

Impact of asphaltene chemistry on bitumen properties

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Abstract

It is known that asphaltenes have a large influence on bitumen properties and consequently pavement performance. Many studies have focused on the asphaltenes as a single solubility class with no differentiation between the types of asphaltenes. Recent research has looked at sub-dividing asphaltenes, based on their molecular weight or chemistry. Separation of asphaltenes into sub-fractions using the asphaltene determinator, has opened further possibilities to study the impact of asphaltene chemistry on bitumen properties. Our studies have focused on the quantitative separation of asphaltenes into their respective sub-fractions using a hot extraction technique with cyclohexane and toluene as the extraction solvents. The asphaltene sub-fractions obtained, referred to as ACYC and ATOL for the fractions soluble in cyclohexane and toluene respectively, were analysed for their chemical composition, stacking behavior and influence on basic bitumen properties. Interestingly, laboratory prepared bitumen based only on ATOL were found to be stiffer than those which contained only Acyc, at similar asphaltene concentration levels. This highlighted the effect of asphaltene chemistry on the performance of bitumen. Asphaltenes formed on maltene oxidation was also studied. Interestingly, it was observed that the rate of formation of new asphaltenes was not influenced by the penetration of the original bitumen. The influence of the asphaltenes formed by the oxidation of the maltenes, as compared to the oxidation of the asphaltenes present in the parent bitumen, on bitumen properties was also studied. It was seen that the oxidation of the asphaltenes already present in the bitumen had a greater impact on the properties of the bitumen as compared to the asphaltenes formed on oxidation of the maltenes. The chemistry of asphaltene sub-fractions on the performance of bitumen will be further investigated to enable tailoring of bitumen from the molecular level, allowing for bitumen to be manufactured with specific properties and maintaining quality.

1. INTRODUCTION

Asphaltenes are known to influence bitumen properties. The studies looking at the effect of asphaltenes on the softening point and penetration [1], viscosity [2][3][4] and temperature susceptibility and thermal stability [5] have shown that the asphaltenes have a large influence on these properties. A number of studies have focussed on the effect of asphaltene concentration as well as their source on bitumen properties [1] [6].

The composition of bitumen, focussing on the asphaltene fraction, was further studied and the impact of compositional variations was discussed by Read et. al., which showed that the rheological properties of bitumen was strongly dependant on the asphaltene fraction [7]. Artificial bitumen samples were prepared by Hofko et. al., with varying asphaltene concentrations to study creep and viscoelastic behaviour [8][9], which again demonstrated the impact of the asphalt fraction on bitumen properties. Hofko et. al. also studied the morphology of the samples as a function of the asphaltene content using atomic force microscopy. These studies indicated that the asphaltene fraction of the bitumen was responsible for imparting stiffness and elasticity to the bitumen.

Recent studies have shown a statistical correlation between the molecular weight and aromaticity of asphaltenes and the zero-shear viscosity [10]. Recent work by Schabron et. al. has shown that asphaltenes can be divided into sub-fractions based on their solubility parameters [11][12]. The separation of asphaltenes involved deposition on a non-interacting chromatographic column, followed by sequential extraction of the asphaltene sub-fractions in solvents with increasing solvent power i.e. ability to dissolve a solute – in this case the asphaltenes. It was seen that the aromaticity of the extracted asphaltenes increased along with the solubility parameters of the solvents used to separate the asphaltene sub-fractions.

The ability to separate the asphaltenes into sub-fractions based on their solubility allows the study of the effect of asphaltene chemistry on bitumen properties. The question of the impact of differences in asphaltene chemistry, of asphaltenes from the same bitumen, on the properties of the bitumen remains largely unanswered in available literature. The present study investigates the impact of asphaltene sub-fractions by preparing a model bitumen at comparable asphaltene concentrations. This would allow the impact of the chemistry of the asphaltene on bitumen properties to be studied.

Chemical changes, predominantly oxidation, are a major factor which influence bitumen properties after ageing. This is an important aspect as ageing occurs during asphalt production and pavement installation, as well as the during the life of the pavement. As the bitumen in pavements oxidises it leads to an increased pavement stiffness which could potentially result in premature pavement failure or a shorter pavement life [13]. A deeper understanding of the asphaltenes formed upon ageing, and their impact on the behaviour of aged bitumen, would be the first step in trying to influence the ageing of bitumen and hence potentially increasing the life and performance of pavements, by controlling the increase in stiffness and elasticity caused by bitumen ageing.

2. MATERIALS AND METHODS

2.1. Raw materials

Six bitumens were chosen for the study, the properties are given in Table 1. The penetration and the softening points were measured following the ASTM D5/ EN1426 and ASTM D 36 methods respectively. The penetration index of the prepared model bitumen was calculated using the measured penetration and softening point values [1]. The composition of the samples, reflected by the saturate, aromatic, resin and asphaltene contents (SARA), was determined using the IP143 followed by the IP368 protocols. The saturate, aromatic and resin fractions had a repeatability of 1%, while that for the asphaltene fraction was found to be 0.1%.

