Binder performance and testing

Towards a better understanding of the chemical changes of in-service bitumen and the chemistry of recycled asphalt pavements (RAP). Recent studies of RAP chemistry after in-service life of more than ten years.

Richard Taylor[1], Dawid D'Melo[2]
[1]Shell Internaitonal Petroleum Company Limited, [2]Shell Projects and Technology, Bangalore, India

Abstract

Recycling of asphalt pavements at the end of their lives is an essential aspect of road construction and a key facet of the economics and sustainability of asphalt pavements. Recycled Asphalt Pavement (RAP) has been the subject of countless studies and levels of RAP have steadily risen in many regions over the last twenty years, as well as the increased use of softer grades of bitumen this has also given rise to a host of additives many of which claim to rejuvenate or restore the rheological properties of the bitumen in the RAP. Such claims range in their sophistication from the restoring of simple rheological tests such as penetration or viscosity to some claiming that the bitumen is fully restored to its original properties. Bitumen chemistry is complex with hundreds of thousands of different molecules present, such chemistry varies as a result of crude oil sources at the refinery and refinery processing. Furthermore, the chemistry of bitumen changes during the asphalt mixing process and during its service life. An understanding of these changes is vital in realising the potential of RAP in constructing durable roads. This paper examines the chemical properties of RAP taken from three countries, United Kingdom, France and India after service lives between ten and twenty years. Chemical analysis of the binder, including asphaltene structure, polarity and solubility, was studied and the potential impacts on blends of these aged binders with fresh binders were also investigated. The studies show that asphaltenes become more polar over time and that this is largely related to the age of the pavement. The impact of this increased asphaltene polarity can be observed in the laboratory in terms of increased physical hardening in the blended bitumen when aged binders are combined with fresh materials.

This paper was first published in 2020 in version 1.0 of the proceedings of the 7th E&E Congress. This second edition (version 1.1.) of the proceedings is published in June 2021. The content of this paper has not changed, but the author(s) may have provided additional information in the form of an annex.

1. INTRODUCTION

Asphalt is one of the most widely recycled materials in the world [1] and road surfaces at the end of their service life provide a valuable material for society in subsequent pavements meaning that asphalt is widely considered a "circular" material. At low concentrations, for example less than 25% by mass of Recycled Asphalt Pavement (RAP), only minor changes are required to mixture design however as the quantity of RAP increases more sophisticated techniques are required in order to ensure that the pavement layer containing the RAP performs as expected.

Some RAP will contain bitumen from previous generations which may have already been recycled multiple times and in order to understand the properties of RAP, and in particular the bitumen component of RAP, a fundamental understanding of the chemistry of bitumen as it ages is required as well as an understanding of what happens when aged bitumen is mixed with new bitumen to produce new road paving layers.

In this study RAP from four sources in three different countries were taken from roads between 10 and 20 years of age and the bitumen analysed to understand the range of properties. Additionally, the aged bitumen was blended with fresh bitumen and observations made of the rheological behaviour over time.

2. SAMPLES INVESTIGATED

Bulk samples of RAP were received from four pavements with differing climatic conditions. Two samples were from India and taken from regions with both high temperatures and high rainfall. Two samples were taken from NW Europe where the climate can be considered moderate. The exact age of the RAP and starting materials were known from three of the samples (India samples plus UK samples) however the provenance of the RAP obtained from France was not known, it is believed that the RAP was taken from a pavement layer at the end of its service life and likely starting material for the bitumen was a 35/50 penetration grade. A summary of the RAP sample locations is given below in Table 1

Table 1: Locations, age and general climatic conditions of the RAP samples in the study.

RAP Binders	Source of material	Time in pavement (years)	Hottest month in the year with high/ low temperature* (ºC)	Coldest month in the year with high/low temperature* (ºC)	Average annual rainfall (cm)
RAP1	Sambalpur, India	10	May, 41 high /27 low	January, 24 high/ 12 low	91
RAP2	Kharagpur, India	20	May, 36 high /25 low	January, 27 high/ 14 low	150
RAP3	France	Unknown	July, 26 high/ 14 low	January, 5 high/ 0 low	36
RAP4	M6 Motorway, UK	16	July, 20 high/ 12 low	January, 5 high/ 2 low	36

3. EXPERIMENTAL PLAN

Binder was extracted from the RAP using ASTM D6847 followed by ASTM D5404. All RAP extracted bitumen samples were tested for the following properties

- SARA Analysis (METHOD) (IP143 followed by the IP368 protocols)
- Penetration (ASTM D5)
- Softening Point (ASTM D36)
- Ageing (RTFOT D2872)
- Calculation of Penetration Index [2]
- Rheological Characterisation using Dynamic Shear Rheometer

- Asphaltene Determinator [3]
- Elemental Analysis (Carbon, Hydrogen and Nitrogen content - ASTM D5291 Oxygen content - ASTM D5622, Sulphur content ASTM D5453)

Finally, RAP1 and RAP2 (Aged 10 years and 20 years respectively) were blended with fresh bitumen, the following were used to investigate the behaviour of the blends.

