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Effects of Aging on the Physical, Rheological and Chemical Properties of Virgin Bitumen Incorporating Recovered Reclaimed Asphalt Pavement Binder

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Abstract: This paper focuses on a physico-chemical analysis on virgin bitumen incorporating recovered binder from reclaimed asphalt pavement (RAP) subjected to various aging conditions. The recovered binders extracted from three sources were blended with virgin bitumen in two proportions, namely 15% and 30%, by mass of total bitumen. Penetration, softening point and viscosity values were measured to characterize the physical and rheological properties of the RAP modified binders. The evolution in RAP modified binder chemistry before and after aging process was determined by using the Fourier Transform Infrared Spectroscopy. The penetration and softening point consistently decrease and increase, respectively at each level of oxidation. The penetration index and viscosity aging index increase as the RAP modified binders were further aged. The process of aging has chemically altered the structure of the RAP modified binders. This chemical change has produced a distinct increase in area ratio especially at 1700 cm^{-1} and 1030 cm^{-1} wavelengths which were dominated by C=O and S=O functional groups, respectively. There is a significant correlation between penetration index with viscosity aging index and area ratio of RAP modified binders.

Key words: Asphalt, Aging, FTIR, RAP modified binder, Recovered binder

INTRODUCTION

Nowadays the use of reclaimed asphalt pavement (RAP) as secondary material in the production of asphalt mixes has become a norm and a cost effective method of pavement construction and rehabilitation. Utilizing reclaimed asphalt pavement is found to be very beneficial from the technical, economical, and environmental perspectives. Some of the advantages include reduce waste, preservation of the existing pavement geometrics and conservation of energy and reduction in life-cycle cost. Many laboratory and field studies have shown that asphalt mixtures containing RAP performed similar if not better than conventional asphalt materials in terms of indirect tensile strength, moisture susceptibility, permanent deformation and fatigue (Su *et al.,* 2009; Widyatmoko, 2008).

During mixing, RAP materials are heated and blended at high temperature with hot virgin bitumen and fresh aggregates. It is expected that the highly oxidized RAP binder will melt off from RAP aggregate and intimately blended with the virgin bitumen and fresh aggregates. During this blending process, the virgin bitumen is supposed to rejuvenate the RAP binder such that the resultant binder meets the target viscosity. However, the chemical change that takes place in the RAP binder and virgin binder blends after mixing in-plant and during pavement service life is very much unknown. This is particularly of great concern since the RAP binder is known to be readily oxidized and the mixing process further aged the RAP binder. Under extreme aging conditions, even conventional binder is prone to lose its binding capacity. Subsequently it becomes less adhesive but more cohesive, and make it increasingly brittle (Valcke *et al.,* 2009). The oxidation of binder further contributes to change in the structural and functional grouping that is responsible for chemical and physical aging (Lamontagne *et al.,* 2001). A study by Zhang *et al.,* (2011) found that after the short-term aging, the proportion of bitumen compounds such as asphaltene and resins were increased. Further aging the bitumen by subjecting to Pressure Aging Vessel (PAV), caused the asphaltenes and resins content to continually increase while the saturates content remained constant. Apparently, severe oxidation on bitumen produces more asphaltenes which are present in the micelle form in a colloidal structure of bitumen, directly influencing physical, rheological and chemical properties of the bitumen (Lu X, and U. Isacsson, 2002; Lesueur D., 2009; Le Guern *et al.,* 2010). Fourier Transform Infrared Spectroscopy (FTIR) is an excellent and popular

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tool to identify chemical evolution in bitumen and able to indicate the severity of oxidation experienced by the bitumen after aging. It has been a major analytical technique to study aging mechanism in asphalt through the characterisation of oxygen-containing functional and hydrocarbon groups. The FTIR can also yield quick qualitative and quantitative results that are highly reproducible. This technique can easily differentiate stretching vibration of carbonyl mode which is largely dominated by asphaltenes compound after the aging process (Toteva *et al.,* 2009).

There appear to be a gap in the literature on studies characterising the physico-chemical of RAP modified binder resulted from blending of virgin and recovered binder from RAP materials subjected to short term and long term aging. Bridging the gap is essential to help understand better the aging effects especially on the evolution of RAP modified binder chemistry. This paper focuses on three RAP binders extracted from cold milled RAP obtained from three major road authorities in Malaysia. The characteristics of RAP modified binders before and after aging are investigated in terms of penetration, softening point, viscosity, and chemical properties.