Table 1: Characterisation of bitumen

Property	B1	B2	B3	B4	B5	B6
Penetration at 25 °C, dmm	180	20	7	15	77	81
Softening point, °C	46.4	70.0	92.5	70.8	49.4	49.2
Composition of bitumen						
Saturate content (%)	11.5	11.6	8.1	9.1	10.9	13.1
Aromatic content (%)	55.8	52.9	40.3	43.3	58.2	58.5
Resin content (%)	16.8	27.1	17.5	25.8	17.6	15.6
Asphaltene content (%)	15.9	8.3	34.1	21.8	13.3	12.8

2.2. Separation of asphaltene sub-fractions

The asphaltenes were separated from the bitumen using n-heptane (1:40 w/vol), refluxed for 30 minutes. The n-heptane – bitumen mixture was then allowed to cool and once cooled to ambient temperature, the asphaltenes were separated by filtration, using a 0.45 µm cellulose acetate filterpaper. The separated asphaltenes were washed with hot heptane in a Soxhlet extraction apparatus to remove any residual maltenes. These asphaltenes have been referred to as A_{HEP} . The A_{HEP} were dried and extracted with hot cyclohexane using the Soxhlet setup. The asphaltenes soluble in the hot cyclohexane have been referred to as the A_{CYC} . The remaining asphaltenes were then dried and extracted with toluene, using a similar technique. These asphaltenes have been referred to as A_{TOL} . It was seen that after extraction with hot toluene there was no asphaltene residue in the filterpaper. The solution of asphaltenes in the various solvents were concentrated using a rotary evaporator and then the concentrated solution was poured into n-heptane (1:40 volume ratio of concentrated solution to n-heptane) to precipitate the asphaltenes from the solution. The precipitated asphaltenes were filtered, dried and used further.

2.3. Preparation of model bitumen

A model bitumen was prepared by following the procedure outlined by Yu et al [14]. The A_{HEP} was blended back into the maltenes of B1 and B3 at the asphaltene mass fraction of the original bitumen. The penetration and the softening point of the reconstituted model bitumen were found to be comparable with those of the original bitumen. This indicated that the process followed to prepare the model bitumen did not result in changes to the components which were reflected in the bitumen properties.

A range of model bitumen samples were prepared by blending the asphaltene sub-fractions into the maltenes at a 25, 50, 75 and 100 % mass fraction of the original concentration of A_{HEP} present in the individual samples. For example, for a sample which had 10 % A_{HEP} , a model bitumen was prepared with 2.5, 5, 7.5 and 10 % of the asphaltene sub-fractions.

2.4. Methodology

The asphaltenes and bitumens (B1 to B6) were analysed for their carbon, hydrogen and nitrogen content following ASTM D5291. The oxygen content was determined using the ASTM D5622 method and sulphur determined using ASTM D5453. The reproducibility of the carbon content was 0.1 % and that of hydrogen and oxygen was 0.05 %. The nitrogen and sulphur content had a repeatability of 0.08 %. The results of the elemental analysis were used to calculate the hydrogen to carbon (H/C), oxygen to carbon (O/C) and oxygen to hydrogen (O/H) atomic ratios.

The powder X-ray diffraction spectrum of the asphaltenes was measured using a Cu $K\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) in the scan range of $2\theta = 5^\circ - 80^\circ$. The spectrum obtained showed poor resolution of the peaks corresponding to the aromatic and aliphatic ordering and hence a deconvolution was carried out following a Lorentzian fitting equation [15]. The three major bands γ , [002], and [100] peaks positioned at around $2\theta = 20, 25, \text{ and } 44^\circ$ respectively were used as the initial estimates for the Lorentzian fitting. Then the peak positions, full width at half-maximum (FWHM) were calculated. The average aromaticity (f_a), interlayer distance between the aromatic sheets $d[002]$, distance between the aliphatic portions (d_y), diameter of the aromatic portions (L_a), for asphaltenes was calculated using the protocol set out by Fu Yen et. al. [16] and Schwarger et. al. [17].

The concentrations of asphaltene sub-fractions present in the bitumen used in the study were determined using the asphaltene determinator method outlined by Schabron *et al.* [11][12].

2.5. Rheological characterisation

The rheological measurements were conducted on a strain-controlled dynamic shear rheometer fitted with an air bearing mechanism which applies torque to the specimen being tested. The dynamic shear rheometer could measure rheological properties of materials within a torque range of 0.1 μNm - 230 mNm . In case of bitumen samples, the lowest torque value up to which data was taken is 1 μNm . The upper PG temperatures were those temperatures at which the stiffness of the material, as reflected by the $G^*/\text{Sin}\delta$, were greater than 1.0 kPa.

2.6. Asphaltene formation on short term ageing

The rate of asphaltene formation on oxidation of the sample was studied by conducting multiple rolling thin film oven tests (RTFOTs) on the maltene fraction of the sample. The aged maltenes were sampled and analysed at intermediate time intervals using the Asphaltene Determinator, SARA content and the elemental composition.

2.7. Method to oxidise asphaltenes

A pressure ageing vessel (PAV) was used to oxidise asphaltenes which were dispersed in *a*-methylnaphthalene (AMN). AMN was chosen as the solvent as it would not vapourise during the course of experiments in the PAV. 5 % (w/v) solutions of asphaltenes were prepared in AMN. The PAV containing the solutions of the asphaltenes in AMN was maintained at 60 °C for 24 hours. After oxidation in the PAV, the AMN solutions were allowed to cool and then the asphaltenes were precipitated in *n*-heptane. These asphaltenes were then dried and a model bitumen prepared using the procedure outlined in section 2.3.