- Predicted versus actual complex modulus (G*) and examination of short-term steric effects using a dynamic shear rheometer

- Long term steric hardening effect by measuring penetration and softening point on samples over a period of one year. For this exercise all samples were fully prepared in advance and conditioned at 25°C for a twelve-month period.

4. RESULTS AND DISCUSSION

4.1. Basic Bitumen Properties

The basic bitumen properties are given below in Table 2.

Table 2: Basic bitumen properties of the four RAP Samples.

Binder property	**RAP1**	**RAP2**	**RAP3**	**RAP4**
Penetration (dmm @ 25 °C)	18	8	7	12
Softening point (°C)	63.4	59.8	78.4	73.2
Penetration index (penetration, $T_{R\&B}$)	-0.5	-2.3	0.2	0.4
Ageing, RTFOT ASTM D2872				
Softening point (°C)	67.2	65.2	85.6	78.6
Change in softening point (°C)	3.8	5.4	7.2	5.4
Compositional analysis				
Saturates (%)	11.7	10.2	12.6	8.1
Aromatics (%)	47.3	40.9	36.4	42.6
Resins (%)	24.5	28.5	28.4	24.1
Asphaltenes (%)	16.5	20.5	22.6	25.2

All four RAP bitumens have quite low penetration values with two of the bitumens being very low penetration mixtures. There is a general trend towards lower penetration values for older samples, the ten-year-old RAP at 18dmm, 15 years old RAP at 12dmm and 20-year-old RAP at 8dmm albeit this represents a limited data set.
For softening point there was a wide range of values recorded, accordingly the penetration index values ranged from -2.3 to +0.4, however this would be considered a reasonable range for a set of fresh bitumens. After short term ageing (RTFOT) all bitumen samples showed that further ageing was possible, the range of increase in softening point would meet the ageing requirement for bitumen in European standards. Similarly, the SARA analysis does not throw up any significant insights except for RAP 4 being relatively high in asphaltenes.

Although there are one or two observations which can be drawn from the basic properties other than the wide range of softening points and the relatively high asphaltene content of RAP 4 there are few insights into the RAP which can be gained using such basic tests.

4.2. Rheological Characterisation of the RAP binders

The penetration values for the bitumen recovered from the RAP falls into a relatively narrow range, albeit it is worth noting that penetration is a logarithmic scale and that this range encompasses a wide range of stiffnesses indicating that penetration value, especially of RAP within a low penetration range may not be a good discriminator. Two of the RAP binders, those with the highest degree of ageing when considering oxygen uptake in service, were analysed using a dynamic shear rheometer and the data compared to the fresh rheology of an oxidised bitumen and a fresh 10/20 penetration grade bitumen. An Anton Paar MCR 501 was used to do the rheological measurements, the rheometer had a torque range of 0.1µNm to 230mNm and uses an air bearing to apply stress/strain on the samples. In case of all the rheological experiments any results with a torque value below 1µNm was ignored. The frequency sweep measurements were performed within a frequency range of 0.1rad/s to 100rad/sec in between a temperature range of 25°C – 100°C. The strain amplitude used in these measurements were kept constant at 6% (within the Linear Viscoelastic region for all the samples). The time sweep measurements were done at equal shear viscosities for all the tested samples in between a temperature range of (20°C – 45°C) at a strain amplitude of 0.5%. The strain amplitude was limited to 0.5% to limit the effects of generated stress on steric hardening.

Black space diagrams were used to compare the rheology, these are presented in Figures 1 to 4 below. It can be seen clearly that the rheological response is very different when comparing aged bitumen extracted from RAP and fresh bitumen of similar penetration. RAP, which showed the highest degree of oxidation has several discontinuities in the black space indicative of a rheologically complex material. Some unusual characteristics were also noted in the black space diagrams, for example, the apparent inversion in black space of RAP bitumen plus the relatively high complex modulus of RAP bitumen at the cross over frequency (45 degrees). These traits may indicate that RAP binders can exhibit a different rheological response to fresh bitumen of a similar penetration.

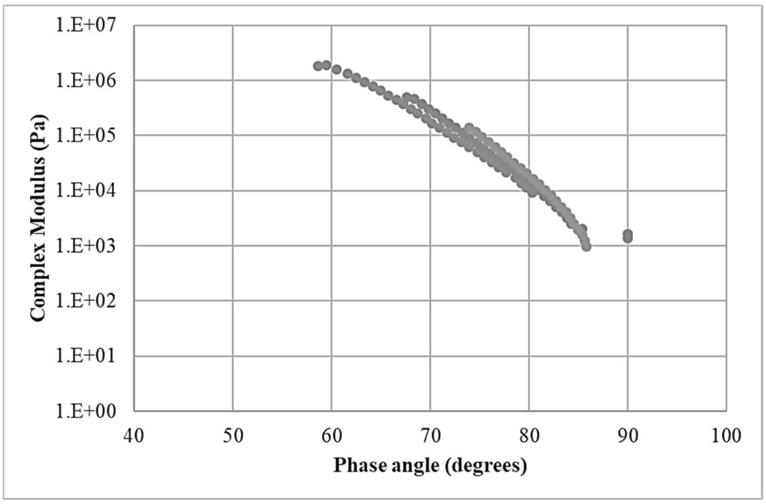

Figure 1: RAP 2 Black space diagram.