2. Materials and Test Procedures:

2.1 Materials:

Milling waste of aged and deteriorated pavements from the Malaysian North South Expressway (NSE), Damansara Puchong Expressway (DPE), and Public Work Department (PWD) roads were used in this study. RAP samples from these three sites were sent to IKRAM Sdn. Bhd. for binder extraction to obtain approximately 400 gram of recovered binder (RAP binder) from each RAP source. A conventional virgin binder grade 80/100 (PG64) supplied by PETRONAS, a Malaysian Oil Company was used as the base binder. The virgin binder was blended with RAP binder in quantities of 15% and 30% of recovered RAP binder by mass of total bitumen at 140°C. Table 1 shows the physical and rheological properties of the virgin and RAP binders.

Table 1: Physical and rheological properties of virgin and recovered binders

Binder	Penetration at 25°C (dmm)	Softening point °C	Viscosity at 135°C (Pa.s)	G*/Sin δ at 64˚C (kPa)
Virgin	90	46.0	0.34	1.14
NSE	14	67.5	3.06	38.0
DPE	13	67.5	4.33	36.1
PWD	11	72.0	2.14	47.8

2.2 Binder Aging Protocol:

The RAP modified binders were subjected to short term and long term aging. The short-term aging, which simulated aging during construction was achieved by using the Rolling Thin Film Oven (RTFO) Test according to ASTM D 2872 (2006) procedures. Binders were aged at 163°C for 85 minutes while 4,000 ml/min of hot air was blown into the rotating bottles lined by the bitumen.

Long-term aging, which simulated field aging in the first 5 to 10 years of pavement service was achieved using the Pressure Aging Vessel (PAV) according to procedures outlined in ASTM D6521 (2006). The RTFO aged binders were placed in the PAV chamber at 100°C and a pressure of 2.1 MPa was applied to the binders for 20 hours.

2.3 Penetration and Ring and Ball Tests:

The penetration test provides a measure of the consistency or hardness of the bitumen. In this test, a needle of specified dimensions was allowed to penetrate a sample of bitumen, under a 100 g load at 25°C temperature for 5 seconds as outlined in ASTM D5 (2006).

In the Ring and Ball test, a standard 3.5 g steel ball was placed onto a sample of bitumen confined in a brass ring that was suspended in a water bath. The water bath temperature was raised at 5°C per minute, the bitumen softened and eventually deformed slowly with the ball moving through the ring. At the moment the bitumen and the steel ball touch a base plate 25 mm below the ring, the temperature was recorded. This temperature was designated as the softening point of the bitumen and represents an equi-viscous temperature. The test was carried out to conformed ASTM D36 (2006).

2.4 Viscosity Test:

A Brookfield Viscometer was employed to measure the viscosities of RAP modified binders according to ASTM D4402 (2006). The test operating speed of the rotational viscometer was set to 20 rpm. The temperature controller of the thermo-chamber was set at 135°C.

2.5 Fourier Transform Infrared Spectroscopy:

A FTIR spectrometer, PerkinElmer model SpectrumOne, was used to determine the functional characteristics of RAP modified binders before and after ageing. All spectra were obtained by 32 scans with 5% iris and 4 cm^{-1} resolution in wavelengths ranging from 4000 to 550 cm^{-1}.

The FTIR spectroscopy allows analyzing functional and structural changes in the fraction of binders due to severe oxidation process by the RTFO and PAV tests. The area of the peak was determined by using the baseline method. The area ratio (AR) for carbonyl and sulfoxide compounds was calculated as in Equations (1) and (2) (Siddiqui and Ali, 1999). The area of particular mode of vibration was measured from valley to valley of the peak by using Spectrum version 5.0.1 software supplied by PerkinElmer™ Instruments.

$$AR_{C=O} = \frac{Area\ of\ the\ carbonyl\ band\ centered\ around\ 1700\ cm^{-1}}{Area\ of\ the\ CH_3\ centered\ around\ 2954\ cm^{-1}} \quad (1)$$

$$AR_{S=O} = \frac{Area\ of\ sulfoxide\ band\ centered\ around\ 1030\ cm^{-1}}{Area\ of\ the\ CH_3\ centered\ around\ 1376\ cm^{-1}} \quad (2)$$

2.7 RAP Modified Binder Designation and Characterising Flow Chart:

A designation system summarised in Table 2 was adopted for easy reference. The RAP modified binder designation consisted of 4 alphanumeric characters in which the first alphanumeric character is an alphabet followed by two numbers or values, and ends with an alphabet. For instance, a designation N15R refers to virgin binder blended with 15% recovered binder from NSE that has been subjected to RTFO test or short term aging. Further detailed explanation of the designation is available in Table 2.