It was observed that the change in softening point obtained for bitumens B1 and B3 using the PAV oxidation method was similar to that obtained after subjecting the samples to the RTFOT (ASTM D 2872/ EN 12607-1).

3. RESULTS AND DISCUSSION

3.1. Asphaltene separation

The asphaltene determinator is an analytical tool and is not suitable to separate the quantities of asphaltene sub-fractions required to prepare the model bitumen, which could then be used for some of the standard bitumen tests. Similarly, the use of a preparatory asphaltene determinator column, as set up by Schabron *et al* [11], would not be suitable to separate the quantities of asphaltene sub-fractions required. An alternate method, based on the principles of the asphaltene determinator, was used and referred to as the hot extraction method.

It was observed that there was a difference between the quantities of the A_{TOL} and A_{CYC} extracted using the hot extraction method and the asphaltene determinator, see Table 2. The asphaltene determinator uses a sequential series of solvents with increasing solubility parameters at ambient temperatures. However, the hot extraction method, as the name suggests, extracts asphaltene sub-fractions using hot solvent. The difference between the amount of asphaltene sub-fractions extracted using the two methods could be due to the use of hot solvent as compared to solvent at ambient temperatures.

Of the six samples considered only three could be separated into A_{TOL} and A_{CYC} sub-fractions (explained in Section 3.2), while the asphaltenes of the other three samples were completely soluble in cyclohexane. The asphaltenes from samples with the lowest starting penetration values and the other with the highest penetration value were separated into the two sub-fractions. The penetration value of the original bitumen samples was not related to the presence of the asphaltene sub-fraction.

Table 2: Separation of asphaltenes into sub-fractions

Asphaltenes extracted from	Asphaltene Determinator			Reflux Extraction Method		
	<i>A_{CYC}</i> fraction (%)	<i>A_{TOL}</i> soluble fraction (%)	<i>A_{DCM}</i> soluble fraction (%)	<i>A_{CYC}</i> fraction (%)	<i>A_{TOL}</i> soluble fraction (%)	<i>A_{DCM}</i> soluble fraction (%)
B1	31.20	57.73	11.08	23.62	76.38	0
B2	41.08	53.16	5.76	100	0	0
B3	11.37	59.30	29.33	29.83	71.17	0
B4	15.63	63.99	20.39	24.41	75.59	0
B5	42.39	49.72	7.89	100	0	0
B6	35.08	54.92	10.00	100	0	0

3.2. Asphaltene characterisation

The elemental composition of the bitumens used in the study is given in Table 3. The degree of aromaticity of the samples are reflected by the atomic ratio of the hydrogen to carbon atoms i.e. the H/C atomic ratio. It was seen that the presence of the asphaltene sub-fractions in the bitumen was not related to the H/C atomic ratio of the bitumen. Asphaltene sub-fractions were present in samples B1, B3 and B4. Samples B5 and B6 had a H/C atomic ratio greater than samples B3 and B4, while sample B2 had a H/C atomic ratio lower than that for samples B3 and B4.

Table 3: Elemental composition of bitumen

Bitumen	C (%)	H (%)	O (%)	N (%)	S (%)	H/C
B1	83.97	10.18	0.59	0.51	4.75	1.45
B2	82.95	9.44	2.66	0.61	4.35	1.37
B3	83.24	8.65	2.85	0.70	4.57	1.25
B4	83.03	9.34	1.93	0.41	5.28	1.35
B5	82.93	9.85	1.39	0.42	5.4	1.43
B6	82.94	9.83	1.52	0.4	5.31	1.42

The A_{HEP} separated from the bitumen were also investigated for their elemental composition, see

Table 4. There was no clear link observed between the presence of the asphaltene sub-fractions and the degree of aromaticity, reflected by the A_{HEP} H/C atomic ratio. Although A_{HEP} from B2 and B3 has a higher aromaticity than A_{HEP} from B1, it was completely soluble in cyclohexane while sub-fractions could be separated from A_{HEP} from B2 and B3. Although the A_{HEP} from B1 had a lower aromaticity as compared to B2 and a comparable aromaticity to B5, B1 could be separated into asphaltene sub-fractions while the A_{HEP} present in B2 and B5 were completely soluble in cyclohexane.

In addition to the aromatic nature of the asphaltenes, the ratio of electro-negative atoms to carbon atoms was determined. The asphaltenes from B1 were not highly aromatic but had a larger concentration of electro-negative atoms as compared to asphaltenes from B2, B5 and B6. This could explain the presence of the asphaltene sub-fractions in B1. On the other hand, the A_{HEP} from B3 and B4 were the most aromatic and this could explain the presence of asphaltene sub-fractions in these samples.

The results indicate that a combination of aromaticity and presence of electro-negative atoms in the asphaltenes could result in the presence of the asphaltenes sub-fractions. This is in line with the theory of the separation of the asphaltenes into the sub-fractions explained by Schabron et al. The solubility parameters of the solvents used take into account both the aromaticity and the electro-negative atom content of samples [11]. Elemental composition of the asphaltene sub-fractions which were present in samples B1, B3 and B4 were determined, see

Table 4. The A_{CYC} , denoted as B- A_{CYC} , had a lower degree of aromaticity and electro-negative atom content than those in the A_{TOL} fraction, denoted as B- A_{TOL} . The combination of the increased aromaticity and electro-negative atom

content in the A_{TOL} could explain their insolubility in cyclohexane. This is in line with the hypothesis that a combination of aromaticity and heteroatom present in the asphaltenes would indicate the presence of A_{CYC} and A_{TOL} .

