ANALYTICAL TECHNIQUES TO QUANTIFY MODIFIERS IN BITUMEN FOR THE SOUTH AFRICAN ASPHALT PAVEMENT INDUSTRY

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ABSTRACT

Modifying bitumen is currently a common practice in South Africa. The asphalt pavement industry has seen an increase in use of different types of modifiers in an attempt to improve or extend the properties of bitumen. Common modifiers used in South Africa include plastomers (e.g. ethylene vinyl acetate or EVA), elastomers (e.g. styrene-butadiene-styrene or SBS) and warm mix additives (e.g. waxes). Bitumens are already complex materials which can be represented mechanically and rheologically with mathematical models. Recently, the need to also characterise the *in situ* structural and chemistry effect of modifiers within bitumen has been appreciated, in order to determine their influence on modified bitumen performance. This paper explores the analysis of bitumen with various modifiers using Fourier Transform Infra-Red (FTIR) spectroscopy and Differential Scanning Calorimetry (DSC). Special attention is paid to quantification of these modifiers in bitumen as a quality control and forensic investigative tool, due to the current asphalt failure challenges facing the industry. The aim is to accurately determine the extent of modification through analytical techniques as a monitoring tool for the better construction of asphalt pavement roads. The paper shows such analytical scientific techniques have the potential to quantify locally used modifiers in South African bitumen.

Keywords: Modified Bitumen, Modifier Quantification, Fourier Transform Infra-Red (FTIR) spectroscopy, Differential Scanning Calorimetry (DSC).

1. INTRODUCTION

The current practice in the asphalt pavement industry utilises empirical physical tests such as softening point, elastic recovery (TG1, 2019) and force ductility (Mturi & Ngkapele, 2013) to give an indication of the level of modification in bitumen. With the increase in grades of modifiers, this approach can be misleading (Mturi et al., 2017). More scientific techniques

are required that can accurately quantify modifiers, both as a quality control and a forensic investigative tool.

Enthalpy changes during heating/crystallization of wax modifiers can be measured using Differential Scanning Calorimetry (DSC) techniques (Sellers, 2009). Based on the Fourier Transform Infra-Red (FTIR) absorbance, ethylene vinyl acetate (EVA) and styrene-butadiene-styrene (SBS) modifiers can be detected. When the pure modifier is available, standards of known quantities can be prepared and the percentage modifier content in unknown bitumen samples can be determined.

This paper introduces analytical techniques for the quantification of commonly used modifiers in South Africa, for bitumen refined nationally. Commonly used grades for wax, EVA and SBS modifiers were selected and added in bitumen as per the typical ranges used by the South African asphalt pavement industry. Calibration curves were developed and used to quantify modifiers present in unknown bitumen samples obtained from industry.

2. BACKGROUND

DSC evaluates the heat flow of a sample enabling the detection of a physical transition in a material. The principle involves heating both the test sample and a reference at the same temperature and measuring the difference in heat flow. Previously, the heat flow was done with DTA (Differential Thermal Analyser) which involved a thermometer being placed in a material inside an oven. The technique was further developed to Boersma DTA, which consists of a fixed thermocouple differential thermal analyser. Further improvements resulted in a technique named DSC which is power controlled (PerkinElmer, 2013). The use of the DSC technique to measure enthalpy changes of waxes has been widely reported in literature (Noel et al., 1970, Edwards et al., 2003, Lu et al., 2004, Soenen et al., 2013 and Alcazar-vara et al., 2013).

Infrared spectroscopy is based on the absorption of infrared light by a sample and measuring the absorbed radiation at different frequencies. The bonds of molecules absorb light at unique frequencies, resulting in characteristic peaks. Traditional infrared spectroscopy was based on splitting light with a prism and the spectrum was photographed. Modern spectroscopy records the spectrum digitally (Hunt R, 2017) and these have notably improved the characterisation of samples. For unknown samples, these peaks can be compared to the spectral database for identification, and the standard curve of known concentrations enables quantification (Mathias, 2015). FTIR has been successfully used in the quantification of EVA and SBS polymers (Yu and Buttons, 1988, Curtis et al., 1995, Choquet and Ista, 1992 and Masson J.F, 2001).

3.   MATERIALS AND METHOD

3.1. Bitumen preparation

The binder was heated in an oven until fluid and stirred using a spatula to ensure a homogenous sample. Once fluid, the sample was placed on a hot plate, stirred using a pedal stirrer and heated to temperature as per TG1 (2019) recommendations. Once it had reached the set temperature, the required amount of modifier was added and the mixture was then blended for a further 2-4 hours.

The base bitumen was an unmodified 50/70pen grade bitumen. In instances where more than a single source of the base bitumen was used, the samples were labelled as bitumen 1, 2, etc. Commonly used grades of wax (i.e. Sasobit®), EVA (i.e. Arkema Evatane® 20-20) and SBS (i.e. Kraton) were selected. They were blended with bitumen in the typical range used by the industry of between 1- 5% (m/m).

