

Innovative approach to evaluate the oxidative ageing resistance of bituminous binders

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Abstract

A methodology, based on the use of specially-designed long-term aging protocols, was developed in order to discriminate binder formulations with respect to their resistance to oxidative ageing. The conditioning involved two protocols, an extended PAV under standard temperature and pressure conditions, for durations up to 72 hours, and a precision oven test developed by the Western Research Institute (WRI) under a contract with the Federal Highway Administration. This oven aging test ages 100 micrometer thick films at 70°C for a duration up to 84 days, to ensure no oxygen diffusion effect. The methodology uses indicators from infrared spectroscopy and rheology to fit an advanced oxidation kinetics model also developed by WRI with the FHWA: this oxidation model allows to obtain rate constants for the first (fast) and secondary (slow/constant) reactions, and determine if various additives are showing an effect on which phase of the chemical oxidative aging reaction. The methodology heavily relied on changes in rheological behavior with an emphasis on the low-temperature end of the spectrum, to determine if the modifiers reduce the low temperature cracking potential through the determination of the ΔT_c , Glover-Rowe Parameter, Rheological Index, and crossover frequency and temperature. These cracking indicators are getting more attention in the asphalt community, particularly in North America. The DSR-4mm was used to conduct the low temperature measurements in lieu of the bending beam rheometer. The study also involved thermal analysis as low-temperature thermal events such as the binder glass transition are known to evolve upon ageing. Overall, the impact of binder formulation on oxidative aging resistance was clearly observed and confirmed through this multi-technique approach which allowed to differentiate various binders and show the efficiency of modification systems with respect to given oxidation indicators. Results discerned between additives that may chemically retard oxidation from additives with merely softening effect.

1. INTRODUCTION

Improving oxidative aging resistance in bitumen is paramount for improving its durability, however it remains an elusive goal. Several ways are envisioned towards improving aging resistance: better compaction to reduce of air voids and oxygen diffusion in the asphalt mix [1], judicious selection of low aging sensitive bitumen (low asphaltene content, less sensitive aromatics, low sulfur content, etc.) [2], blending of bitumen with less aging susceptible components (reduce the volume fraction of oxidizable material in bitumen through dilution), to reduce components prone to significant structuring upon aging, treatment with antioxidants, treatment with sacrificial additives that preferentially oxidize and decompose into softer materials, treatment with acid-base modulating additives such as hydrated lime [1-2], etc. Some of these methods for improving aging resistance do not intervene specifically in the oxidation chemistry, but rather seek to mitigate, or slow down, the irreversible effects of oxidation [1].

Of the many ways to mitigate the effects of long-term aging, antioxidants are appealing since they occur naturally in biological systems, but are also produced and deployed at very large scales for many different industries. They are also attractive because they can be quite effective in many materials at levels below 100s of ppm which can make them cost efficient for paving while being compositionally and rheologically marginal in the bitumen. So far, no such effective antioxidants have been found for use in bitumen at these levels with most additives needing to be used in the 1-10% range to show a positive effect in reducing the effects of aging. At these concentrations it is unclear if these additives are clearly participating to intervene in the chemical pathway leading to oxidation by two main routes: electron donors or acceptors to scavenge free radicals, or reactive compounds which react to decompose peroxide or hydroperoxides.

Long-term aging occurs during the service life of the asphalt pavement and deals with the diffusion of oxygen from ambient air to reactive molecules within the bitumen to undergo oxidation and propagation at a molecular level, which is of course accelerated with increasing temperature [1-7]. Upon oxidation, the higher viscosity fractions that are produced are significantly more polar as they have incorporated oxygen functional groups (mainly ketones and sulfoxides) which can participate in additional specific bonding which is not present to a significant degree within the original bitumen [2,6]. Loss of volatiles also contributes to stiffening and is most pronounced during short-term aging (mixing, paving and compacting) resulting in a stiffening effect in the bitumen [2].

During this study, resistance to oxidative aging was investigated for different bitumen formulations, including a base bitumen treated with different additives. Chemical and physical methods were used to quantify the effectiveness of the formulations and rank their aging resistance. Advanced oxidation kinetics were also applied to the chemical data to show differences in the reactivity with aging severity.

2. EXPERIMENTAL PLAN

One base bitumen, from a commercial grade (35/50 penetration) product used in Europe, was modified with 5 different additives at less than 5wt% of each additive. Bitumen 1 (medium level of modification) and bitumen 2 (low level of modification) were modified with SBS polymer additive according TOTAL know-how. Bitumen 4 was modified with natural clay. Bitumen 6 and bitumen 8 were modified with TOTAL patented additives to prone specifically low kinetic of oxidation for bituminous binders. The base bitumen was also formulated as a soft bitumen. Bitumen samples were aged by two different conditions to simulate accelerated long-term aging (pressure aging vessel, PAV) and at conditions more similar to pavement in-service conditions (thin-film oven aging, TFOA). The samples were then analysed by FTIR to track the effects of the additives on chemical oxidation through the evolution of their carbonyl (C=O) and sulfoxide (S=O) content [1-7]. Rheological evolution was tracked using DSR with 8 and/or 4 mm parallel plates to determine the oxidation effect on the low, mid and upper parameters and critical temperatures used to in the Superpave Performance Grade (PG) system, and on the overall rheological behaviour as presented in the Black space [1-13]. C=O and S=O indices were used to follow long-term oxidation and fit kinetics models developed at the Western Research Institute (WRI) and also studied by others [1-2, 4-6, 14, 15]. Select details about the samples are provided in Table 1. Note: the so-called PG temperatures are not exactly PG temperatures as they were measured at the unaged stage. They are meant to compare the various binders before aging, in a similar way as penetration (PEN) and softening point (SP).

Table 1. Selected samples used to evaluate aging resistance.