Table 4: Elemental composition of n-heptane asphaltenes and asphaltene sub-fractions

Asphaltenes separated from	C (%)	H (%)	O (%)	N (%)	S (%)	H/C	(SNO)/(CH)	(ON/C)
B1	82.78	7.28	1.18	1.21	1.45	1.06	0.015	0.023
B2	84.94	7.35	0.80	1.24	5.67	1.04	0.022	0.019
B3	84.88	6.97	1.44	1.21	5.90	0.99	0.026	0.025
B4	87.01	6.97	1.68	1.15	3.19	0.96	0.020	0.026
B5	83.20	7.42	0.77	1.00	7.62	1.07	0.025	0.017
B6	82.77	7.58	1.52	0.83	7.3	1.1	0.027	0.022
A_{CYC} asphaltene sub-fraction								
B1- A_{CYC}	82.89	7.51	1.21	1.15	7.23	1.09	0.027	0.023
B3- A_{CYC}	84.46	7.35	1.61	0.94	5.64	1.04	0.024	0.024
B4- A_{CYC}	86.49	7.56	1.6	1.12	3.2	1.05	0.019	0.025
A_{TOL} asphaltene sub-fraction								
B1- A_{TOL}	82.68	7.11	1.69	1.2	7.32	1.03	0.030	0.028
B3- A_{TOL}	84.98	6.09	1.94	1.08	5.92	0.86	0.029	0.028
B4- A_{TOL}	87.01	6.37	1.88	1.34	3.41	0.88	0.024	0.029

The two asphaltene sub-fractions i.e. A_{CYC} and A_{TOL} , are chemically dissimilar with respect to elemental composition. The impact of the elemental composition of the A_{CYC} and A_{TOL} on molecular aggregation was studied using the XRD, see Table 5. A representative comparison of XRD spectra obtained for A_{HEP} , A_{CYC} and A_{TOL} sub-fractions for B3 can be seen in Figure 1. It should be noted that the y-axis of the spectrum does not have any units as Figure 1 shows the differences in the shape of the spectrum observed between asphaltenes and asphaltene sub-fractions. The XRD spectra of the other asphaltenes and sub-fractions were similar to the ones seen for sample B3 and are not shown. It has been proposed that the ordering in the asphaltenes are a result of the stacking of the individual asphaltene molecules through the $\pi - \pi$ interaction of the aromatic rings [18]. The interlayer distance of the aliphatic and aromatic portions of the individual asphaltene molecules in the asphaltene aggregate was similar for A_{HEP} extracted from the various bitumen, see Table 4 and Table 5.

The average stack height of aromatic portion of the A_{HEP} aggregates was seen to be the highest in the samples which contained A_{TOL} and A_{CYC} . Aliphatic chains present on an aromatic core would restrict the number of molecules which can be stacked due to steric hindrance. This could indicate that asphaltenes present in these samples have shorter aliphatic chains or possibly a lower number of aliphatic chains. The stack height of samples B1, B3 and B4 are greater than that of the other samples and these asphaltene aggregates contain a high number of molecules than those present in the other samples. The samples, which have a larger number of molecules in the asphaltene aggregate, are also those which contain A_{CYC} and A_{TOL} . This could indicate a difference in ordering of the molecules within the asphaltene aggregate when both A_{CYC} and A_{TOL} are present as opposed to only A_{CYC} .

The interlayer distance between the aliphatic chains and between the aromatic sheets of A_{TOL} was marginally lower than that A_{CYC} , see Table 5. This indicated that the asphaltenes of A_{TOL} could result in stacks where the individual molecules were closer together as compared to A_{CYC} . The average stack height and the number of molecules in each asphaltene aggregate were higher for A_{TOL} as compared to the corresponding A_{CYC} . This could be due to the increased aromaticity of the molecules which comprise A_{TOL} allowing for a closer packing with reduced steric hinderance. This would result in an asphaltene aggregate with increased height as well as one with a higher number of individual molecules per aggregate.

Table 5: Analysis of XRD spectra

Asphaltenes extracted from	Interlayer distance for the aliphatic chains, (d_l) Å	Interlayer distance between two aromatic sheets, ($d_{[002]}$) Å	Average stack height, (L_c) Å	Number of molecules in the stack, (M)	Average diameter of the aromatic sheets, (L_a) Å	Aromaticity, (f_a)
B1	4.36	3.53	15.81	5.48	12.04	0.306
B2	4.36	3.53	15.69	5.44	11.85	0.315
B3	4.39	3.53	17.42	5.93	12.53	0.388
B4	4.46	3.51	17.43	5.96	13.67	0.363
B5	4.15	3.55	14.47	5.07	8.73	0.255
B6	4.43	3.57	13.34	4.73	13.68	0.337
Cyclohexane soluble asphaltene sub-fraction						
B1- A_{CYC}	4.38	3.60	10.81	4.00	12.77	0.387
B3- A_{CYC}	4.30	3.64	9.08	3.50	10.70	0.431
B4- A_{CYC}	4.46	3.66	9.08	3.48	11.84	0.434
Toluene soluble asphaltene sub-fraction						
B1- A_{TOL}	4.28	3.53	12.38	4.51	10.36	0.399
B3- A_{TOL}	4.24	3.49	17.43	5.99	13.90	0.505
B4- A_{TOL}	4.41	3.52	13.80	4.92	11.89	0.440