3.2. Apparatus and procedure

FTIR spectrometer:
- Two different models of FTIR spectrometers were used in this paper: a Bruker V70 (figure 1) and a Perkin Elmer Spectrum 100 (figure 2).
- After setting-up the instrument, the following criteria were used: wavenumber ranging from $550cm^{-1}$ to $4000cm^{-1}$, 32 scans and a resolution of $4cm^{-1}$
- To run a test, the following procedure was followed:
  - Run the background spectrum.
  - Add a spatula tip of a sample directly on the germanium crystal.
  - Twist the sample press to ensure that the diamond is in contact with the sample.
  - Set the pressure gauge to 130 (percentage based) for each run.
  - Baseline correct the obtained results.
  - When using the ATR, take the smallest amount of sample should be enough to cover the ATR crystal.

Figure 1: **FTIR spectrometer (Bruker V70)**

Figure 2: FTIR spectrometer (Perkin Elmer Spectrum 100) with an ATR

Differential Scanning Calorimetry (figure 3):
- About 5.7 – 7.1mg of sample gets weighed into a DSC sample pan and hermetically sealed, with a matching pan and lid used as a reference.
- The sample gets heated to 120˚C at 10˚C/min and kept at this temperature for 5min.
- Sample then cooled to -20˚C at 10˚C/min and heated again at the same rate to 120˚C and kept at that temperature for 5min.
- The melting enthalpies are then calculated

Figure 3: The DSC instrument used for thermal analysis of samples

4. RESULTS AND ANALYSIS

4.1. Modifier Characterisation

Waxes exhibit notable melting and crystallization peaks (see figure 4). The melting peaks are a result of an endothermic process during heating, where a solid-liquid transition of a sample is observed. The crystallization peak is due to an exothermic process which occurs during cooling and results in a phase transition of liquid to solid. When energy is absorbed or released by a sample, it results in the melting and crystallization peaks observed with a DSC.

The FTIR spectra of pure unmodified bitumen (see figure 5) and a pure EVA are combined in figure 6. The EVA FTIR spectrum consists of characteristic peaks at $1739cm^{-1}$ and $1242cm^{-1}$ that corresponds to C=O and C-O-C ester groups, respectively. Other notable peaks occur at $1376cm^{-1}$, $1456cm^{-1}$, $2851cm^{-1}$ and $2921cm^{-1}$. A distinctive peak at $1601cm^{-1}$ is associated with double bonds of benzene rings in unmodified bitumen, and this peak is absent in the EVA spectrum. The absorbance peaks at $1376cm^{-1}$ and $1456cm^{-1}$ are common in both EVA and the bitumen spectra, therefore these two peaks cannot be utilized as distinctive peaks.

The presence of SBS in bitumen is characterised by peaks at 966 cm^{-1} and $699/700 \text{ cm}^{-1}$ (see figure 7). The peak at 966 cm^{-1} is due to the carbon double bonds (C=C) in butadiene while the $699/700 \text{ cm}^{-1}$ peak indicates the presence of C-H bond in styrene.
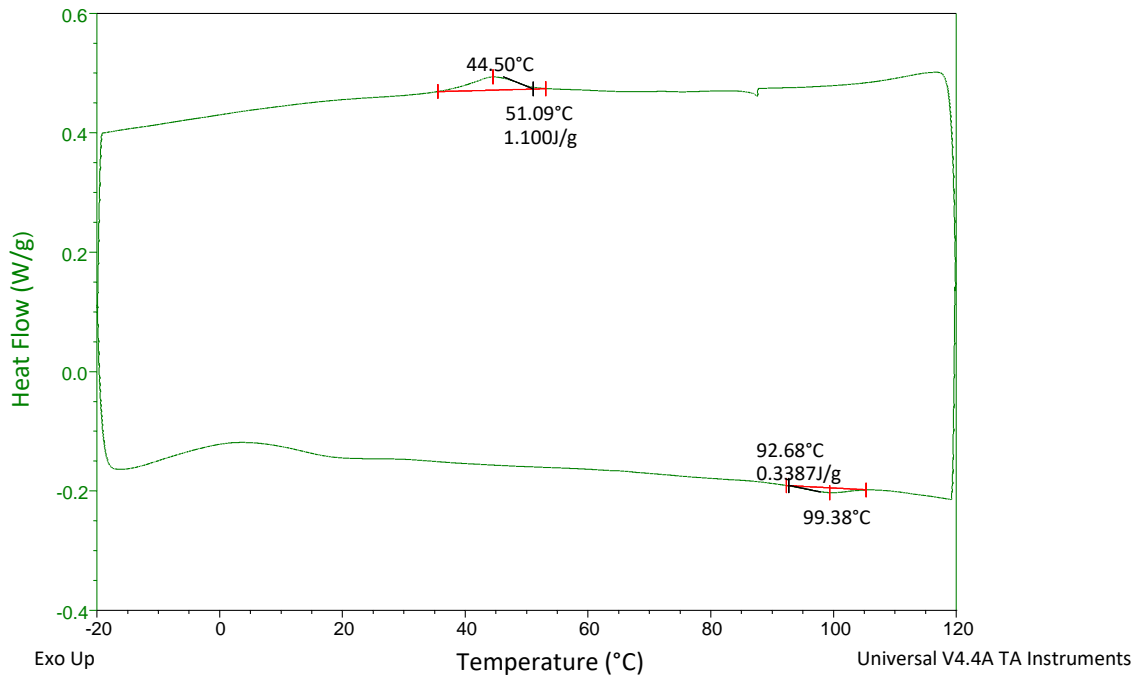
Figure 4: A DSC curve showing melting and crystallization peaks of a wax
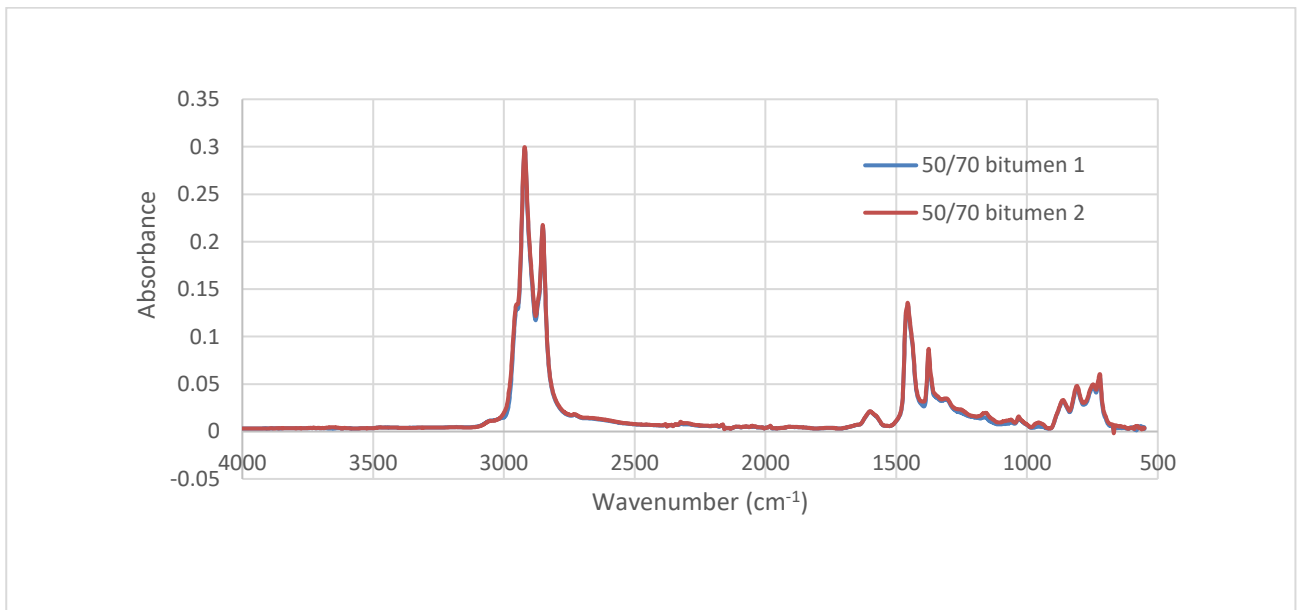