Sample	Type of Modification	Upper PG (Unaged)	Intermediate PG (Unaged)	Lower PG (Unaged)
Control	Commercial bitumen (35/50)	70.5	20.0	-26.0
Bitumen 1	Control + SBS polymer additive	83.5	20.2	-26.0
Bitumen 2	Control + SBS polymer additive	72.3	20.6	-26.5
Bitumen 4	Control + additive	70.3	20.8	-25.5
Bitumen 5	Softer base of the control (160/220)	53.2	9.4	-34.8
Bitumen 6	Control + additive	72.5	20.4	-25.4
Bitumen 8	Experimental bitumen formulation	81.5	14.4	-32.8

Sample	Type of Modification	Class	PEN (dmm)	SP (°C)
Control	Commercial bitumen (35/50)	35/50	38	52,5
Bitumen 1	Control + SBS polymer additive	25/55-60	30	64
Bitumen 2	Control + SBS polymer additive	25/55-50	35	61
Bitumen 4	Control + additive	35/50	36	52,2
Bitumen 5	Softer base of the control (160/220)	160/220	185	40,2
Bitumen 6	Control + additive	35/50	38	54,2
Bitumen 8	Experimental bitumen formulation	35/50	43	57,8

2.1. Aging Protocols

Two long-term oxidation protocols were used to age the bitumen. The first protocol was accelerated aging by standard PAV conditions for 16, 24, 40, 72 hrs; and the second protocol was TFOA at 70 °C for 3, 15, 28, 63 and 84 days under ambient pressure. TFOA is designed to perform oxidation at temperatures more similar to in-service pavement conditions. By using thin films (100 microns) the diffusion limitation of oxidation penetrating the bitumen becomes insignificant and oxidation occurs more rapidly and uniformly [2,6]. TFOA allows aging to occur at significantly lower temperatures and at ambient pressure and is useful for validating any perceived aging resistance observed during PAV results. It is important to check that the antioxidant activity is not sensitive to different aging procedures. FTIR determination of C=O + S=O from TFOA provides data for the WRI oxidation model with already established activation energies and other constants.

2.2. Chemical Analysis

It has been long established that oxidation in bitumen can be tracked using FTIR by quantifying the growth of oxygen C=O (carbonyl) and S=O (sulfoxide) bands [2]. Several studies at WRI have shown better correlation with rheology and direct oxygen uptake when both oxidation species are tracked [2,6]. For analysis, samples were dissolved in CS₂ and tetrachloroethylene and the absorbance spectrum obtained using a Perkin Elmer Frontier FTIR spectrometer.

2.3. Rheological Analysis

Low-temperature properties of the bitumen such as the stiffness (S), rate of stiffness change with loading time (m-value)—an indicator of bitumen relaxation—and the newly developed cracking parameter ΔT_c ($\Delta T_c = T_c(S) - T_c(m)$) [11] were measured using the 4mm parallel plate method developed at WRI [9-10]. Using the 4mm-DSR, $T_c(G)$ is the critical temperature at which the relaxation modulus G is equal to 143 MPa and $T_c(m)$ is the critical temperature at which the slope m is equal to 0.28. Both criteria are strongly correlated with BBR standardized criteria based on 300MPa stiffness S and 0.3 m-value limits [9-10]. This testing allows for evaluation of small samples sizes (25 mg) under several temperature sweeps for a single sample in a few hours. The ability to use such a small sample size makes it possible to measure the rheological properties of small amounts of TFOA samples. The PAV samples rheology was monitored by 4, 8 and 25mm plates up to higher temperatures providing complete rheological behaviour. In addition to Black space analysis (not covered in this paper), various rheological parameters were

investigated such as ΔT_c , Glover-Rowe (G-R), crossover temperature (T_c), crossover frequency (ω_c), complex modulus (G^*), phase angle (δ), the rheological index (R) from the Christensen- Anderson (CA) model and the mastercurve to track the effectiveness of the various additives in the bitumen [1-2,7,10-13]. Finally, $\log G^*$ at 10 rad/s and 64°C was used to track the extent of aging, as proposed by the NCHRP 09-54 project [1,3,5,7].

Note: the Glover-Rowe (G-R) index was calculated from the equation: $G-R = G^* \times (\cos \delta)^2 / \sin \delta \times \omega$, [11, 12] and obtained under measurement conditions of 15°C temperature and 0.005 rad/sec angular frequency (ω).

2.4. Oxidation Kinetics

Oxidation models using TFOA at temperatures from 50, 60 and 70°C were developed at WRI under work performed for the Federal Highway Administration [2,6]. The model originally uses the build-up oxidation species determined from FTIR C=O and S=O absorbance, but it can be adapted to fit other data, like rheology for example [1,5]. TFOA data is appropriate for this kind of modelling because uncertainties due to the diffusion rate of oxygen is dependent upon the stiffness of the bitumens and this diffusion limitation is negligible for very thin-films [2,6].

The fit used to model oxidation is as follows:

$$\Delta[C = O + S = O] = RM \times \left(1 - \frac{k_2 \times p_{O_2}^n}{k_1 \times p_{O_2}^m} \right) \left(1 - e^{(-k_1 \times p_{O_2}^m \times t)} \right) + k_2 \times p_{O_2}^n \times RM \times t$$

The oxidation model fits the change in oxidation reaction products (C=O and S=O) relating to two different oxidation events. The initial oxidation event is a fast reaction rate (k_1) that tapers off as a second long-term oxidation event builds up at a considerably slower, but relatively constant rate (k_2) [1-2,4-6]. t is aging time, m and n are the pressure exponents for fast and constant reactions and P_{O_2} is the oxygen partial pressure. The reactive material (RM) is the rate limiting portion of an unknown class of compounds within bitumen that readily reacts with oxygen under the testing conditions.

C=O and S=O data generated from PAV samples can be used with the oxidation model as well, but assumptions about the pressure, activation energies and other terms need to be applied. Given enough aging points and bitumens, many of these terms can be solved, however the diffusion limitation experienced within PAV pan thickness need to be assumed as a constant among the different materials. Nevertheless, with reasonable assumptions meaningful comparisons can be made using PAV data.