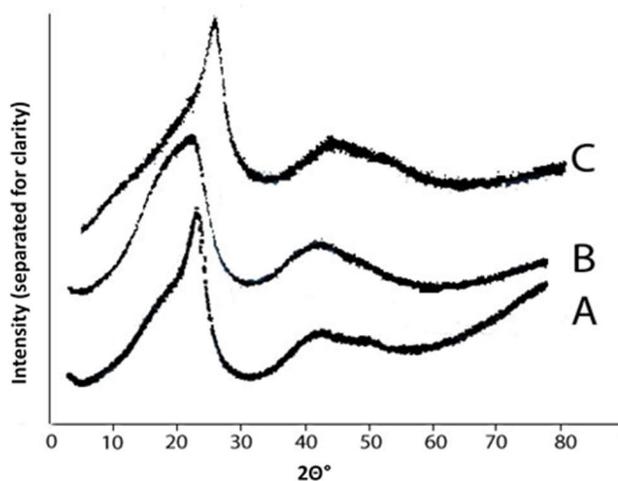


Figure 1: XRD spectra of n-heptane asphaltenes and asphaltene sub-fractions from B3; A is B3- A_{HEP} ; B is B3- A_{CYC} ; and C is B3- A_{TOL}

3.3. Effect of asphaltene sub-fractions on bitumen properties

The analysis of the effect of asphaltene sub-fractions on the penetration and softening point values of the model bitumen prepared showed that A_{TOL} resulted in harder bitumen as compared to A_{CYC} , at similar mass fractions, see Figure 2 and Figure 3. This indicated that A_{TOL} had a greater degree of interaction with the maltene phase. It was observed A_{CYC} and A_{TOL} influenced the penetration and softening point to different degrees at similar concentration levels, as seen from the variations in the penetration indices. At lower asphaltene concentrations, i.e. 25 %, the two asphaltene sub-fractions resulted in a model bitumen with similar penetration indices. However, at asphaltene concentrations of 50 % and higher, the B- A_{TOL} samples showed higher penetration indices. The higher penetration

index of B- A_{TOL} samples also indicated that it had a greater interaction with the maltene phase as compared to corresponding B- A_{CYC} samples.

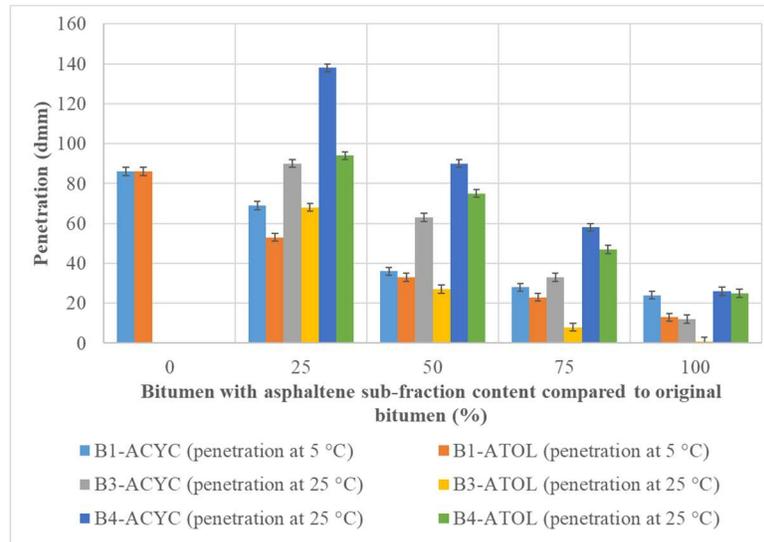


Figure 2: Relationship between asphaltene sub-fraction content and penetration

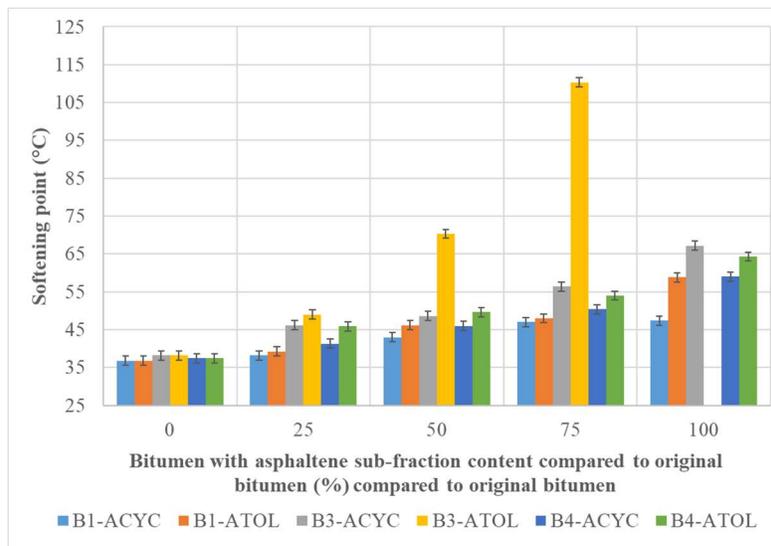


Figure 3: Relationship between asphaltene sub-fraction content and softening point

