SBS modified binders based on a 50/70pen grade base binder (Kraton® D1184) and based on a 70/100pen grade base binder.

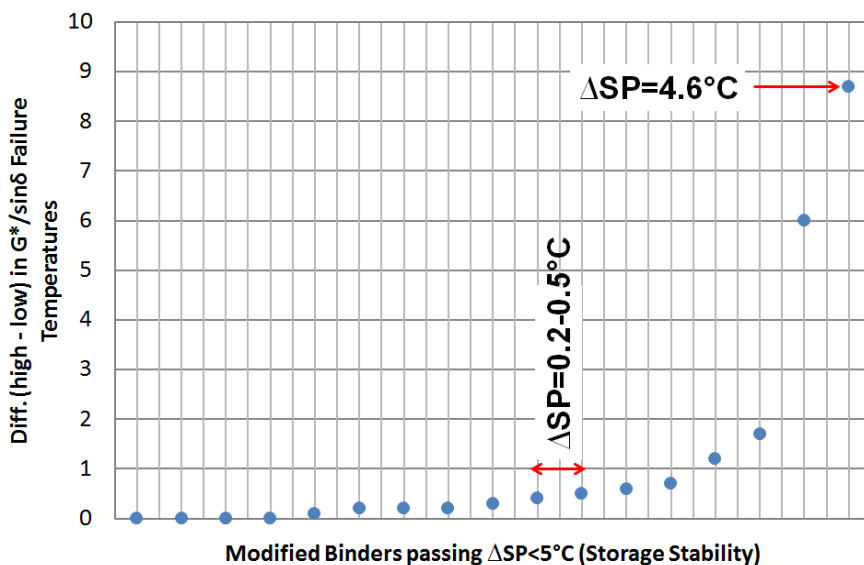


Figure 17: Storage stability of modified binders from various sources in South Africa.

3.3. Stability

Having determined and classified the morphology of PMBs, the change in morphology during storage stability and ageing conditioning can be characterised.

Based on the analysis of SBS modified binder samples submitted to the lab (from the South African asphalt industry) over the years, a pattern emerges:

- Storage stable blends tend to have a finer dispersion of the polymer, see Figure 18.
- Storage unstable blends tend to have larger discrete polymer agglomerates. During storage stability conditioning, they undergo further agglomeration to form large continuous units of the polymer towards the top of the storage stability glass tubes, see Figure 19.

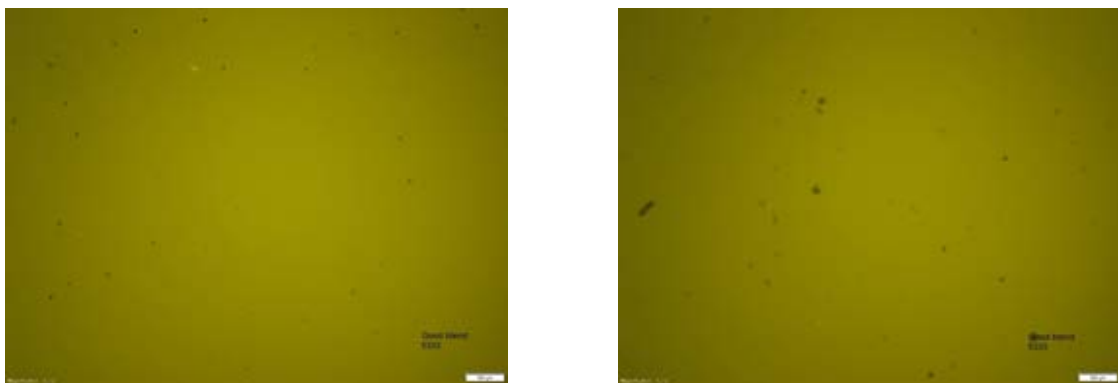
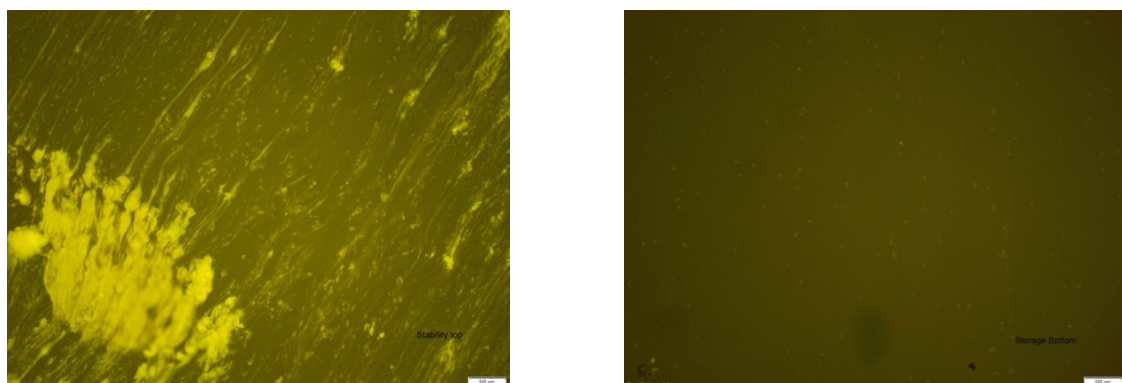


Figure 18: Fluorescent images of a storage stable SBS modified binder samples from past projects done at the CSIR.