3. RESULTS AND DISCUSSION

3.1. Chemical Analysis

FTIR spectra were acquired on all of the samples and the absorbance of the C=O, S=O and C=O + S=O were used to track oxidation. Figure 1 shows their evolution during TFOA for the control bitumen.

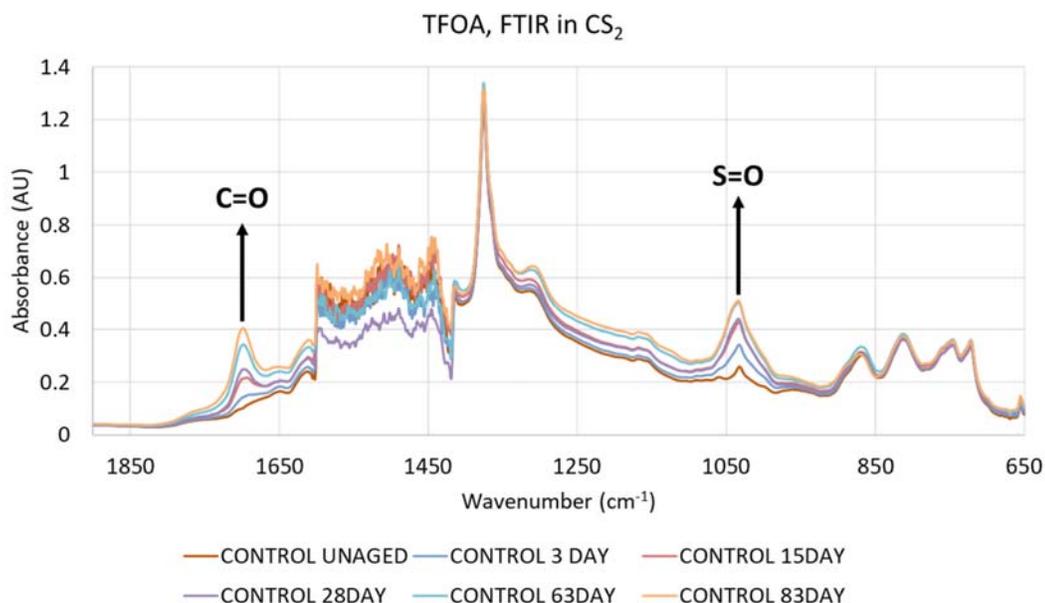


Figure 1: Select region of FTIR spectra obtained in CS₂ of the control bitumen after TFOA.

Bitumen 6 contained an additive with significant IR absorbing functionalities in the region completely overlapping the S=O band at 1034 cm⁻¹. Consequently easier comparisons could be achieved by examining the C=O data for all samples. It is necessary to subtract the amount of aged C=O from the initial amount of C=O from the unaged material to account for any changes during blending with the additives. From both the PAV and the TFOA experiments, Bitumen 1 clearly generated less oxidized (C=O) products than the Control or the other treatments, as shown in Figure 2.

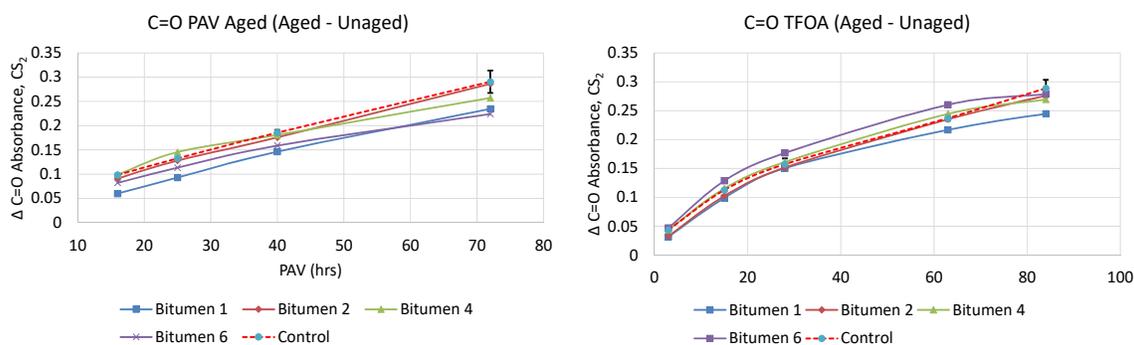


Figure 2: Change in C=O from aged vs. unaged bitumen for PAV and TFOA aged samples containing the same base bitumen.

For the testing of the other bitumen formulations, there was a significant decrease in the oxidation evolution for Bitumen 8 compared to the Control and Bitumen 5 as shown in Figure 3. The FTIR data trends are similar for the C=O+S=O data and for other samples prepared in TCE, providing duplicated validation. For the sake of space and simplicity only the C=O evolution is presented in this paper. A more complete presentation of the data will be presented in a future paper.

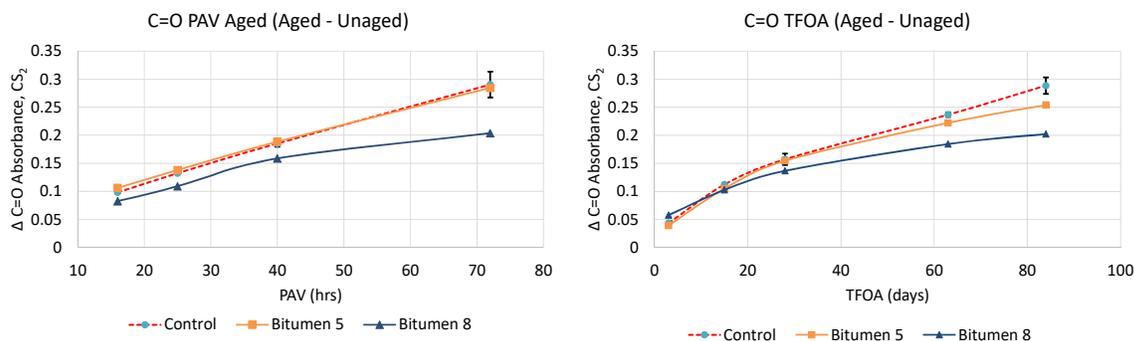


Figure 3: Change in C=O from aged vs. unaged bitumen for PAV and TFOA aged samples with different formulations.