3.4. Rheological characterisation

The upper PG temperatures of the model bitumen can be seen in Figure 4. B- A_{TOL} samples had higher stiffness values than B- A_{CYC} samples at equivalent asphaltene concentrations, reflected by a higher upper PG temperature. The thermal susceptibility of the model bitumen prepared was determined from the slope of the line obtained when the $G^*/\text{Sin}\delta$ was plotted against the test temperature. The thermal susceptibility of upper PG temperature of B- A_{TOL} was lower than that of B- A_{CYC} , at similar asphaltene concentrations.

The higher upper PG temperature of B- A_{TOL} as compared to B- A_{CYC} can be attributed to the higher degree of interaction between the A_{TOL} and the maltenes than that between A_{CYC} and maltenes. The lower thermal susceptibility of B- A_{TOL} compared to B- A_{CYC} can also be explained by this higher interaction between the A_{TOL} and maltenes. It should be noted that waxes can also impact the thermal susceptibility of bitumen. Since the same maltenes were used to prepare B- A_{TOL} and B- A_{CYC} the difference in thermal susceptibility would not be due to wax.

The elastic component (G') of the B- A_{TOL} was found to be higher than that of the corresponding B- A_{CYC} , see Table 6. The results for model bitumen based on B1 are shown. Since similar trends were obtained for model bitumen based on B3 and B4, they have not been shown. The combination of a lower thermal susceptibility and higher stiffness in a sample could indicate that this sample would have a higher cracking tendency. The Glover-Rowe (G-R) parameter for the model bitumen was also determined [20]. The B- A_{TOL} samples was found to have lower ductility and potentially higher cracking tendency as compared to B- A_{CYC} samples.

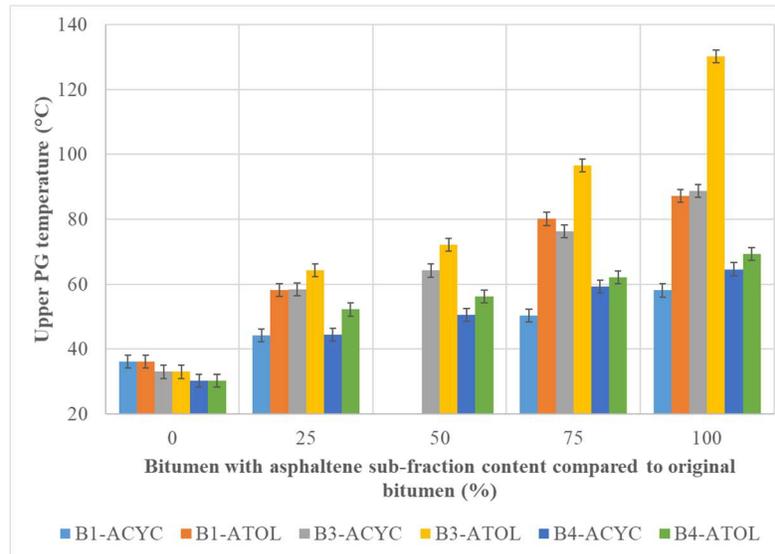


Figure 4 : Influence of asphaltene sub-fractions on upper PG temperature at various concentrations

Table 6: Effect of asphaltene sub-fractions on G-R parameter for bitumen B1

Sample Details	G' (MPa)	Predicted ductility at 15 °C (cms), 0.005rad/sec
25 % B1- A_{CYC}	0.025	>10
25 % B1- A_{TOL}	0.041	6 to 8
75 % B1- A_{CYC}	0.037	8 to 10
75 % B1- A_{TOL}	0.090	5 to 6
100 % B1- A_{CYC}	0.065	6 to 7
100 % B1- A_{TOL}	0.105	5 to 6
B1	0.015	>10

The rheological behaviour of these model bitumen samples containing A_{TOL} and A_{CYC} were studied using master curves. The master curves for bitumen based on 75% B3- A_{CYC} and 75% B3- A_{TOL} are shown in Figure 5 and Figure 6. The B3- A_{CYC} sample demonstrated typical Maxwell behaviour at low frequencies, indicating that the sample behaved as a viscoelastic liquid. 75% B3- A_{TOL} showed an elastic plateau at lower frequencies potentially arising because of greater interaction between the asphaltene and maltene phases, which was not seen for the A_{CYC} sample. Similar observations were made for the 50, 75 and 100 % A_{TOL} and A_{CYC} based model bitumen based. Since the trends are similar the individual graphs for the different bitumen are not shown. The 25 % A_{TOL} and A_{CYC} based model bitumen did not show a difference in viscoelastic behaviour, which could be attributed to the low mass fractions of the asphaltenes in these compositions.

The model bitumen based on A_{TOL} showed a slight inflection of the storage modulus at higher frequencies which was not observed with the model bitumen based on A_{CYC} or a typical bitumen sample. The inflection indicates that the temperature susceptibility of the material changes over a frequency range. The higher degree of interaction between the A_{TOL} and the maltene phase could possibly lead to such behaviour. Since the penetration index and the thermal susceptibility measured using the rheometer indicate that the A_{TOL} based bitumen have a higher degree of interaction with the maltene phase as compared to A_{CYC} . This could be a credible explanation for the observed behaviour. Similar

behaviour has been observed with clay modified polymer systems, which has been attributed to an increased interaction between the clay and the polymer phases [21].