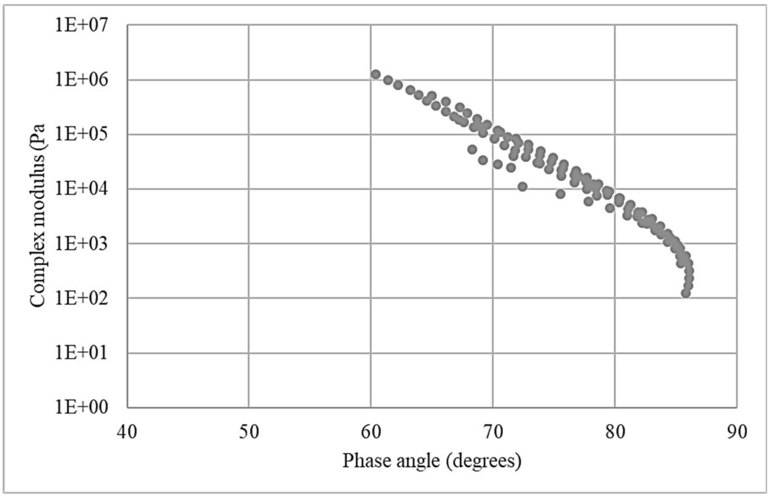

Figure 2: RAP 4 Black space diagram

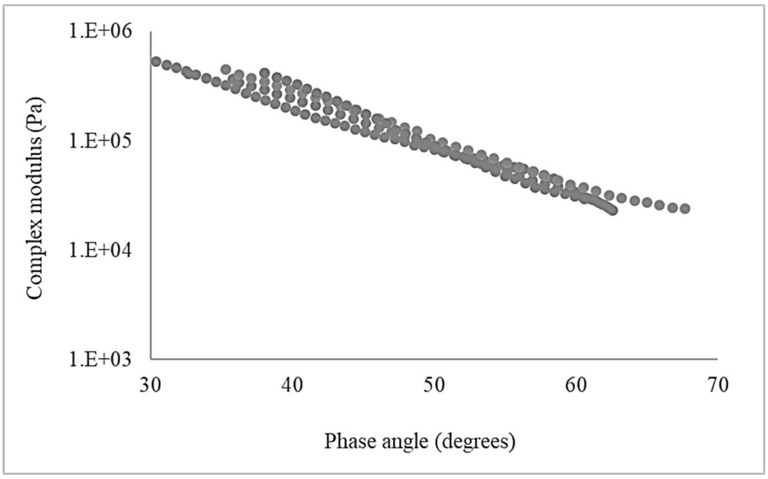

Figure 3: Black space diagram of an unaged 15dmm penetration oxidised bitumen

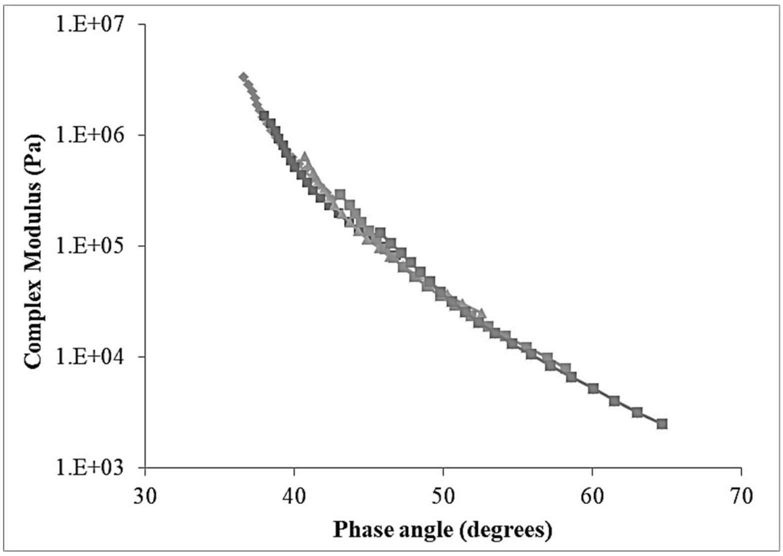

Figure 4: Black space diagram of an unaged 15dmm penetration grade paving bitumen

4.3. Chemical Analysis of the bitumens

The elemental analysis of RAP1 and RAP2 binders is given in Table 3 below. The highest accumulation of oxygen is found in the toluene subfraction and the least in the maltene fraction. It should be noted that it will be the quantity of oxygen in the asphaltene subfraction that will drive the solubility and the identification of the subfraction to an extent.