3.2. Rheological Analysis

For the PAV samples, all continuous PG parameters were measured at all aging conditions, as shown in Figure 4. Once again this is not meant to compare the PG grades themselves but to follow the evolution of the parameters and critical temperatures upon aging.

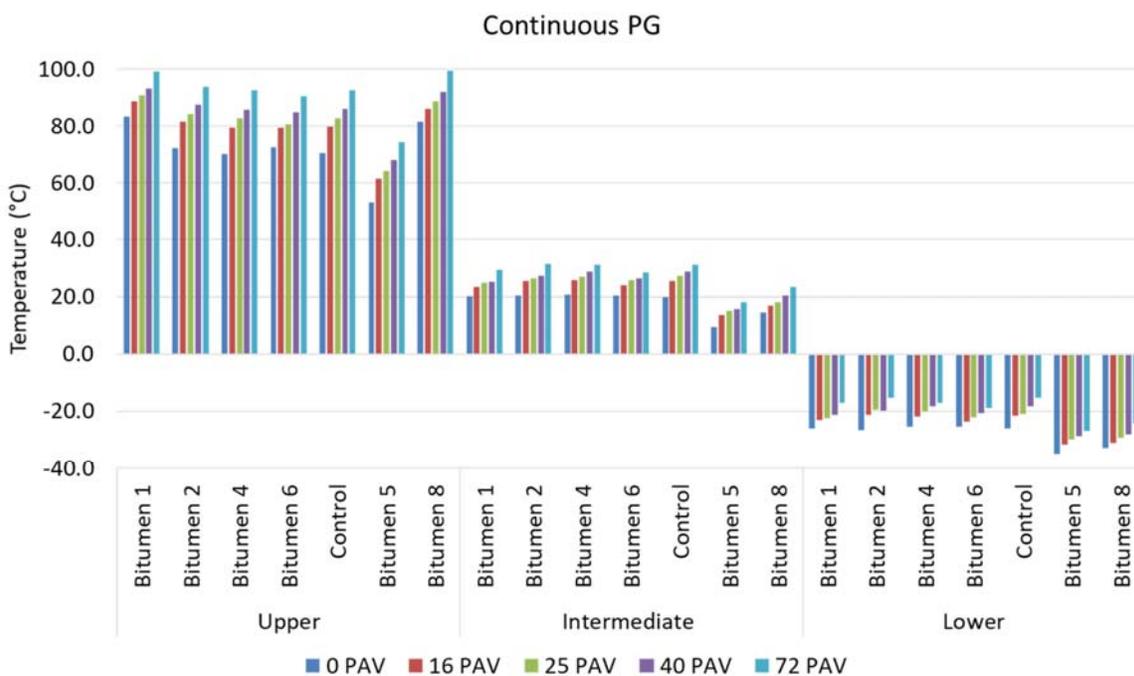


Figure 4: Evolution of upper, intermediate and lower continuous PG with PAV aging time (0 to 72 hrs).

If additives, or formulations, can reduce aging they should ideally reduce the stiffening experienced by the bitumen upon aging, relative to its unaged form. For maximum effect the stiffening reduction should occur at both the upper and lower temperature ranges. Figure 5 shows that Bitumen 1, 6 and 8 exhibit less stiffening upon aging for their upper temperature range while Bitumen 1, 5, 6 and 8 show the least amount of stiffening and/or relaxation loss upon aging for their lower temperature range.

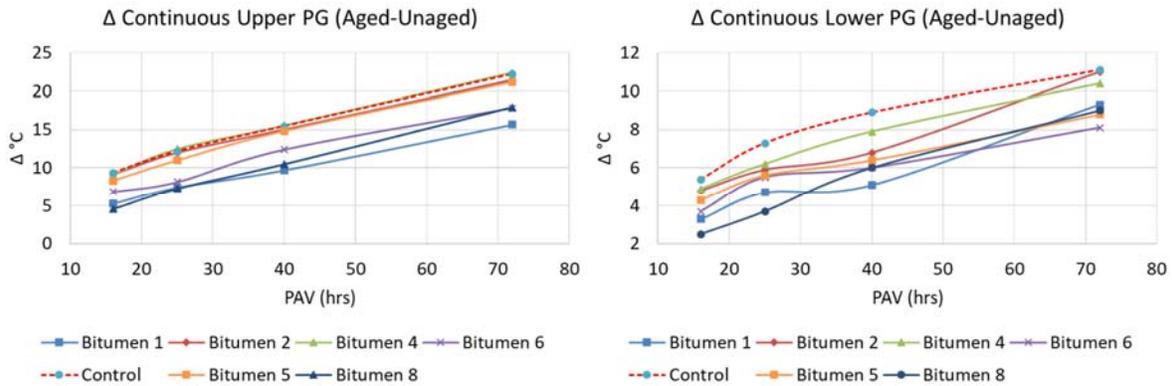


Figure 5: Change in upper (left) and lower (right) PG temperature from aged vs. unaged bitumen for PAV aged samples.

Analysis of mastercurve data (reference temperature at 15°C) showed that formulations resulting in less overall stiffening of the bitumen did not flatten the mastercurve as severely relative to the Control. This can be observed by plotting the bitumen shear modulus G^* as a function of the reduced frequency. When plotting the various unaged bitumen against the respective 72 hrs PAV aged bitumen and comparing to the Control, the stiffening effect from oxidation is more obvious in the low frequency/ high temperature range. At a given reduced frequency, 1×10^{-5} rad/s for instance, if the G^* value is smaller than the control bitumen this indicates that the material is not as stiff after the same aging conditions and duration, as shown in Figure 6.