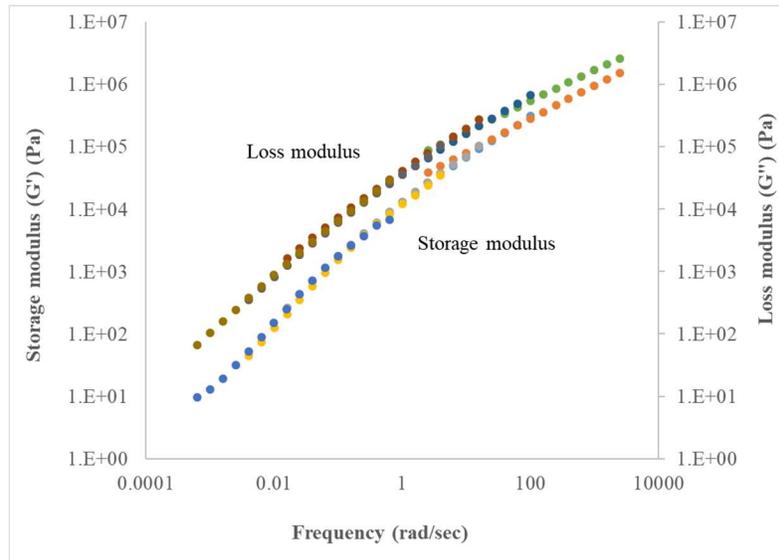


Figure 5 : Master curve for bitumen B3 (75% ACYC fraction) at 40°C

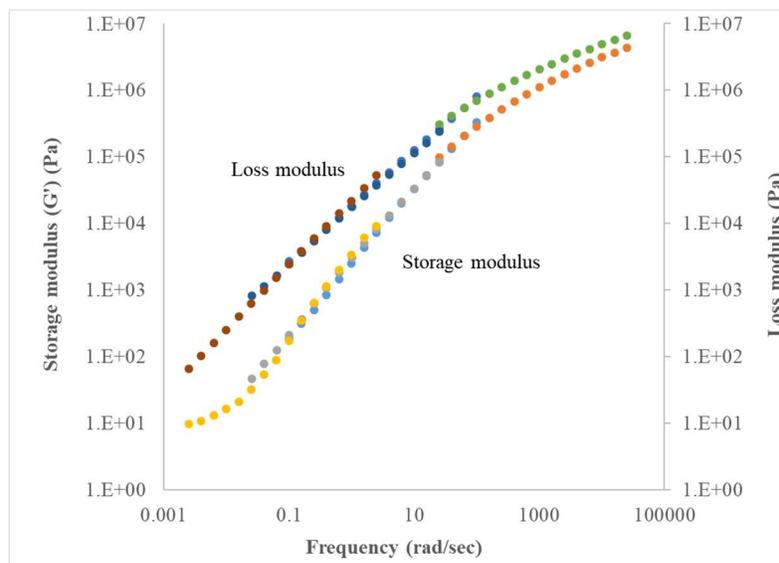


Figure 6 : Master curve for bitumen B3 (75% ATOL fraction) at 40°C

3.5. Effect of oxidative ageing on bitumen

During the oxidation of bitumen, the asphaltenes present in the bitumen are oxidised and new asphaltenes are formed through the oxidation of the maltenes [13]. Maltenes were oxidised to study the new asphaltenes formed upon oxidation. The formation of asphaltenes, based on the mass fraction in the oxidised bitumen, were seen to be comparable for all the samples tested. The penetration grade or composition of the bitumen, from which the maltenes were separated, did not have an influence on the rate of asphaltene formation, see Figure 7.

The nature of the asphaltenes formed upon oxidation of the maltenes was studied using the asphaltene determinator, see Figure 8. The concentration of ACYC formed on maltene oxidation increased at a higher rate than the ATOL and ADCM fractions over time. There was an increase in the H/C atomic ratios for the asphaltenes with oxidation time. The H/C ratio of the asphaltenes for B3 increased from 0.99, for the original asphaltenes present in the bitumen, to 1.07

and 1.11 after 6 and 12 hours in the RTFOT. Similar increasing trends were seen for all the other bitumen, though the data is not shown in this paper. The asphaltenes formed on oxidation would be classified as an asphaltene, as the molecules would be insoluble in n-heptane due to the addition of oxygen atoms to more aliphatic and lower polarity molecules.