Table 2: RAP modified binder designation

Description	First Alphabet	Number/Value	Last Alphabet
Possible Alphabet/Number	N/D/P	15/30	U/R/P
Denotation	The letter refers to the source of the RAP binder as follows; N – NSE D – DPE P – PWD	The figures reflect percentage of recovered RAP binder blended with virgin bitumen by mass of total bitumen, namely 15% and 30%	The last letter indicates the aging process the sample has been subjected to; U – Unaged R – RTFO P – RTFO+PAV

Figure 1 shows a flow chart to characterize the physical, rheological and chemical properties of the RAP modified binders after subjected various aging conditions.

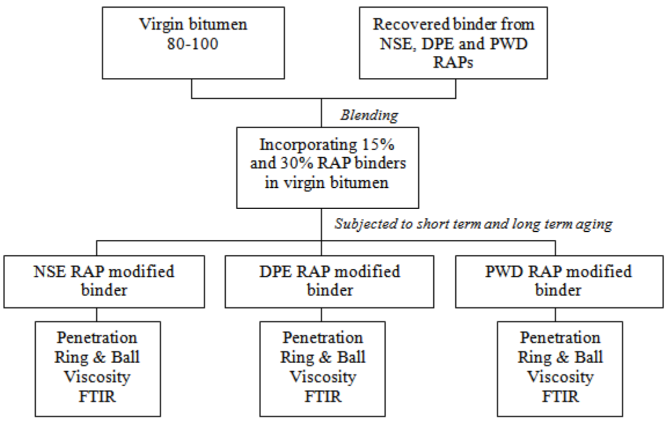


Fig. 1: A flow chart to characterize the physical, rheological and chemical properties of RAP modified binders

RESULT AND DISCUSSION

3.1 Penetration:

Figure 2 shows the penetration values of RAP modified binder after subjected to short term and long term aging. The penetration of RAP modified binder decreases as the RAP modified binders were further aged.

The hardening trend of RAP modified binders is consistent with all RAP binder sources and proportions. For the respective RAP binder proportions, the penetration values of D15 and D30 RAP modified binders after the long term aging are 28 dmm and 24 dmm respectively, and are the lowest.

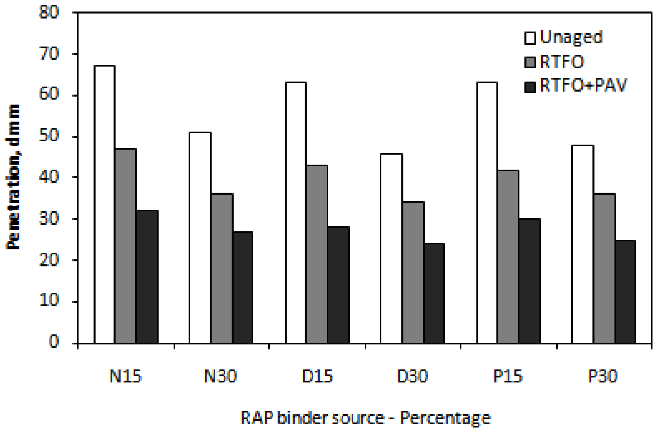


Fig. 2: Penetration of RAP modified binder under different aging conditions

3.2 Softening Point:

The softening point of all RAP binder sources and proportions increase as they undergo aging as shown in Figure 3. For the respective RAP binder proportions, the D15 and D30 RAP modified binders exhibit the highest softening point at 64°C and 67°C, respectively after subjected to long term aging.