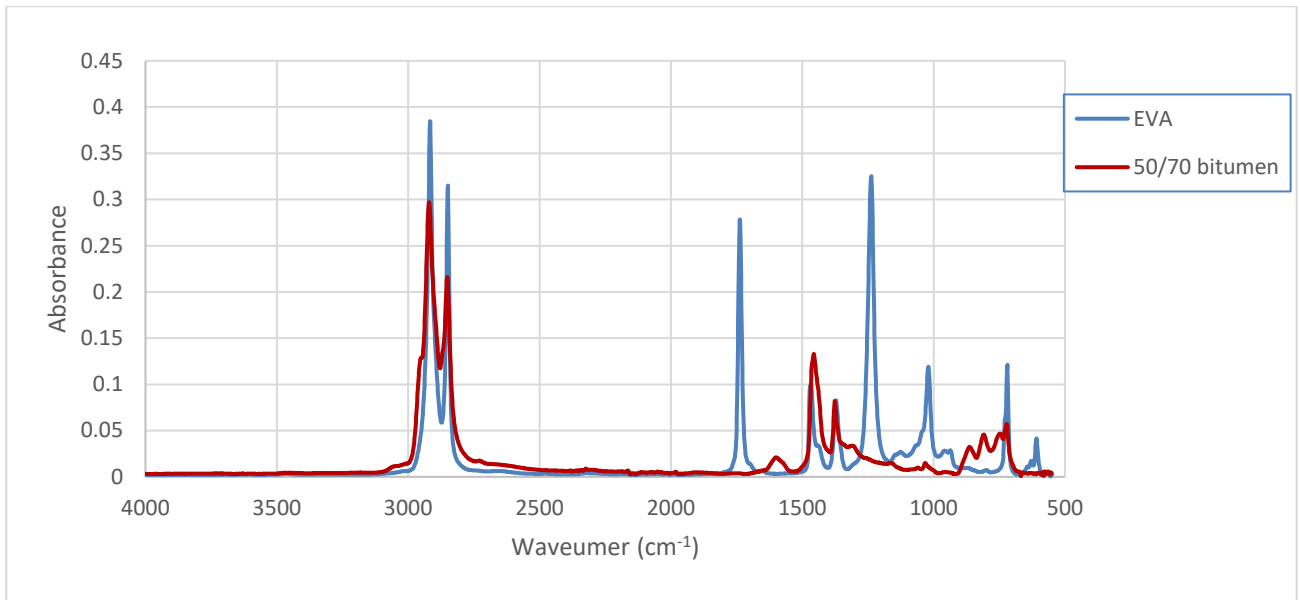**Figure 5: FTIR spectra of a pure 50/70pen grade bitumen**