Table 3: Elemental analysis of RAP binders 1 and 2.

	RAP1	**RAP2**		**RAP1**	**RAP2**
Chemical composition of n-heptane insoluble asphaltenes			Chemical characterisation of toluene soluble asphaltene sub-fraction		
C (%)	82.56	81.23	*C (%)*	80.97	81.06
H (%)	7.69	7.36	*H (%)*	7.32	7.37
O (%)	2.90	4.55	*O (%)*	4.17	6.15
N (%)	0.77	0.76	*N (%)*	0.82	0.88
S (%)	6.09	5.30	*S (%)*	5.75	6.02
Chemical characterisation of cyclohexane soluble asphaltene sub-fraction			Chemical composition of the maltene fraction		
C (%)	82.05	82.15	*C (%)*	85.00	84.51
H (%)	7.47	7.45	*H (%)*	10.26	10.75
O (%)	2.58	3.75	*O (%)*	0.15	0.50
N (%)	0.92	0.90	*N (%)*	0.26	0.36
S (%)	5.81	6.11	*S (%)*	4.33	3.88

Table 4 shows a summary of the elemental analysis of the n-heptane asphaltenes of all four RAP bitumens. The magnitude of levels of oxygen present are quite high when compared to fresh bitumen, which has typically low levels of oxygen [2]. Testing for oxygen levels in asphaltenes could be an important indicator of aged bitumen or the degree of ageing in a pavement.

Table 4: Elemental analysis of n-heptane asphaltenes extracted from RAP bitumen.

n-Heptane asphaltenes	**RAP1**	**RAP2**	**RAP3**	**RAP4**
C (%)	82.56	81.92	82.39	70.98
H (%)	7.69	7.42	7.59	6.69
O (%)	2.90	4.55	3.64	8.33
N+S				3
H/C atomic ratio	1.11	1.08	1.10	1.12
O/C atomic ratio	0.026	0.042	0.033	0.088

Bitumen extracted from RAP 4 is worthy of further comment as it has a very high content of oxygen in the asphaltenes compared to the other RAP bitumen samples, there are several potential reasons why the value recorded could be elevated

- The mixture from which the RAP and subsequently the bitumen was extracted was a thin surface course material with a relatively open structure in order to meet local skid resistance requirements, this open structure may lead to higher ageing through a higher availability of oxygen compared to the dense mixtures from which bitumen from RAP1-3 was extracted.
- The mixture may have already contained RAP from a previous pavement
- The original bitumen may have contained a proportion of blown or oxidised bitumen
- The bitumen may have been sensitive to ageing and oxygen uptake.

4.4. SARA and Asphaltene Subfractions

The asphaltenes and their subfractions were extracted from RAP1 and RAP2 binders and their aromaticity and oxygen to carbon ratio determined from the elemental analysis. The results are given in Figures 5 and 6 below.

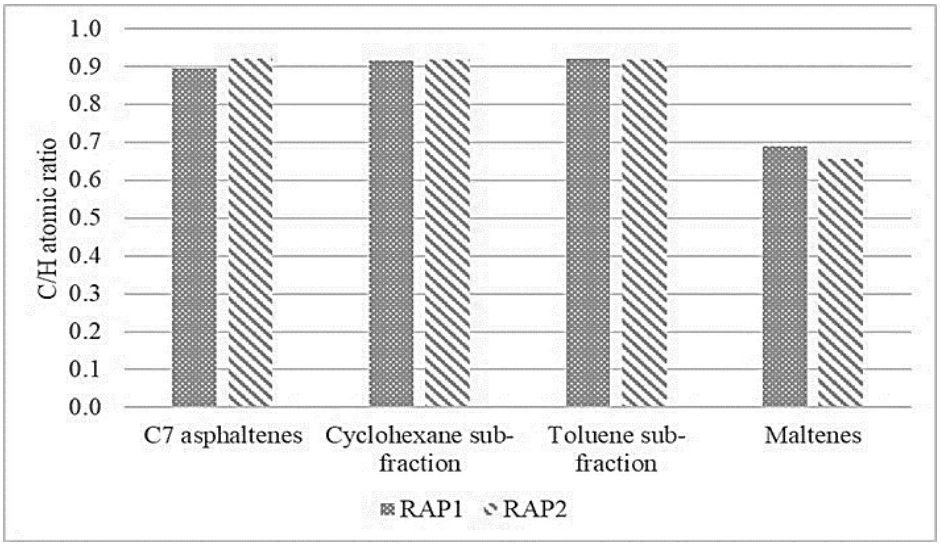

Figure 5: Aromaticity (expressed as C/H atomic Ratio) asphaltenes and asphaltene subfraction of bitumen extracted from RAP1 (10 Years old pavement) and RAP2 (20 Years old pavement)