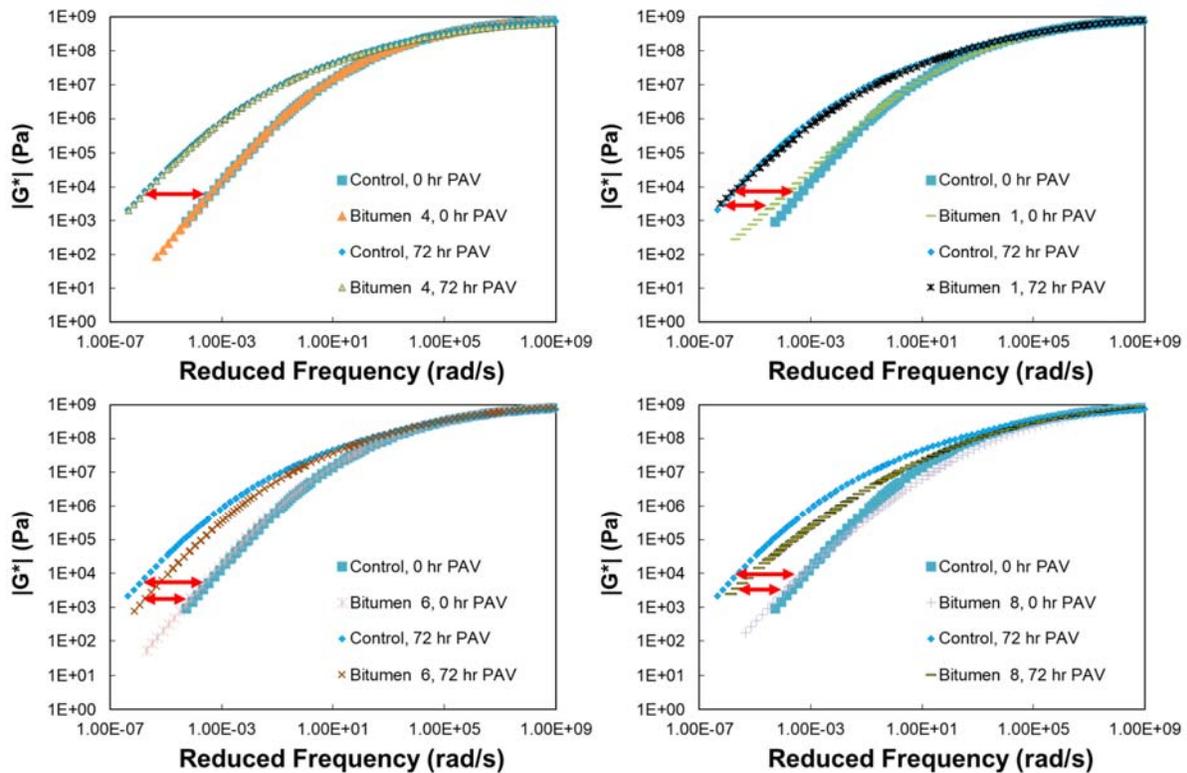


Figure 6: Mastercurve data ($T_{ref}=15^\circ\text{C}$) showing how an ineffective formulation (upper left) which shows no distinction between the Control and the other formulation which showed less stiffening at the same level of aging relative to the Control.

Many different rheological parameters are currently being proposed as metrics to measure aging and cracking propensity which increases upon aging. The parameters ΔT_c , G-R and the crossover temperature are being investigated heavily for their ability to predict cracking in the field, and/or their sensitivity to aging. ΔT_c in particular appears to be also quite sensitive to bitumen compatibility as well as an indicator of low- and intermediate-temperature cracking and durability [11]. ΔT_c is particularly attractive, from the practical point of view, since the S and m-value must already be obtained for Superpave PG specifications. Materials with poor inherent relaxation

behaviour are unable to relax stress, which become compounded by oxidative aging and physical hardening. ΔT_c shows some limitations like any rheological parameter measured under the linear-viscoelastic domain, particularly for polymer modified bitumens which can have a lower ΔT_c than the base bitumen which decreases further with aging, but this does not necessarily translate to cracking in actual field samples. Additional exceptions are being studied as part of the NCHRP 9-60 project led by WRI. Nevertheless, ΔT_c shows good correlations for a wide range of bitumens and field conditions and a high sensitivity to changes in bitumen. Similar to ΔT_c , G-R was initially developed as a surrogate for measuring ductility and has been used in several studies as a cracking parameter [12], however some classes of binders, polymer modified bitumens (PMB's) in particular and very soft bitumen, do not show agreement between both parameters. G-R derivation and temperature sensitivity are being investigated under NCHRP 9-60 and the WRI Asphalt Industry Research Consortium. However, G-R sensitivity to aging remains useful for this study [1,7]. The crossover temperature represents the temperature where material transitions from a more elastic solid-like state to a more viscous liquid-like state, which occurs at a phase angle of 45° . Above the bitumen's crossover temperature the material is able to flow and relax stress, whereas below the crossover temperature the material becomes more brittle and prone to cracking [10,13]. From these various metrics, Bitumen 1 and 8 show consistent aging resistance over all aging levels compared to the control and other formulations, yet for some metrics and various aging levels, Bitumen 6 also showed significant aging resistance (Figure 7).