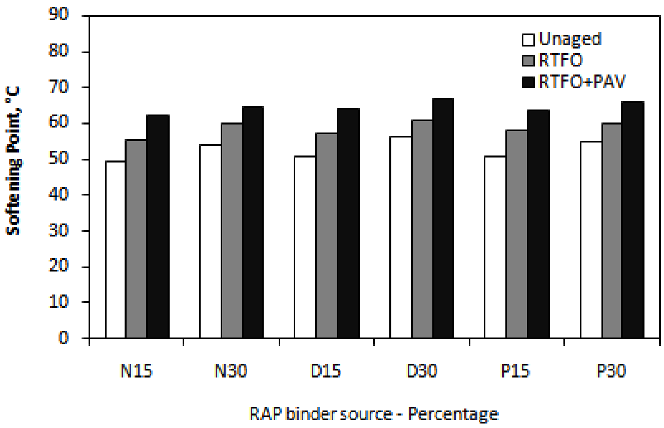


Fig. 3: Softening point of RAP modified binder under different aging conditions

Table 3 shows the percentage decrease and increase of penetration and softening point values, respectively of RAP modified binders after the short term and long term aging. It can be seen that the percentage decrease of penetration from unaged to short term and long term is nearly doubled for all RAP modified binders. Similar trend is also observed for percentage increase of softening point for all RAP binders. It is interesting to note that for RAP modified binder N15P, P15P, D30R, P30R, N30P, D30P and P30P have similar magnitude of percentage decrease within their RAP binder proportion groups and aging conditions. This relates well with similar magnitude of percentage increase in softening point in the groups. The effect of doubling the RAP binder content is to slightly reduce the percentage decrease and increase in penetration and softening point, respectively.

3.3 Viscosity:

Viscosity is a measure of a fluid's resistance to flow. Figure 4 shows consistent increase in RAP modified binder viscosity with percentage of RAP binder as well as level of oxidation increase regardless of RAP binder sources. The N15U and P15U, and N30U and P30U RAP modified binders exhibit similar viscosity values of 0.45 Pa.s and 0.58 Pa.s, respectively. The viscosities of the D15P and D30P samples are the highest which corresponds to the most viscous binders among the RAP modified binders tested. The N15P and P30P RAP modified binders exhibit 61.5% and 60.8% increase respectively and are the highest in their groups. However, P15R and P30R have the lowest viscosity increments at 35.7% and 34.8%, respectively.

Table 3: Percentage change in penetration and softening point of modified RAP binders

RAP Modified Binder	Percentage Decrease in Penetration	Percentage Increase In Softening Point
N15R	29.9	10.8
N15P	52.2	20.2
N30R	29.4	10
N30P	47.1	16.3
D15R	31.7	11.4
D15P	55.6	21.1
D30R	26.1	8.2
D30P	47.8	16.4
P15R	33.3	12.9
P15P	52.4	20.5
P30R	25	8.3
P30P	47.9	16.7

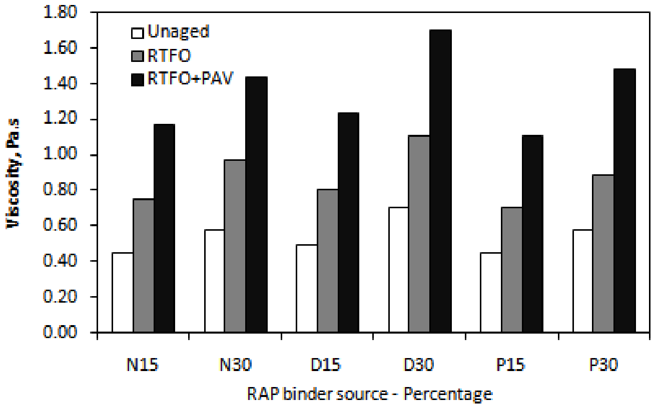


Fig. 4: Viscosity of RAP modified binder under different aging conditions at 135°C

3.4 Penetration Index:

The penetration index (PI) is a measure bitumen susceptibility to temperature and is calculated using Equation 3 (Read and Whiteoak, 2003). The PI for all modified RAP binder lies between +1 and -1 as depicted in Table 4, which is within the PI range for conventional bitumen (Roberts *et al.,* 1991).

$$PI = \frac{1952 - 500 \log pen - 20\, SP}{50 \log pen - SP - 120} \tag{3}$$

where pen = penetration at 25°C
SP = softening point

The table also indicates that as RAP modified binders are further aged, the penetration index is also increased. This means that the RAP modified binders are less temperature susceptible. It can be seen that for the respective RAP binder proportions, P15P and D30P RAP modified binders exhibit higher penetration index at 0.52 and 0.66 respectively, after long term aging.