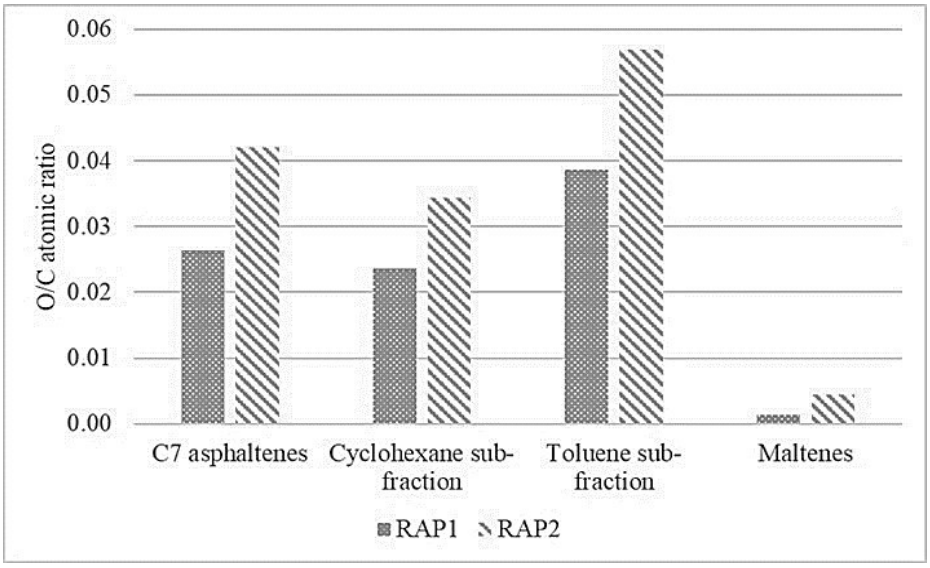

Figure 6: Oxygen to carbon content of asphaltenes and asphaltene subfraction of bitumen extracted from RAP1 (10 Years old pavement) and RAP2 (20 Years old pavement)

The figures show that aromaticity (C/H ratio) does not discriminate between the RAP samples of different ages, both samples show broadly the same aromaticity regardless of the fraction examined. Conversely the oxygen to carbon ratio clearly shows a difference between the two samples with a higher ratio of oxygen to carbon with the increase in age from 10 to 20 years of the RAP. The oxygen to carbon ratio is highest in the toluene asphaltene subfraction and the maltene fraction, although showing an increase with age of the RAP, attracts little of the oxygen on ageing and there is a clear elemental partitioning on ageing.

A further experiment was conducted to demonstrate this using laboratory ageing, a sample of bitumen (Indian origin, VG30 grade) was analysed for oxygen content in the fresh state, after short term RTFOT ageing and after successive days of ageing in a Pressure Ageing Vessel. The oxygen is largely taken up by the asphaltene fraction and the level of oxygen in the asphaltene fraction could be a potentially important measure of the degree of ageing of a bitumen. The results from the laboratory ageing simulation are given below in Figure 7.

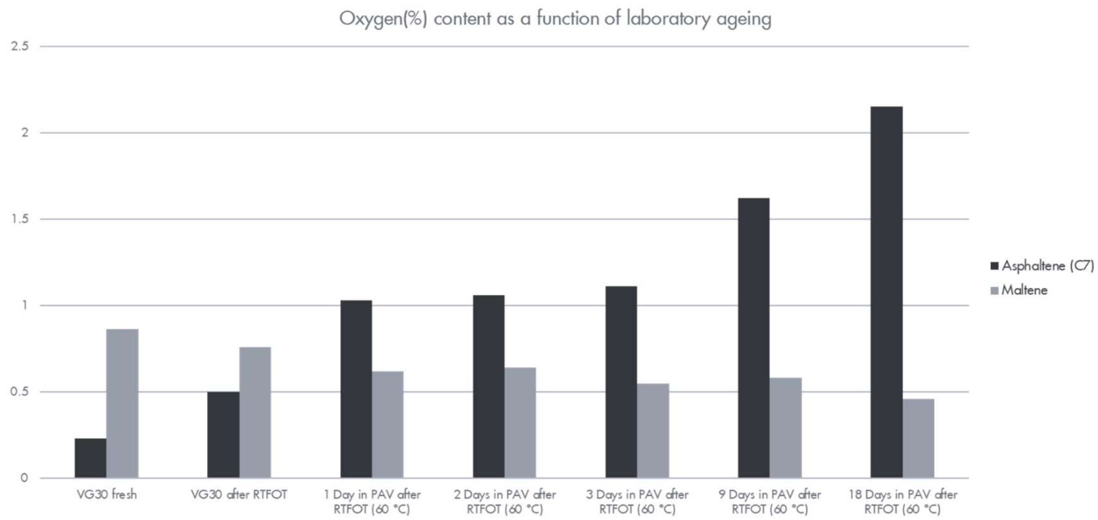

Figure 7: Oxygen Uptake by Asphaltenes and Maltenes During Long Term Laboratory Ageing

The magnitude of oxygen taken up by the laboratory aged samples also provides some insights into the representative nature of long-term laboratory ageing protocols such as pressure ageing vessels and field ageing. After a significant period in the pressure ageing vessel (18 days) the total quantity of oxygen present in the n-heptane asphaltene fraction was around two percent and after one cycle this value was around one percent, this compares with a range of 2.9 to 9.4% in the n-heptane asphaltenes extracted from field aged binder in the RAP1 to 4 samples. Taking a single cycle of PAV in terms of oxygen content indicates that the field ageing has higher oxygen contents, in this study the field ageing ranged from three to ten times higher in terms of oxygen uptake.