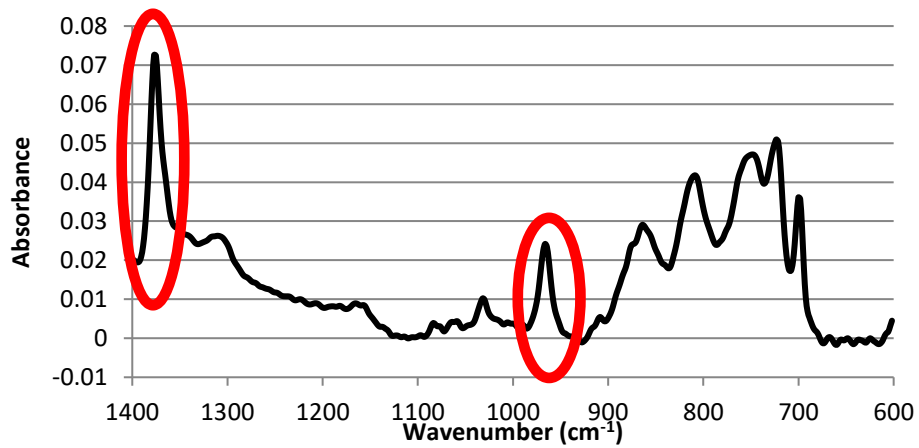**Figure 6: Comparison of FTIR spectra of pure EVA and unmodified binder**

Figure 7: FTIR spectra of an SBS modified bitumen showing characteristic SBS peaks at 966cm^{-1} and 1375cm^{-1}

4.2. Calibration Curves

In order to develop calibration curves, pure bitumen had to be tested with different percentages of modifiers.

4.2.1. Wax quantification

With an increase in wax content, the modified bitumen exhibited an increase in peaks observed during both the melting and crystallization cycle – see Figure 8. The calculated melting temperatures and enthalpy values are shown in Table 1. The developed calibration curve is shown in figure 9, which can be used to calculate the wax content of any unknown blend of the wax modifier in bitumen.

As a commonly used empirical property in South Africa, the softening points of the blends were tested and are shown in Table 2. They show the blend at 5% wax needs to be re-blended using a different procedure to achieve better homogeneity that would result in an increase in softening point. This highlights the need to characterise the dispersion during such exercises.
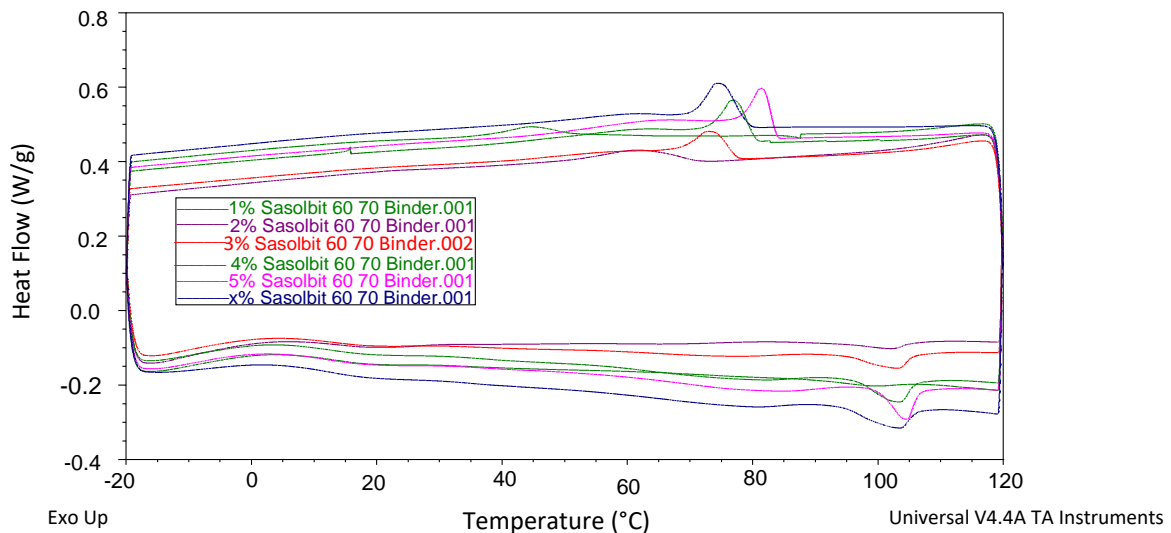

Figure 8: The DSC results of 1-5% blended samples and the unknown sample

Table 1: Calculated results of the bitumen samples

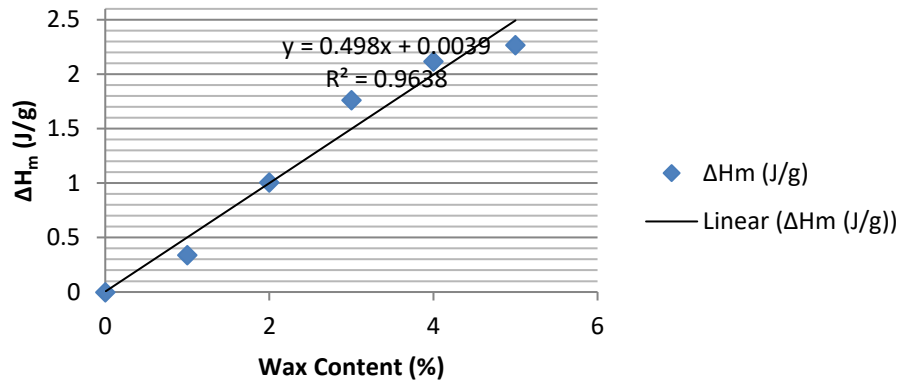| Wax Content (%)	Melting enthalpy (J/g)	Melting temperature (°C)
0	0	-
1	0.339	99.38
2	1.007	102.09
3	1.762	103.24
4	2.119	103.44
5	2.267	104.43