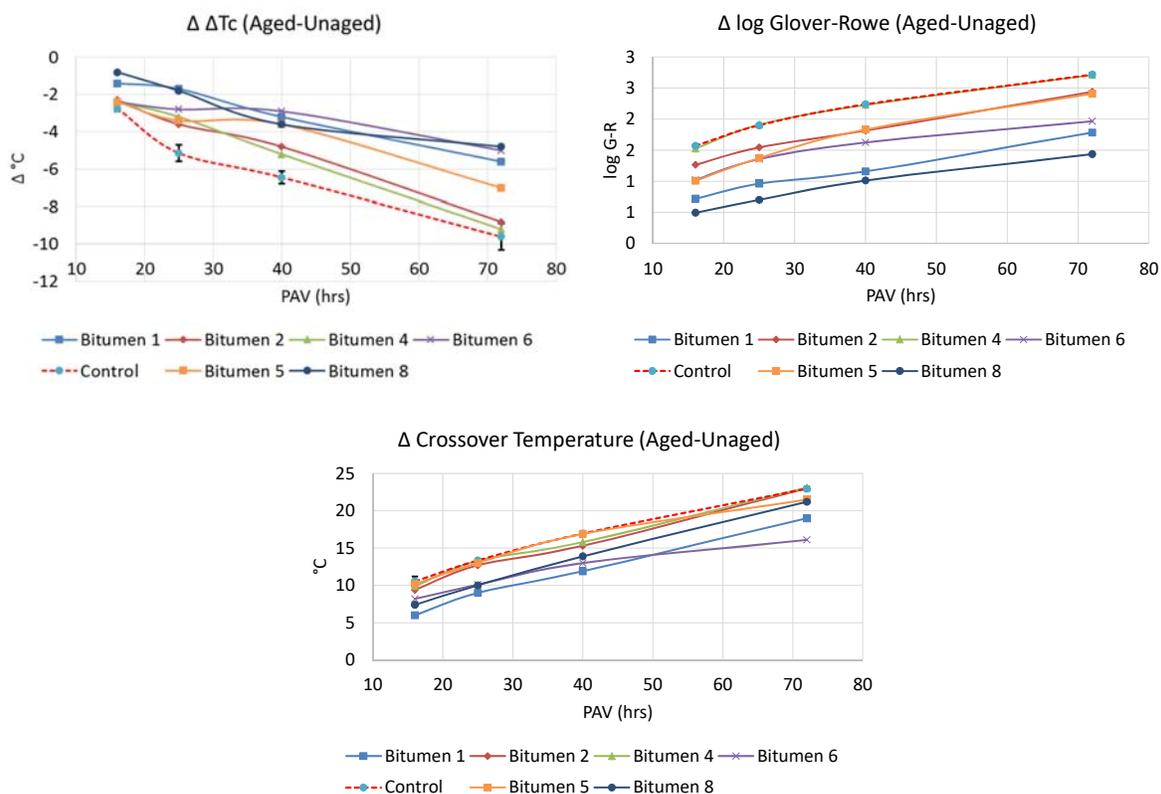


Figure 7: Evolution of various cracking parameters— ΔT_c (top left), G-R (top right) and crossover temperature (bottom) under PAV exposure. The difference in aged vs. unaged of the same bitumen is used to remove initial rheological changes imparted by the formulations.

Aging has been tracked following changes in the G^* and δ , one such sensitive metric for tracking oxidation was developed extensively under NCHRP 9-54. Within that work, larger changes in G^* in the viscous domain were exploited to develop a sensitive aging metric for G^* at 64°C and 10 rad/s [1,3,5,7]. For other analysis, assuming the glassy modulus and considering the crossover frequency, as in the case of the CA model, allows determination of the R-value which provides a measurement of the shape of the relaxation spectrum and mastercurve. When bitumens age their R-value increases and their crossover frequency decreases. Both the CA model and the G^* at 64°C and 10 rad/s methods have limitations, especially for bitumens exhibiting PMB phase behaviour, however they are effective at tracking the evolution of aging, especially for a single bitumen. Both of these aging metrics showed that Bitumen 1, 6 and 8 performed better under all aging conditions than the control bitumen and other formulations, as shown in Figure 8.

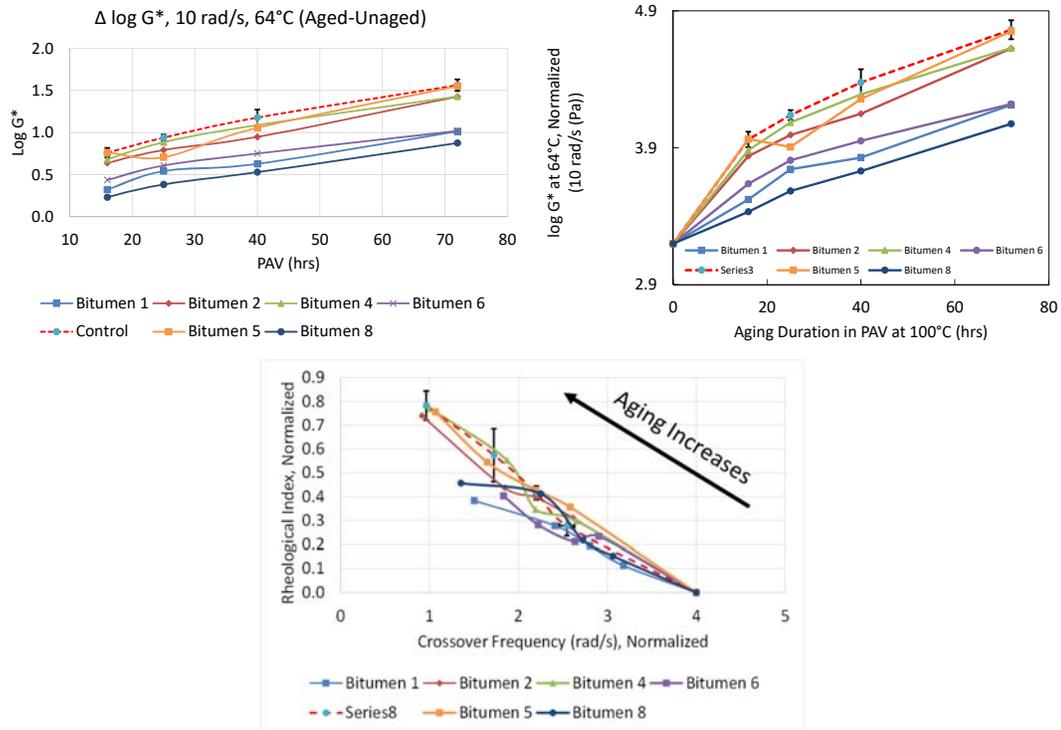


Figure 8: Evolution of aging followed by G^* at 64 °C and 10rad/sec (top plots) and the CA R-value and crossover frequency. In the top left plot the difference in aged vs. unaged of the same bitumen is used to remove initial rheological changes imparted by the formulations.