4.5. Blends of RAP bitumen with fresh bitumen

Having established that in terms of bitumen, and in particular asphalt, chemistry that oxygen uptake is a potential indicator of age and degree of ageing in asphalt pavements the next phase of the study examined the implications of blending aged bitumen with elevated oxygen contents with fresh bitumen.

4.5.1. Blending ratios

Bitumen blending follows simple blending rules [2]. In this study, field aged binders from RAP1 and RAP2 (10 and 20 years old respectively) were blended with fresh bitumen and their predicted blend complex modulus compared to the actual complex modulus, as measured by DSR. Measurements were taken at 0.1, 1 and 10 rad/s.

Figure 8 below shows a deviation between the predicted stiffness and the measured stiffness of blends of aged and fresh binder suggesting that aged binders may behave differently during blending than fresh bitumen. Table 5 shows the deviation from the predicted value for different levels of RAP1 bitumen with varying frequency, in all cases the measured level of modulus was significantly higher than the predicted stiffness. This may present an insight into differences between blending of fresh bitumens and blending of RAP aged binder with fresh binder.

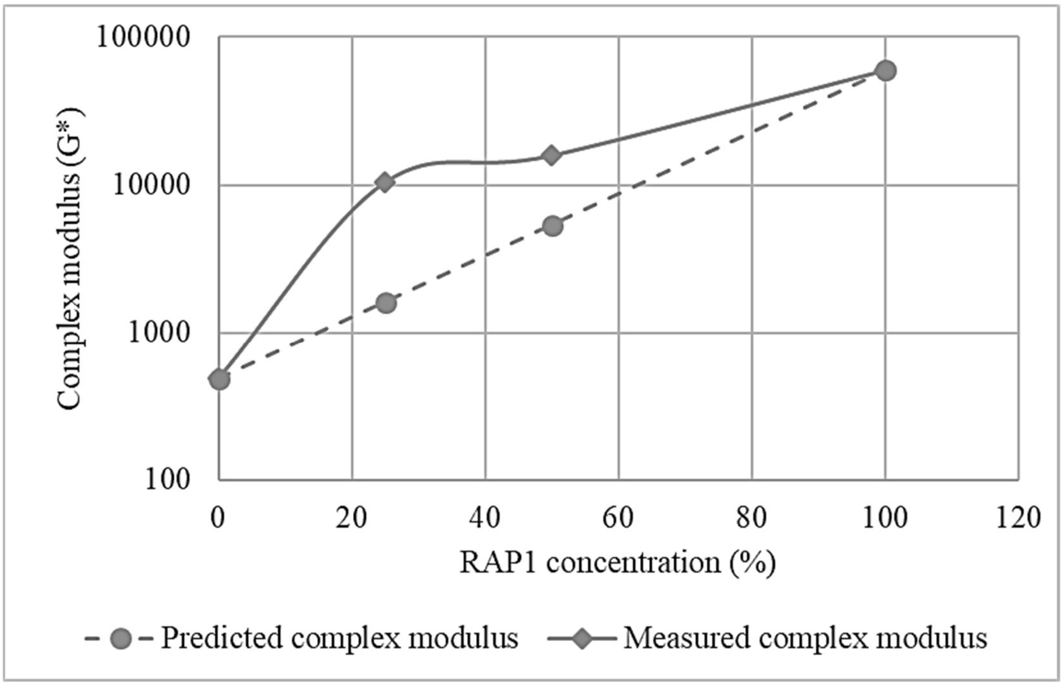

Figure 8: Example of deviation between measured and predicted complex modulus

Table 5: Example of deviation between predicted and measured complex modulus of RAP binder blended with fresh binder.

Frequency (rad/sec)	Percentage deviation for 25 % RAP 1 + VG30 blend	Percentage deviation for 50 % RAP 1 + VG30 blend
10	84	65
1	84	65
0.1	82	63

4.5.2. Short term Steric Effects

Steric hardening of bitumen describes the hardening of bitumen over time at low to moderate temperatures (e.g. room temperature) [4]. The ordering of asphaltenes over time and the subsequent structuring of the bitumen leads to a stiffening and a change in bitumen properties. When considering aged bitumen from RAP it could be hypothesised that the increased oxygen content in the asphaltenes, and the subsequent increase in polarity of asphaltenes, may drive a higher propensity for ordering in a blend of aged and fresh bitumen and increased steric hardening.