Figure 9: Calibration curve of the melting enthalpies of the known blended samples

Table 2: Softening points at different wax contents

Wax Content (%)	Softening Point (°C)
0	48.2
1	54.4
2	63.4
3	74.2
4	82.6
5	82.2

4.2.2. SBS quantification

Figure 10 shows FTIR spectra of 1-5% SBS in bitumen. For the quantification of SBS in bitumen, calibration curves are developed from the absorbance ratio in Table 3, using peaks at 966 cm^{-1} and 1375 cm^{-1}. The use of absorbance ratios minimizes errors from baseline correction and peak area resolution. The developed calibration curve is shown in figure 11, and the correlation is adequate for the quantification of unknown samples of the SBS modifier in bitumen.
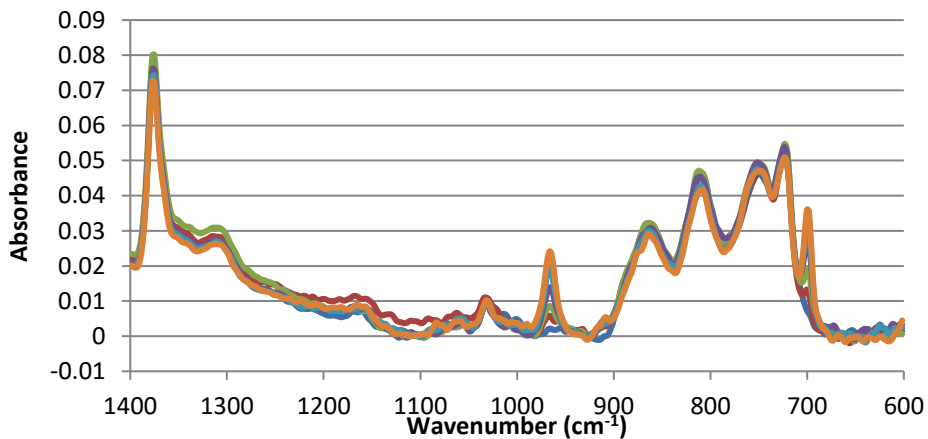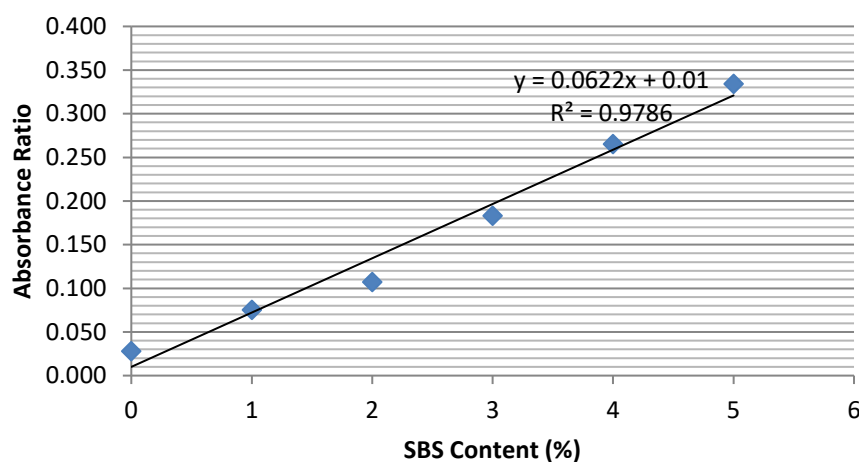

Figure 10: FTIR spectra of 1-5% SBS in bitumen

Table 3: Peak ratio results

	966	1375	Ratio
0%	0.0022	0.0776	0.028
1%	0.0059	0.0779	0.075
2%	0.0086	0.0801	0.107
3%	0.0139	0.0759	0.183
4%	0.0197	0.0741	0.265
5%	0.0242	0.0723	0.334

Figure 11: A calibration curve using the absorbance ratio at the wavenumbers of 966 cm^{-1} and 1375 cm^{-1}.