3.5 Viscosity Aging Index:

The viscosity aging index is defined by Equation (4). Table 4 also shows the viscosity aging index of the RAP modified binders from the three sources after short term and long term aging.

$$VAI = \frac{Viscosity\ of\ aged\ RAP\ modified\ binder}{Viscosity\ of\ unaged\ RAP\ modified\ binder} \tag{4}$$

It can be seen that for the respective RAP binder proportions, N15P and P30P RAP modified binders exhibit higher viscosity aging index at 2.60 and 2.55 respectively, after subjected to long term aging. This high rate of hardening is contributed to the increasing asphaltene compounds in the modified RAP binder due to severe oxidative process

Table 4: Penetration index and viscosity aging index of RAP modified binders

Modified RAP Binder	Penetration Index	Viscosity Aging Index
N15R	-0.06	1.67
N15P	0.38	2.6
N30R	0.26	1.67
N30P	0.48	2.46
D15R	0.05	1.63
D15P	0.47	2.51
D30R	0.33	1.59
D30P	0.66	2.43
P15R	0.21	1.55
P15P	0.52	2.47
P30R	0.26	1.53
P30P	0.58	2.55

3.6 Fourier Transform Infrared Spectroscopy:

During the artificial aging processes, the modified RAP binders were severely oxidized in which aromatization, dehydrogenation and intermolecular and intramolecular hydrogen bonding of polar groups were substantially increased. The chemical functional and structural changes are precisely analyzed through infrared at vibration modes of C=O and S=O. Figure 5 illustrates the infrared spectra of the RAP modified binders for the three RAP sources. The figures clearly show the increasing trend of spectra at carbonyl and sulfoxide groups with increased RAP binder content and aging period as well as aging condition. It can be observed that the absorbance value increases at every level of oxidation at carbonyl and sulfoxide regions.

3.6.1 Carbonyl Groups of Modified RAP Binders:

Carbonyl and/or carboxyl groups were detected by IR spectra with the presence of distinct C=O absorption at 1700 cm^{-1} wavelength. The area of the carbonyl absorption was measured from valley to valley of the peak between 1726 and 1675 cm^{-1} by using Spectrum version 5.0.1 software, which corresponds to the region containing the absorption peaks for carboxylic acid, ketones and anhydrides. Carboxylic acids occur naturally in bitumen while ketones and anhydrides form on oxidative aging. The oxidative aging is well related to the existence of these three functional groups which are an integral part of large asphalt molecules (Siddiqui and Ali, 1999).

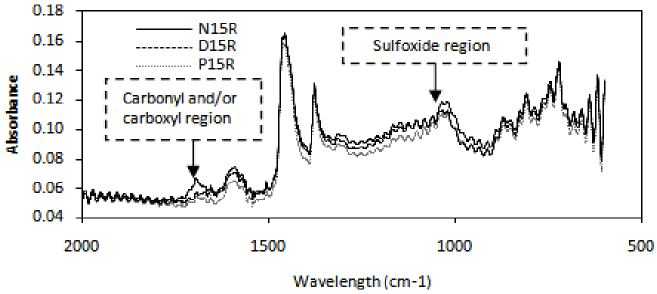
Table 5 shows the area ratio of unaged and aged RAP modified binders. It can be seen that the area ratio of all carbonyl groups increased consistently in both short term aging and long term aging for the three RAP sources. The D15P and P30P RAP modified binders exhibit the highest ratio at 0.124 and 0.175 after long term aging, respectively. The unaged RAP modified binder, N15U and P15U have the lowest C=O area ratio value. On the contrary, the area ratio of N15U and P15U increased by 63.1% and 58.2%, respectively after long term aging, representing the higher percent increase in area ratio among the RAP modified binders tested. This indicates that the evolution of RAP modified binder structures has taken place after extreme aging conditions. During that period, the amount of asphaltene compound has increased due to oxygenation of resin. During the aging process oxygen was being taken up by asphaltene molecular structure. This is similar to the findings of Siddiqui and Ali, (1999) where there was an increase in the percent weight of oxygen in asphaltenes molecules which indicate insertion of substantial amount of oxygen in the asphaltenes after each level of oxidation. Furthermore, the long term aging is attributed to a large quantity of oxygen incorporated in the newly formed oxygen-containing groups such as hydroxyl, carbonyl, and carboxylic groups. The consistent increase in area ratio correlates well to the increase in the level of oxidation which caused a pronounced increase C=O in the carbonyl region.