TFOA provides enough material that can be tested by 4mm DSR to probe low-temperature and intermediate-temperature rheological properties. Figure 9 shows that Bitumen 1 and 8 had the lowest increase in ΔT_c relative to their respective unaged bitumen, confirming the results from the PAV aged samples (see Figure 5). However, TFOA Bitumen 6 did not perform as well as when PAV aged. This contradiction between PAV and TFOA may be an example of the limitation of using only PAV aging to draw conclusions about aging behaviour of certain additives at in-service conditions.

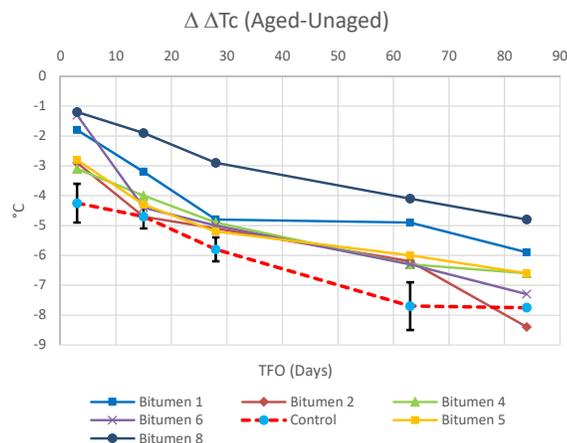


Figure 9: The change in ΔT_c of the various bitumens relative to TFOA time.

3.3. Oxidation Kinetics

One of the important developments that helped lead to a robust oxidation kinetics model was the TFOA procedure which removes the difficulties of modelling oxygen diffusion at different temperatures and viscosities. The model

allows for the quantification of the oxidation sensitive reactive material (RM). Early work showed a relationship between the bitumen aromatics fraction and RM [6].

As a first approximation, the model was applied to the C=O+S=O data from the PAV aged samples assuming the pressure exponents for fast (m) and slow (n) reaction rates to be 0.3 and extrapolating to 100 °C rate constants for the fast and slow reaction from previous data. The only unknown, RM (neglecting relative bitumen-dependent diffusion and pressure dependency effects), was then determined by minimizing the error of the fit to the kinetics model. Figure 10 shows some results of fitting the oxidation model with PAV aging data. Modelling results showed Bitumen 1 and 8 were the most resistant to chemical aging.

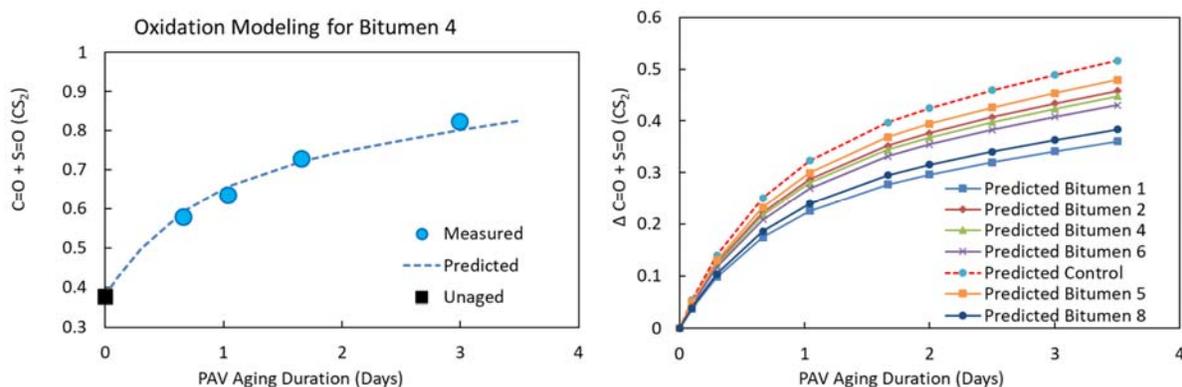


Figure 10: The left plot shows actual measured C=O+S=O data from FTIR for Bitumen 4 after various durations of PAV aging, and predicted data from the oxidation model. The right plot compares the predicted data for the different PAV aged bitumen samples.

Likewise, application of the oxidation model to TFOA C=O + S=O data provided a similar trend showing that Bitumen 1 and 8 were the most resistant to oxidation, as shown in Figure 11. The data modelled using PAV data and using TFOA data showed some discrepancies. For instance the PAV data showed Bitumen 1 as more aging resistant than Bitumen 8, when the TFOA data showed the opposite—both bitumen remaining best ranked. There are other slight discrepancies in the aging resistance order inferred from the RM amount, as seen in Table 2. Analysis of a second set of aged Control bitumen by TFOA showed repeatability within 0.01 for RM, clearly confirming that Bitumen 8 and 1 outperform the other formulations. The ranking difference between the PAV and TFOA data may be related to factors such as unknowns in rates of diffusion, temperature and pressure dependency between different bitumens during PAV aging, possible changes in oxidation behaviour from more severe PAV conditions relative to gentler TFOA or due to experimental error.

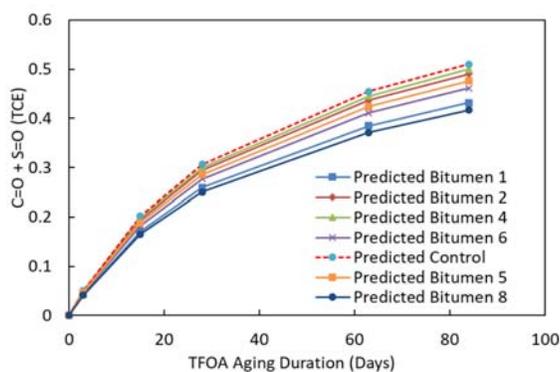


Figure 11: Predicted C=O+S=O evolution for the different bitumen samples data TFOA using the WRI oxidation model. Error bars are not shown as they are too small to be meaningful.

Table 2. Amount of RM in ascending order determined from the WRI oxidation model for C=O+S=O data obtained from PAV (left) and TFOA samples (right).