4.2.3. EVA quantification

Samples containing 0-5% EVA in bitumen were prepared. The absorbance peaks observed at 1242 cm^{-1} and 1739 cm^{-1} indicates the presence of EVA, as shown in Figure 12. The absorbance ratios were calculated from an average of three measurements at the following EVA FTIR wavelengths: 1739cm^{-1} and 1242cm^{-1}; to those at the bitumen FTIR wavelengths: 1601cm^{-1} and 2851cm^{-1}. The use of different peaks to determine absorbance ratios assessed whether the variation in the results could be reduced by the selection of peaks. The resultant calibration curves from the absorbance ratio at the wavelengths of 1739/1601 cm^{-1} are shown in Figure 13; at the wavelengths of 1739/2851 cm^{-1} are shown in Figure 14; and at the wavelengths of 1242/2851 cm^{-1} are shown in Figure 15. All the three calibration curves have appropriate correlations to quantify the EVA modifier in bitumen. The best COV of 1% was achieved at 1739/1601 cm^{-1}, whereas the COV of 4% and 8% were obtained at 1739/2851 cm^{-1} and 1242/2851 cm^{-1} respectively. This highlights the importance of selecting peaks were only a single component absorbs (i.e. either EVA or bitumen), as opposed to wavelengths where both components show absorbance.
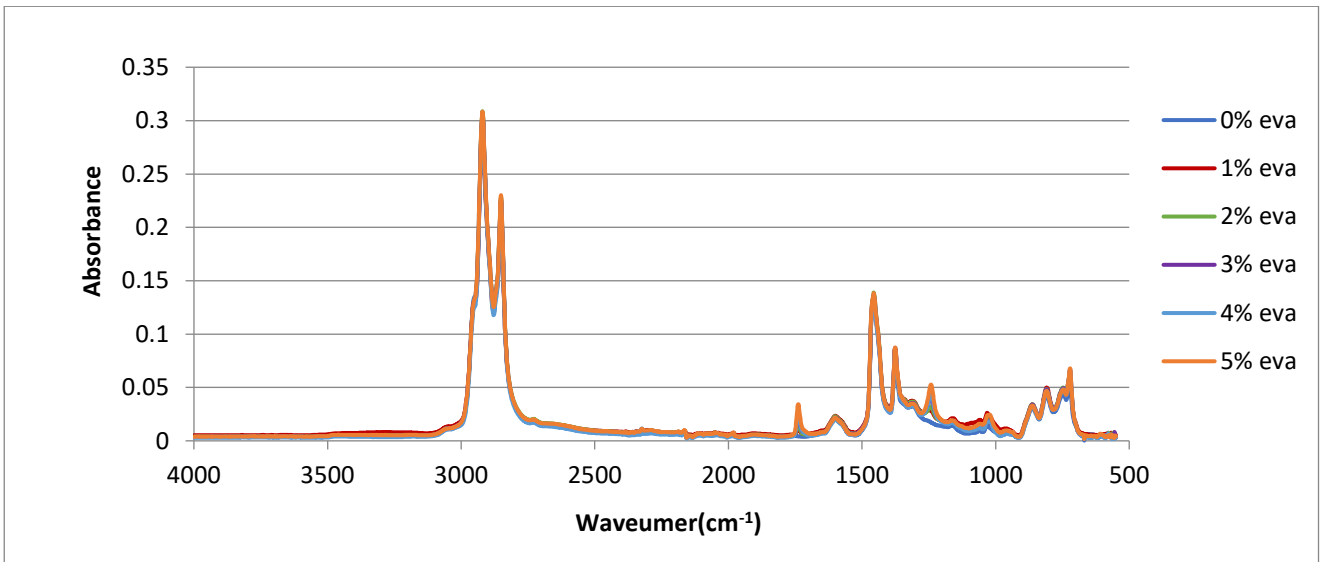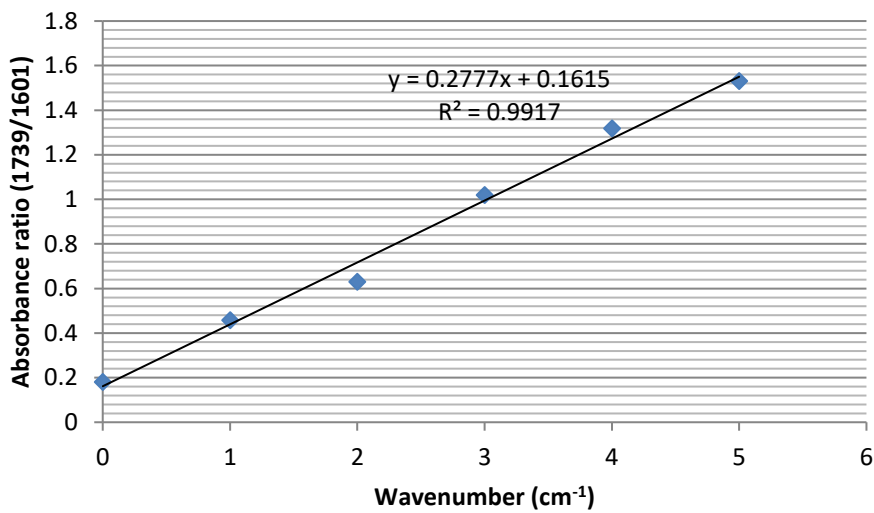
Figure 12: FTIR spectra of 1-5% EVA in bitumen