Table 5: Area ratio of RAP modified binders before and after aging

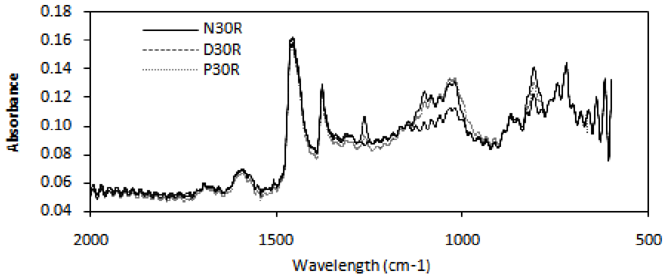
RAP Modified binder	Carbonyl	Sulfoxide
	C=O (1700 cm^{-1})	S=O (1030 cm^{-1})
N15U	0.041	0.51
N15R	0.046	0.54
N15P	0.111	0.55
N30U	0.109	0.54
N30R	0.127	0.543
N30P	0.14	0.56

Table 5: Continue

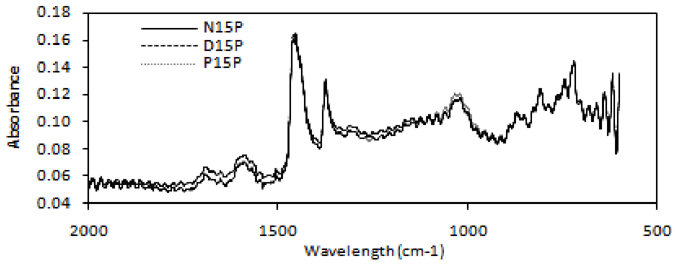
D15U	0.1	0.514
D15R	0.11	0.551
D15P	0.124	0.553
D30U	0.125	0.564
D30R	0.132	0.582
D30P	0.149	0.603
P15U	0.041	0.535
P15R	0.047	0.539
P15P	0.098	0.599
P30U	0.108	0.597
P30R	0.12	0.616
P30P	0.175	0.664



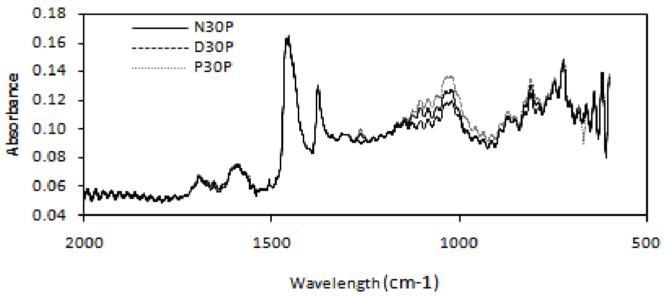
(a) Short Term Aging (15% RAP binder)



(b) Short Term Aging (30% RAP binder)



(c) Long Term Aging (15% RAP binder)



(d) Long Term Aging (30% RAP binder)

Fig. 5: Fourier transform infrared spectroscopy spectrum of RAP modified binders

3.6.2 Sulfoxide Groups of Modified RAP Binders:

Vibration of sulfoxide (S=O), a functional group most easily formed in bitumen upon oxidation of sulphide compound was captured at intense peak 1030 cm^{-1} from the IR spectra. The area of the sulphide absorption covered the wavelength between 1051 and 1027 cm^{-1}.

Table 5 relates similar trend for sulfoxide groups in which the area ratio of all sulfoxide groups increased consistently in both short term aging and long term aging for the three RAP sources. The increase aging time subsequently increase the area ratio in S=O where during the oxidation process, oxygen was absorbed by the sulphide compound of asphaltene molecular structures. This chemical reaction is contributed to further hardening of the RAP modified binder. The P15P and P30P RAP modified binders exhibit the highest S=O ratio at 0.599 and 0.664 at long term aging respectively.

3.7 Correlation Between Penetration Index, Viscosity Aging Index and Area Ratio:

Table 6 shows a high significance and Pearson correlation values between penetration index and viscosity aging index, and between penetration index and area ratio of the RAP modified binders. This is evident by high penetration index well corresponds to high viscosity aging index and area ratio of the RAP modified binders. Even though as viscosity aging index increase, the area ratio of carbonyl groups also increase, however in general there is no significant correlation between the parameters.