PAV			TFOA		
Bitumen	RM	Rank	Bitumen	RM	Rank
1	0.293	1	8	0.293	1
8	0.312	2	1	0.303	2
6	0.351	3	6	0.324	3
4	0.364	4	5	0.334	4
2	0.373	5	2	0.345	5
5	0.390	6	4	0.351	6
Control	0.420	7	Control	0.359	7

4. CONCLUSIONS

A series of bitumen formulations were tested for their ability to resist long-term aging at the bitumen level through two different oxidation methods: standard PAV aging and TFOA (more similar to in-service aging). The aging resistance was evaluated through chemistry using FTIR to quantify oxidation species, and through mechanical properties using DSR through a wide range of temperatures (-30 through 100 °C) using 4, 8 and 25 mm parallel plate geometries.

A reduction in chemical oxidation, as evaluated through FTIR, was most evident for Bitumen 1 and 8 as they produced significantly less C=O+S=O relative to their unaged samples. Bitumen 6 also showed a significant reduction in oxidation products for PAV aged samples but a less significant reduction for TFOA samples. The reason for this discrepancy needs to be further studied as it may be an example of a limitation of using more severe PAV aging to predict additive performance at in-service conditions. In the future it would be important to confirm if the change in aging resistance ranking between the two aging methods is related to the aging methods or to other possible factors, as it could have serious implication for using PAV aging as the sole method to determine aging resistance. Application of the WRI oxidation model showed that Bitumen 1 and 8 had the lowest amount of RM and that Bitumen 6 was the next best performer.

Analysis of the mechanical properties of the bitumens were consistent with the results from the chemical evaluation. Various cracking parameters (ΔT_c , G-R, crossover temperature) and aging sensitivity parameters (mastercurve shifts, R-value, G-R, and G^* at 64°C) all showed that Bitumen 1 and 8 consistently performed the best when compared to their respective unaged bitumen. As with the chemical data, some inconsistencies were seen for Bitumen 6 compared to Bitumen 1 and 8. These discrepancies may be related to a different action mechanism of the additive under different aging conditions.

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REFERENCES

- [1] Kim, Y. R., C. Castorena, M. D. Elwardany, F. Yousefi Rad, B. S. Underwood, A. Gundha, P. Gudipudi, M. Farrar, and R. Glaser. "Long-term Aging of Asphalt Mixtures for Performance Testing and Prediction", NCHRP 09-54 Project, Report No. 871, Transportation Research Board, Washington, D.C., 2018.
- [2] Petersen, J. C. "A Review of the Fundamentals of Asphalt Oxidation", Transportation Research E-Circular, (E-C 140), TRB, Washington, D. C., 2009.
- [3] Elwardany, M. D., F. Yousefi Rad, C. Castorena, and Y. R. Kim. "Evaluation of Asphalt Mixture Laboratory Long-Term Aging Methods for Performance Testing and Prediction", *Road Materials and Pavement Design*, 18(1), 2017: 28-61.
- [4] Glover, C. J., R. Han, X. Jin, N. Prapaitrakul, Y. Cui, A. Rose, J. J. Lawrence, M. Padigala, E. Arambula, E. S. Park, and A. E. Martin. (2014). *Evaluation of Binder Aging and Its Influence in Aging of Hot Mix Asphalt Concrete*. Publication FHWA/TX-14/0-6009-2. FHWA, U.S. DOT.

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- [5] Elwardany, M. D., F. Yousefi Rad, C. Castorena, and Y.R. Kim. "Climate-, Depth-, and Time-Based Laboratory Aging Procedure for Asphalt Mixtures", *AAPT*, Vol. 87, 2018: 467-512.
- [6] Glaser, R., T. F. Turner, J. L. Loveridge, S. L. Salmans, and J. P. Planche, "Aging Mastercurve (FP 10) and Aging Rate Model (FP 11)", *Fundamental Properties of Asphalts and Modified Asphalt*", Volume III, Technical White Paper, WRI, Laramie, WY, 2015.
- [7] Yousefi Rad, F., M. D. Elwardany, C. Castorena, and Y. R. Kim. "Evaluation of Chemical and Rheological Aging Indices to Track Oxidative Aging of Asphalt Mixtures", *TRR*, 2018, 2672: 349-358.
- [8] Farrar, M., C. Sui, S. Salmans, and Q. Qin, "Determining the Low Temperature Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR)", Technical White Paper FP08, FHWA, Washington, D.C., 2017.
- [9] Sui, C., M. J. Farrar, W. H. Tuminello, and T. F. Turner, "New Technique for Measuring Low-Temperature Properties of Asphalt Binders with Small Amounts of Material", *TRR*, 2010, 2197, pp. 23-28.
- [10] Elwardany, M. D., J.-P. Planche, and J. J. Adams. "Determination of Binder Glass Transition and Crossover Temperatures Using Four-mm Plates on a Dynamic Shear Rheometer: Significance and Applications", *TRR*, 2019, DOI: 10.1177/0361198119849571.
- [11] Anderson, M, G. King, D. Hanson, and P. Blankenship. "Evaluation of the Relationship between Asphalt Binder Properties and Non-Load Related Cracking", *AAPT*, 80, 2011, pp. 615-649.
- [12] Rowe, G. "Prepared Discussion Presented in Response to M. Anderson et al., *AAPT*, V.80, 2011".
- [13] Garcia Cocalon, L., Kaseer, F., Arámbula-Mercado, E., Epps, A., Martin, N. M., Pournoman, S., and Hajj, E. "The Crossover Temperature: Significance and Application Towards Engineering Balanced Recycled Binder Blends", *Road Materials and Pavement Design*, 2018.
- [14] Hofko, B., Porot, L., Falchetto Cannone, A. et al.; "FTIR spectral analysis of bituminous binders: reproducibility and impact of ageing temperature" *Materials Structures* (2018) 51: 45. <https://doi.org/10.1617/s11527-018-1170-7>
- [15] J. Lamontagne, P. Dumas, V. Mouillet, J. Kister, "Comparison by Fourier transform infrared (FTIR) spectroscopy of different ageing techniques: application to road bitumens", *Fuel* 80 (2001) 483-488