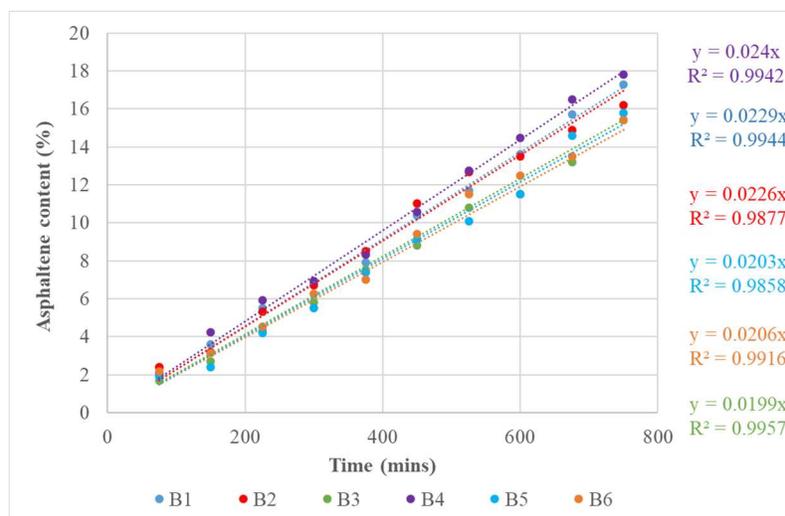


Figure 7 : Variation of asphaltene content on oxidation of maltenes

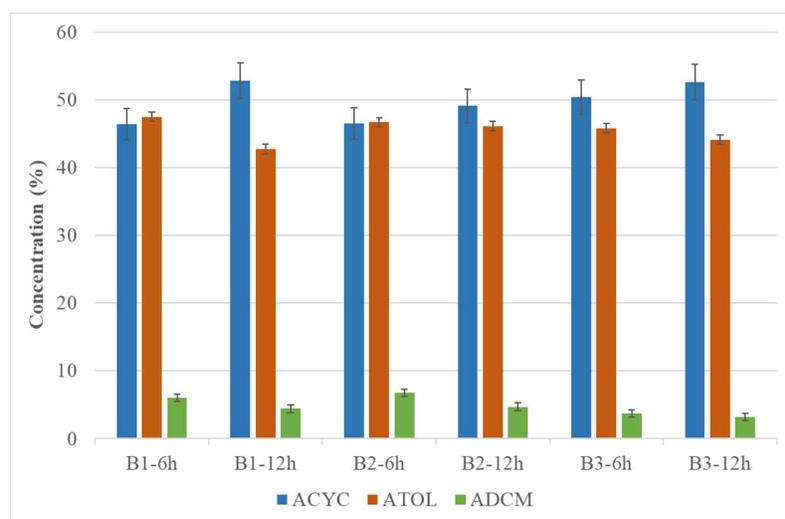


Figure 8 : Variation of asphaltene composition on extended oxidation

3.6. Effect of asphaltene oxidation on bitumen properties

The influence of the newly formed asphaltenes and that of the oxidised asphaltenes already present in the bitumen was studied. The softening point of the sample was used as an initial screening property to study the influence of oxidised bitumen components on bitumen properties, see Table 7. The concentration of asphaltenes after RTFOT was determined and then kept constant for the model aged bitumen prepared.

The presence of the newly formed asphaltenes formed by the maltene oxidation was found to have a marginal impact on the softening point of the model bitumen. The results showed that the softening point of aged bitumen is largely driven by the oxidation of asphaltenes already present in the bitumen. From the study conducted on the impact of A_{TOL} and A_{CYC} on bitumen properties it was seen that asphaltene aromaticity and polarity both lead to an increased impact on bitumen properties. Thus, the asphaltenes formed on oxidation of the maltene fraction would not be as effective in influencing bitumen properties as that of the oxidised asphaltenes already present in the bitumen.

Table 7 : Impact of oxidation on bitumen softening point (°C)

Sample	Before ageing	After PAV ageing	Unoxidised maltene + oxidised asphaltenes	Oxidised maltenes + unoxidised asphaltenes	Oxidised maltenes + oxidised asphaltenes
B1	46.4	49.6	51.2	47.6	52.8
B3	70.8	79.6	85	71.8	86

4. CONCLUSIONS

The presence of asphaltene sub-fractions A_{TOL} and A_{CYC} were not linked to the penetration grades or the chemical composition of the parent bitumen. The A_{TOL} asphaltene sub-fraction was found to have an overall lower H/C atomic ratio and a higher concentration of electro-negative atoms compared to the A_{CYC} sub-fraction. The individual molecules of the A_{TOL} sub-fraction resulted in asphaltene aggregates with a higher number of molecules per aggregate as well as lower gaps between the molecules in the aggregate, driven by the lower steric hinderance associated with these molecules. The A_{TOL} sub-fraction resulted in a stiffer artificial bitumen with a lower thermal susceptibility as compared to that obtained from A_{CYC} , at equivalent asphaltene concentrations. This was due to the increased interaction between the A_{TOL} asphaltenes and the maltene phase in the model bitumen.

The rate of formation of asphaltenes from maltenes was found to be independent of the penetration of the parent bitumen or its chemical composition. Over 24 hours of oxidation in the rolling thin film oven, the rate of asphaltene formation did not change, indicating that the reactive molecules in the maltenes were not sufficiently reduced to influence the rate of reaction.

The properties of aged bitumen were found to be predominantly driven by the oxidised asphaltenes already present in the bitumen and not by the asphaltenes formed upon oxidation, at similar asphaltene concentration levels, as indicated by the softening point. The asphaltenes formed on extended oxidation of the maltenes have a lower aromatic nature which leads to a reduced impact on bitumen properties.

These insights are useful to understand the influence of bitumen chemistry on bitumen properties and potentially pavement performance. This will help build the link between the crude oils used to produce the bitumen and its properties.

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