

Effect of polyphosphoric acid on bituminous binder oxidation

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ABSTRACT

Polyphosphoric acid (PPA) has been successfully used for years in the US and other parts of the world to enhance high service temperature stiffness of paving grade bitumen. Several researches show evidences of PPA interaction with asphaltenes and resins. These interactions typically lead to an increase of the asphaltene content concurrently with a decrease of the resins content. The mechanism describes a dispersion of the asphaltene-resins phase leading to the increase in viscosity of the bituminous binder. Whereas the impact of PPA onto the physical properties of the asphalt at high temperature is reasonably well described, the favorable effect reported by some authors, on bitumen aging remains unclear. In order to study the effect of PPA on bitumen oxidation, two bituminous binders from two different sources were treated with PPA and oxidized as thin films at 70 °C for up to 8 weeks along with the untreated control materials. Oxygen uptake was determined by transmission Fourier-transform infrared spectroscopy for each material, and the rates of reaction of the treated and untreated bitumens were compared. Oxygen diffusivity differences were investigated under the same conditions with thicker films (1000 micron). Molecular weight change differences were measured with size exclusion chromatography. The changes in rheological properties were examined using dynamic shear rheometry. The overall results indicate that PPA alters the oxidation reaction mechanism compared to reference bitumen by slightly reducing the oxygen uptake.

Keywords: Additives, Ageing, Asphalt, Modified Binders

1. INTRODUCTION

Bitumen is subject to chemical oxidation by reaction with dissolved oxygen originating from the atmosphere. Bitumen oxidation results in hardening of bitumen and reduction in its ability to relax stresses. Consequently, oxidized bitumen retain stress for longer times under loading, and that stress is larger than for unaged bitumen. During a cooling event, oxidized bitumen builds stress faster, and fails at a higher temperature. Ultimately, oxidation leads to cracking and failure of bitumen concretes through a combination of thermal stress and loading.

Field observations indicate that bitumen modified with polyphosphoric acid (PPA) often performs as well or better than similarly graded unmodified bitumen with regard to long-term durability when properly used. Previous studies indicate that PPA modification beneficially influences the oxidation of bitumen [1-3]. However, several questions remain concerning as to how PPA affects the oxidation rate:

- 1) Does PPA change the intrinsic oxidation mechanism?
- 2) Does PPA change the mass transfer of oxygen and/or its solubility in the bitumen?
- 3) How does PPA affect the micro structure and resulting mechanical properties as bitumen oxidize?

The influences of PPA concentration on thin-film isothermal aging of neat bitumen (no polymer) were studied. Methods used included RTFO aging, Fourier transform infrared spectroscopy (FTIR), dynamic shear rheometry (DSR), and SAR-AD[®] (proprietary automated fractionation system). Only portions of the study are discussed in this paper.

2. EXPERIMENTAL

2.1 Materials and Approach

Two unmodified bitumens and their PPA-modified counterparts were supplied by Innophos. PPA modifications were made by blending 2% INNOVALT[®] N200 with L-VIS[™] Technology into the unmodified bitumen. This modifier is a proprietary formulation including PPA with the CAS number 8017-16-1 as mentioned in the safety data sheet.

Bitumen 1	PG58-28
Bitumen 1 (PPA)	Bitumen 1 modified as discussed above
Bitumen 2	PG58-28
Bitumen 2 (PPA)	Bitumen 2 modified as discussed above

Control samples for each bitumen type were unmodified base bitumen and PPA-modified bitumen after RTFO treatment to mimic the mix-plant thermal history. The untreated base bitumen samples were aged identically to the PPA treated materials (at the same time in the same ovens). Oxidation was performed in ambient pressure, precision ovens using 50 micron films to eliminate diffusion control, and 1000 micron films to study diffusion effects. Although the two supplied bitumens have the same PGs, they are from different sources and have different chemical compositions as can be seen in Table 2 later.