Storage Stability Top
(SP = 63.3°C)

Storage Stability Bottom
(SP = 55.0°C)

Figure 19: Fluorescent images of the top and bottom of a storage unstable SBS modified binder sample.

The effects of ageing can include a change in morphology and/or agglomeration of polymers in bitumen. This is notably the case for the elastomers more than any other group of modifiers. Rolling thin film oven test (RTFOT) and pressure ageing vessel (PAV) ageing of the elastomers are shown in the fluorescent images in Figure 20. This agrees with the reduced elastic response of SBS modified binders with ageing observed towards

the higher in-service temperatures previously seen in black space diagrams (Mturi and O'Connell, 2012).

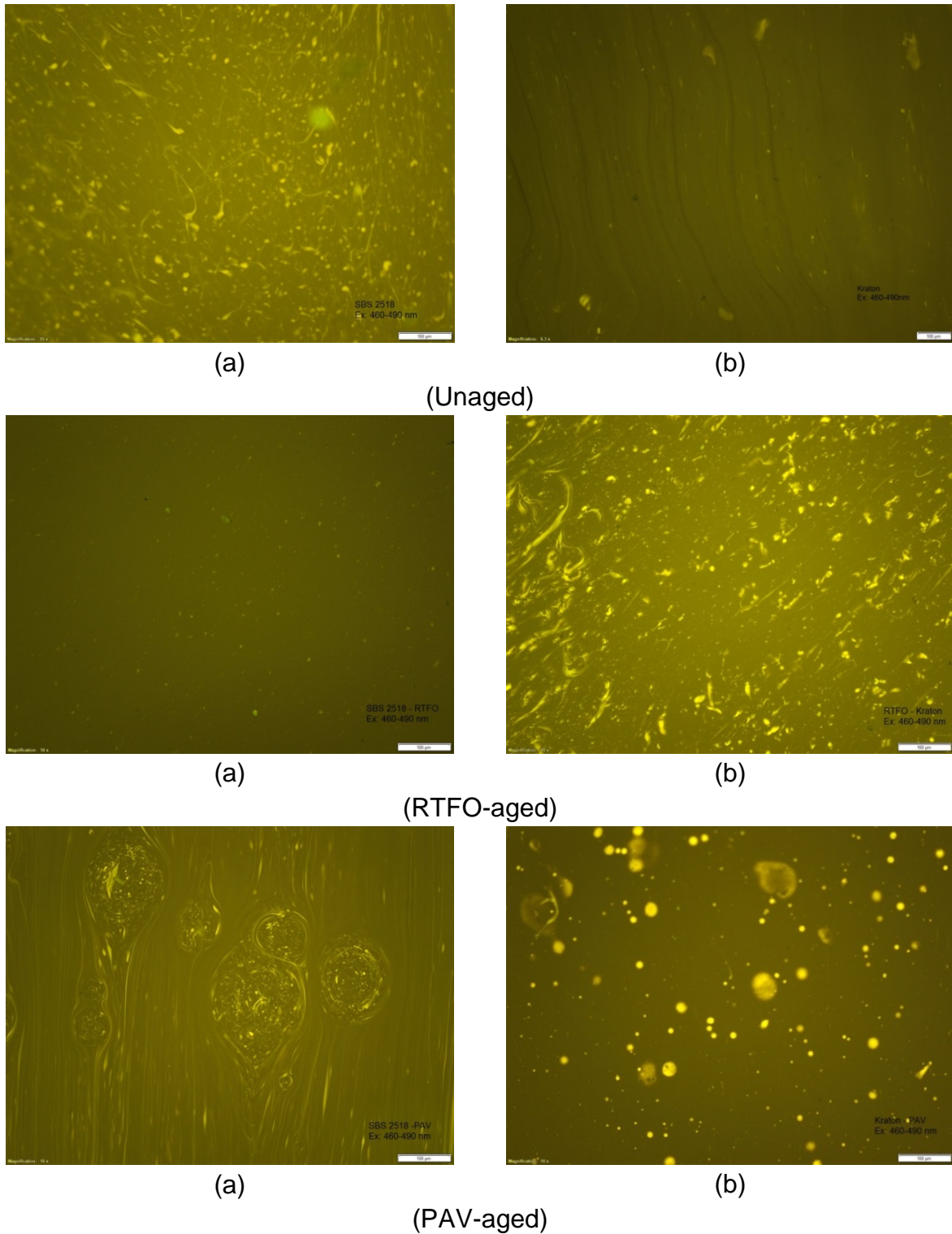


Figure 20: Fluorescent images of (a) SBS (Vector® 2518) and (b) SBS (Kraton® D1184 ASM) in bitumen.

CONCLUSION

Epi-fluorescence microscopy, as discussed in this paper, proves that different modifiers exhibit different morphologies in bitumen. This morphology depends on the nature of the polymer, the nature of the base binder, the polymer content, the compatibility between the bitumen and the polymer and the mixing conditions. Different morphological properties of PMBs will inevitably affect their rheological, storage and ageing properties.

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