Figure 13: The calibration curve of EVA content vs absorbance ratio the absorbance ratio at the wavelengths of 1739 cm⁻¹ and 1601 cm⁻¹
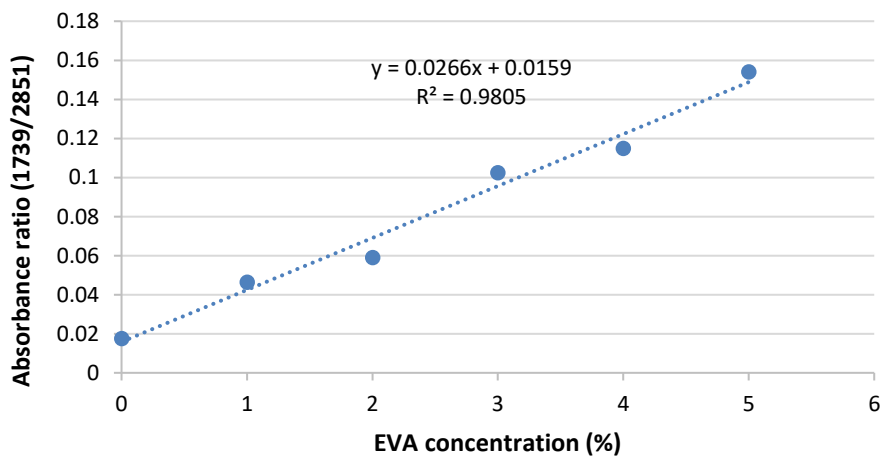

Figure 14: The calibration curve of EVA content vs absorbance ratio the absorbance ratio at the wavelengths of 1739 cm⁻¹ and 2851 cm⁻¹
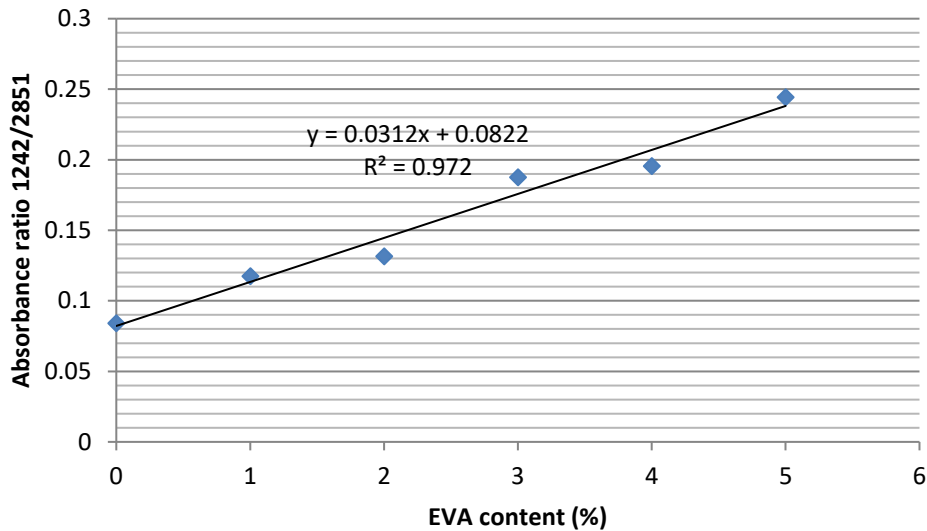
Figure 15: The calibration curve of EVA content vs absorbance ratio the absorbance ratio at the wavelength 1242 cm^{-1} and 2851 cm^{-1}

Using calibration curves; wax, EVA and SBS modifiers were quantified in unknown modified bitumen samples received from industry, as shown in Table 4. The actual modifier contents were obtained by consulting with suppliers and technicians. At times the determined modifier content seems close to that given by the source, but they can vary significantly in other instances.

Table 4: Calculated vs actual modifier content in bitumen

Modifier	Determined Modifier Content (%)	Actual Modifier Content (%)
Wax	4.16	~4.0
SBS	2.81	2.9
EVA	2.59	1.8-2.2
EVA	2.46	1.8-2.2
EVA	2.60	1.8-2.2

4.3.   Ageing Characterisation

The contribution of modifiers in pavement cracking requires characterisation of the chemical (oxidative) and reversible (wax crystallization, free volume collapse, asphaltene precipitation, phase separation) field ageing of the asphalt bitumen in the laboratory.

Chemical changes of bituminous binders can be characterised by analysing the change in functional groups before and after ageing. Oxidation of bitumen results in the formation of carbonyl (ketone) and sulfoxide compounds which are centred at 1700cm^{-1} and 1030cm^{-1} respectively (Dondi, 2016). This is due to the reaction of oxygen with perhydroaromatics resulting in hydroperoxides, which in turn results in the rapid formation of ketones and sulfoxides (Singh, 2017). During ageing, the increase of these   compounds in unmodified binder is more than that of modified binders. PMBs tend to reduce the formation of these compounds thus enhance the ageing resistance (Singh, 2019). This inhibits the oxidation process by disrupting the interaction of oxygen and binder molecules (Singh, 2019). The infrared indexes used to calculate changes in base bitumen and polymer functional groups are calculated according to the equations (Singh, 2017, Singh, 2019) below.

$$I_{C=O} = \frac{Carbonyl\ band\ area\ centred\ at\ 1700cm^{-1}}{\sum area\ of\ spectral\ bands\ between\ 2000\ and\ 600cm^{-1}} \quad\quad (1)$$

$$I_{S=O} = \frac{Carbonyl\ band\ area\ centred\ at\ 1030cm^{-1}}{\sum area\ of\ spectral\ bands\ between\ 2000\ and\ 600cm^{-1}} \quad\quad (2)$$

$$I_{SBS} = \frac{Area\ of\ spectral\ band\ around\ 966cm^{-1}}{\sum area\ of\ spectral\ bands\ between\ 2000\ and\ 600cm^{-1}} \quad\quad (3)$$

$$I_{EVA} = \frac{Area\ of\ spectral\ band\ around\ 1242}{\sum area\ of\ spectral\ bands\ between\ 2000\ and\ 600cm^{-1}} \quad\quad (4)$$

More recently, simple variable-temperature FTIR techniques have been used to study the effect of wax crystallization and melting on thermo-reversible ageing of bitumen at cold temperatures (Ding & Hesp, 2020). Bitumen FTIR peaks at 710-735 cm^{-1} (reflecting the amorphous linear paraffin fraction in bitumen) can be studied throughout the South African in-service temperatures to yield important information on wax behaviour and its contribution towards the in-situ ageing of the asphalt binder, as shown in Figure 16.