To investigate steric hardening in RAP blends a simple short-term experiment was conducted to investigate the aged binders from RAP 1 and RAP2 and compare this with the stiffness build up in an unaged binder. Bitumen samples were tested over a period of three days using a DSR under isothermal conditions.

Considering the “pure” aged binders and a fresh VG30 grade bitumen (India source) there was typically a 5% increase in complex modulus over the three-day period. A 6% increase in complex modulus recorded for the older of the two RAP samples (RAP2, 20 years old). When blends of RAP binder and fresh binder were tested under the same conditions stiffness build up over the three-day period was recorded at 15% with a 21% increase recorded for the older RAP 2. Both pieces of evidence indicate that, as already known, bitumen stiffens over time due to ordering of the asphaltenes and that the aged bitumen samples may structure more than fresh bitumen. Results from these experiments are given in Tables 6 and 7 below.

Table 6: Stiffness build-up over three days of blends of RAP1 with fresh VG30 bitumen

Sample type	Stiffness build-up immediate (%)	Stiffness build-up over 3 days (%)	Temperature (°C)	Shear viscosity (Pa.s)
VG30	95	**5**	30	260000
VG30 +25 % RAP 1	85	**15**	37	260000
VG30 + 50% RAP 1	85	**15**	40	260000
100% RAP 1	95	**5**	45	260000

Table 7: Stiffness build-up over three days of blends of RAP3 with fresh VG30 bitumen

Sample type	Stiffness build-up immediate (%)	Stiffness build-up over 3 days (%)	Temperature (°C)	Shear viscosity (Pa.s)
VG30	95	5	30	33000
VG30 +25 % KGP RAP	79	21	35	33000
VG30 + 50% KGP RAP	85	15	40	33000
100% RAP	94	6	45	33000

4.5.3. Long Term Steric Effects

To further investigate the steric hardening effects of RAP aged bitumen when blended with fresh bitumen a long-term test was carried out over a period of twelve months. Samples of fresh binder plus 75:25 blends of fresh binder with RAP1 Binder (10 years field ageing) and RAP2 binder (20 Years field ageing), to recap the oxygen content in the n-heptane asphaltenes of the RAP binders was 2.9% for RAP1 and 4.6% for RAP.

All samples were tested for penetration and softening point and calculation of penetration index. The samples were prepared ready for testing and kept in a conditioning cabinet at 25°C for the entire period prior to testing. The softening point samples were cut at the beginning of the long-term test and not further trimmed prior to testing to avoid heating the long-term stored samples. Individual penetration specimens were prepared for each round of testing. Samples were tested at zero, three, six, nine and twelve months.

The results show a considerable stiffening over a twelve-month period with an increase in stiffening for samples including RAP binders and an increase in stiffening with more aged, higher oxygen content, bitumen. In terms of magnitude, the softening point increased in the control fresh bitumen from 51 to 63°C over the twelve-month period whereas the blend made from RAP1 saw a softening point rise of 53 to 67°C, the RAP2 blend (the oldest RAP bitumen) saw a rise from 55.6 to 72.6°C over the same time period. A similar trend is apparent for penetration and penetration index where the aged RAP bitumen in the blend and the degree of ageing appear to influence the rate of steric hardening and change of properties during long term 25°C conditioning. The softening point change and the log penetration change are shown in Figures 9 and 10 below.

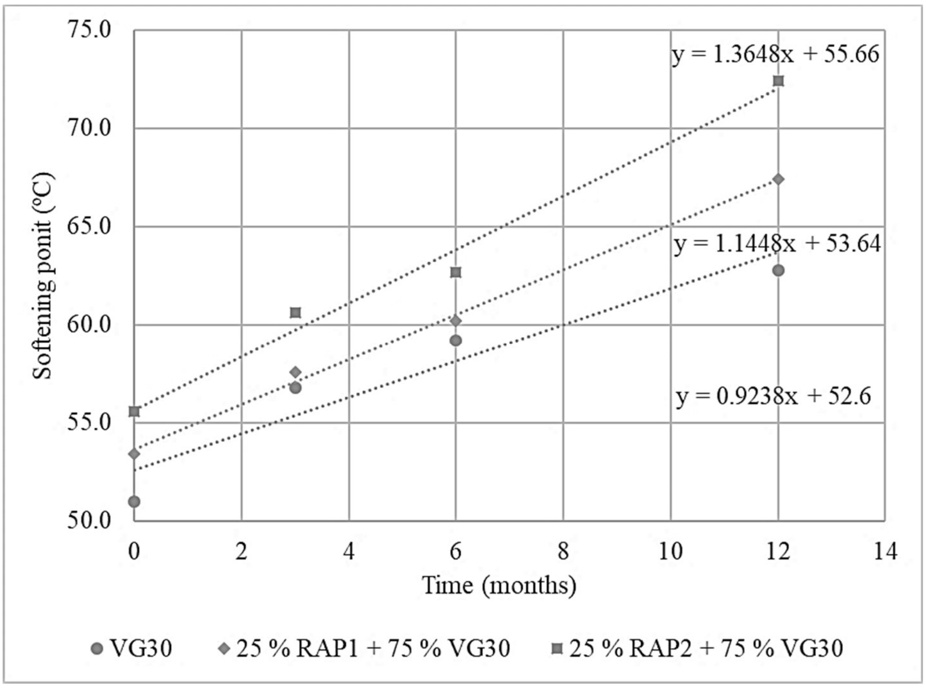

Figure 9: Change in softening point during long term storage at 25ºC for VG30 and RAP blends made with VG30