Table 6: Coefficient of correlation analysis

Correlation between	Pearson correlation	p-value (2-tailed)	Significant
PI*VAI	0.784	0.003	Yes
PI*AR	0.712	0.009	Yes
VAI*AR	0.501	0.097	No

Notes : PI –Penetration Index, VAI –Viscosity Aging Index, A –Area Ratio

Conclusion:

The penetration and softening point consistently decrease and increase, respectively after severe aging conditions for all RAP modified binders. The penetration index and viscosity aging index increase as the RAP modified binders are further aged. The RAP modified binders for all RAP binder sources and proportions exhibit distinct change in binder chemical evolution after subjected to short term and long term aging. The carbonyl and sulfoxide groups namely C=O and S=O consistently show increase in the area ratio at each level of oxidation. For the respective RAP binder content, the DPE and PWD RAP modified binders incorporating 15% and 30% RAP binders respectively are the most aged binders after long term aging. There is significant correlation between penetration index and viscosity aging index, and between penetration index and area ratio of RAP modified binders.

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REFERENCES

ASTM D2872, 2006. ”Standard Test Method for Effect of Heat and Air on Moving Film of Asphalt (Rolling Thin-Film Oven Test)”, ASTM International, West Conshohocken, PA,West Conshohocken, PA, USA.

ASTM D6521, 2006. “Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV)”, ASTM International, West Conshohocken, PA,West Conshohocken, PA, USA.

ASTM D5, 2006. “Standard Test Method for Penetration of Bituminous Materials”. ASTM International, West Conshohocken, PA, USA.

ASTM D36, 2006. “Standard Test Method for Softening Point of Bitumen”, ASTM International, West Conshohocken, PA, USA.

ASTM D4402, 2006, " Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer" ASTM International, West Conshohocken, PA, USA.

Lamontagne, J., P. Dumas, V. Mouillet and J. Kister, 2001. Comparison by Fourier transform infrared(FTIR) spectroscopy of different ageing techniques: application to road bitumen. Fuel., 80: 483-488.

Lesueur, D., 2009. The colloidal structure of bitumen: Consequences on the rheology and on the mechanisms of bitumen modification. Advances in Colloid and Interface Science, 145: 42-82.

Le Guern, M., E. Chailleux, F. Farcas, S. Dreessen and I. Mabille, 2010. Physico-chemical analysis of five hard bitumens: Identification of chemical species and molecular organization before and after artificial aging. Fuel., 89: 3330-3339.

Lu, X and U. Isacsson, 2002. Effect of ageing on bitumen chemistry and rheology. Construction and Building Materials., 16: 15-22.

Read, J., and D. Whiteoak, 2003. The Shell Bitumen Handbook, 5th Edition, Shell Bitumen UK.

Roberts, F.L., P.S. Khandal, E.R. Brown, D.Y. Lee and T.W. Kenneday, 1991. Hot mix asphalt materials, mixture design, and construction. 1st Ed., NAPA Education Foundation, Lanham, Maryland.

Siddiqui, M.N. and M.F. Ali, 1999. Studies on the aging behaviour of the Arabian asphalts. Fuel., 78: 1005-1015.

Su, K., Y. Hachiya and R. Maekawa, 2009. Study on recycled asphalt concrete for use in surface course in airport pavement. Resources, Conservation and Recycling, 54: 37-44.

Toteva, V., A. Georgiev and L. Topalova, 2009. Oxidative desulphurization of light cycle oil monitoring by FTIR spectroscopy. Fuel Processing Technology, 90: 965-970.

Valcke, E., F. Rorif and S. Smets, 2009. Ageing of EUROBITUM bituminised radioactive waste: An ATR-FTIR spectroscopy study. Journal of Nuclear Materials, 39: 175-185.

Widyatmoko, I., 2008. Mechanistic-empirical mixture design for hot mix asphalt pavement recycling. Construction and Building Materials., 22: 77-87.

Zhang, F., J. Yu and J. Han, 2011. Effect of thermal oxidative ageing on dynamic viscosity, TG/DTG, DTA and FTIR of SBS and SBS/sulphur-modified asphalt. Construction and Building Materials, 25: 129-137.