Quantification of these ageing mechanisms in the asphalt bitumen can be used as a quality control and forensic investigative tool to better understand the current asphalt cracking failures facing the industry.

Determination of wax content and WPT (wax precipitation temperature) are accomplished by integration of two peaks area range, 1402 cm^{-1} and 1324 cm^{-1} (S1) and 735 cm^{-1} and 715 cm^{-1} (S2). The reduced spectral area (S2/S1) is determined and plotted against temperature, whereby a WPT is obtained. Oxidation results in an increase of WPT (Ding & Hesp, 2020).
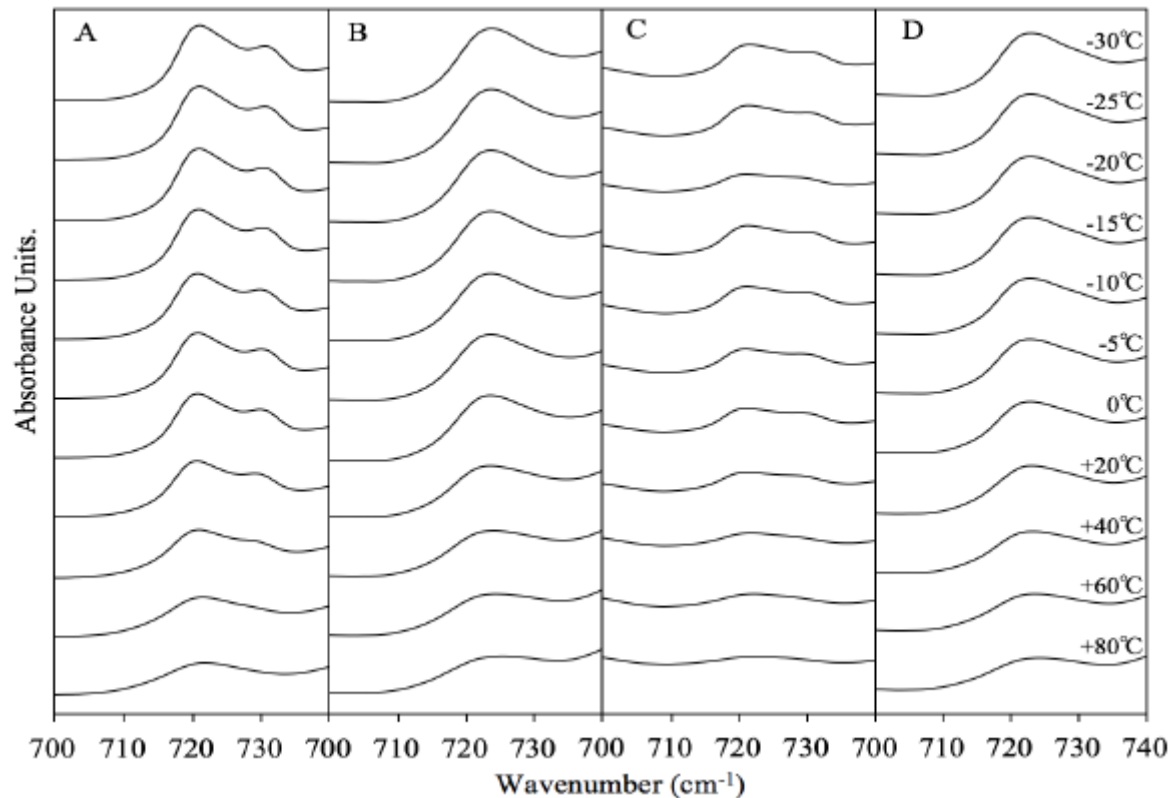
Figure 16: FTIR spectra of PAV-aged asphalt binders cooled from +80 °C to ‑30 °C (Ding & Hesp, 2020).

5.   CONCLUSIONS & RECOMMENDATIONS

Previous South African studies (Mturi et al., 2017) have shown the use of different grades of modifiers makes it a challenge to relate empirical physical properties to the level of modification. Based on the experimental results and discussions, the following conclusions can be given:

(1) Based on the chemistry of the modifier, this paper shows that modern techniques such as spectroscopy and calorimetry have sufficiently advanced to qualitatively as well as quantitatively identify and quantify modifiers, respectively.

(2) The results show these analytical methods have potential, with further development. The investigation also highlights the need for appropriate modifier/bitumen peak selection and repeat testing to identify and eliminate outliers. In addition, method validation can also be determined with modified binders exhibiting different dispersions.

(3) Determination and quantification of the ageing mechanisms of asphalt binders can be used as a quality control and forensic investigative tool to better understand the current asphalt cracking failures facing the industry. It will enable the industry to select asphalt binders less susceptible to the ageing expected locally.

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