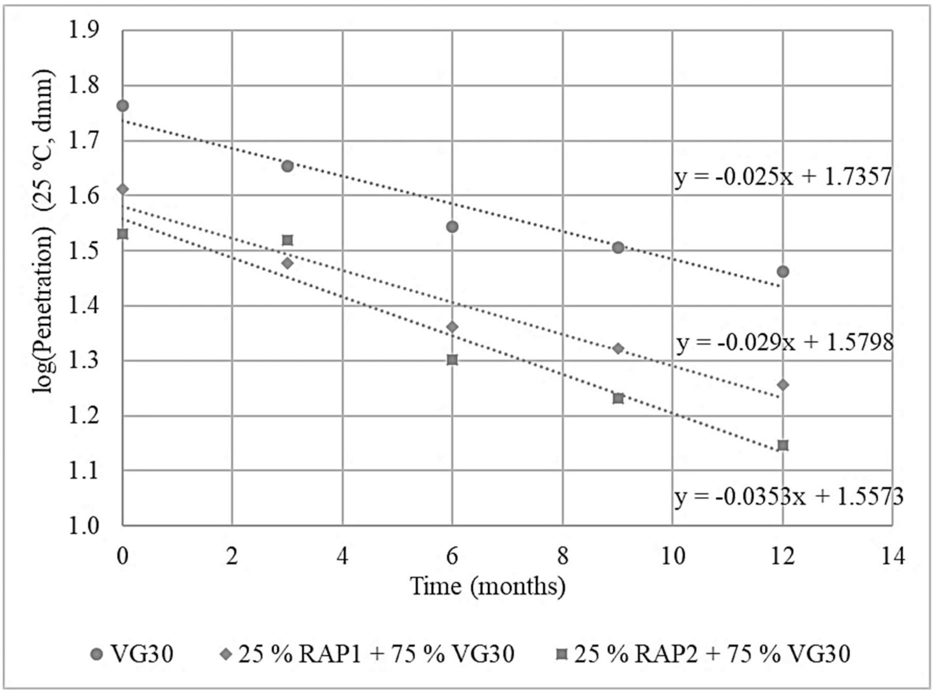

Figure 10: Change in log penetration during long term storage at 25oC for VG30 and RAP blends made with VG30

5. CONCLUSIONS

Binders extracted from four samples of RAP from different geographical regions were examined for chemical and rheological properties and tests were conducted to investigate the properties of bitumen blends made using the RAP extracted binders, the following conclusions were drawn from the study

- Using simple standard tests such as penetration, softening point and SARA, it is difficult to draw conclusions on the behaviour of RAP derived bitumen.
- Aromaticity does not discriminate between RAP bitumen of different ages
- Oxygen tends to accumulate in the asphaltene fraction of the bitumen, the oxygen will also drive the subfractions recovered, higher oxygen contents manifest themselves in a higher toluene asphaltene fraction.
- Oxygen content in a binder has potential to be used as a method to estimate degree of ageing of a bitumen or the presence of aged bitumen.
- Laboratory ageing is unlikely to replicate field ageing and this study has demonstrated that the oxygen contents possible in the asphaltenes using a pressure ageing vessel is only a small fraction of the oxygen contents in asphaltenes extracted from the field.
- In this study, predicted stiffnesses for RAP and fresh bitumen blends did not obey a simple log blending rule. Blends resulted in stiffer bitumen, measured as G* than predicted by the blending rule.
- Blends of RAP bitumen with fresh unaged bitumen show a tendency to higher steric hardening and a larger change in properties over time. Over a twelve-month period, as measure in this study, significant changes in properties can be measured. Samples higher in oxygen content (older RAP) show a higher level of steric hardening.

REFERENCES

[1] EAPA, "Asphalt in Figures 2017", Rue du Commerce 77 B-1040 Brussels, Belgium, 2017

[2] J Read, A Self, et al., Shell Bitumen Handbook, Sixth Edition, ICE publishing, 2015

[3] John F. Schabron, Joseph F. Rovani Jr. and Mark M. Sanderson, "Optimised asphaltene determinator and waxphaltene determinator separations for rapid characterisation of asphalt binders", Pavement Performance and Prediction Symposium, Laramie Wyoming, July 15, 2010.

[4] Masson J F, Collins P, Polomark, G, "Steric Hardening and the Ordering of Asphaltenes in Bitumen", NRCC 47288, 2005