2.2 Thin film aging and FTIR methods

Prior to beginning the aging tests, all of the samples were RTFO aged (AASHTO T240) to simulate oxidation occurring in the mix plant and during pavement placement. All four RTFO treated samples were solvent cast as 50 micron films and were aged in convection ovens at 70 °C for 8 weeks. Splits of the thin film samples (each split in its own pan) were removed from the ovens at 0, 8, 14, 28 and 56 days. After aging for the prescribed time, the changes in composition were monitored by fast Fourier transform infrared spectroscopy (FTIR) using an Agilent Cary 630 FTIR instrument. The FTIR spectra were obtained in transmission mode through sodium chloride windows with a 1 mm beam path length. The aged bitumen was prepared for measurement by dilution with carbon tetrachloride at a concentration of 50 mg bitumen per milliliter of solvent.

Very thin films (50 microns) were employed during oven aging to ensure no rate limitation due to air diffusion into the samples as occurs in PAV aging. Toluene was used as the casting solvent. Removal of the solvent required sweeping with argon for 4 hours at room temperature followed by vacuum-oven treatment for 4 hours at 70 °C. Higher temperatures were avoided to prevent sulfoxide decomposition. The pans used to cast the films were commercially available aluminum weighing pans. For analysis of the data (complicated by the change in composition due to PPA addition), the oxidation effects are best observed by subtracting the RTFO-aged sample FTIR spectrum (time zero) from the oxidized sample spectra leaving just the areas that change. This procedure also removes the distortions caused by the PPA additive (unless the PPA changes as well). Oxidation effects in bitumen are plainly seen in IR at wave numbers 1035 (sulfoxide) and 1700 (carbonyl).

2.3 Oxidation kinetics method

A number of mathematical and/or kinetic expressions and/or chemical mechanisms have been proposed in the past [4-12]. The dual sequential mechanism for oxidation of bitumen proposed by Petersen [13] provides a simplified conceptual view of oxidation chemistry in bitumen. Reducing this chemical path concept to a mathematical form was the approach used in Federal Highway Administration sponsored work at WRI to create the robust model based upon

fundamental chemistry, the WRI oxidation kinetics model [14]. The final integrated form of the model is shown in equation 1:

$$P = C_{fast,0} \left(1 - \frac{k_2}{k_1} \right) (1 - e^{-k_1 t}) + k_2 C_{fast,0} t + P_o \quad (1)$$

where:

P = metric for the extent of oxidation, usually S=O and C=O absorbance sums

P_o = the RTFO time-zero value of P

$C_{fast,0}$ = the reactive material concentration for the fast reaction

k_2, k_1 = the slow and fast reaction rate constants for isothermal aging, temperature dependent according to the Arrhenius equation

The above model is applied to data generated in the ambient pressure oxidation study. Equation 1 is used to fit the isothermal FTIR data to determine the rate constants and amount of reactive material for each binder studied.

The WRI oxidation kinetics model was developed by assuming parallel rate limiting steps, one fast and one slow, that likely share free radical species. The final integrated form of the model has the following parameters: P , a metric for the extent of oxidation, usually S=O and C=O absorbance sums; P_o , the RTFO time-zero value of P ; $C_{fast,0}$, the reactive material concentration for the fast reaction; k_1, k_2 , the slow and fast reaction rate constants for isothermal aging. The model was applied to data generated in the thin film oxidation study. Equation 1 was used to fit the isothermal FTIR data to determine the rate constants and amount of reactive material for each bitumen studied.

2.4 Diffusion method

Diffusion effects were investigated by comparing unmodified 1000 micron samples and modified 1000 micron samples aged for 56 days at 70°C. The differences in the degree of oxidation of the 1000 micron films were then compared to the same materials after eight weeks of oxidation at 70°C using 50 micron films. The 50 micron film oxidation rate is controlled by the chemical oxidation rate alone, as the movement of oxygen into the entire sample is much faster than the chemical reaction rate. The 1000 micron films are sufficiently thick that the oxidation rate is limited by the ability of the oxygen to penetrate the film by molecular diffusion. At the surface, the rate is controlled by the chemistry, but deeper in the film the rate slows down because there is less dissolved oxygen since the reaction is consuming it faster than diffusion can deliver it.

2.5 SAR-AD® method

SAR-AD was developed at WRI with funding from the Federal Highway Administration [15]. It couples a HPLC chromatography-based SAR separation with a previously-developed bitumen analysis method called the Asphaltene Determinator® [16] which characterizes asphaltenes by solubility. The combined system, SAR-AD, generates *saturates, aromatics, and resins* (SAR) chromatographic fractions and elutes cyclohexane soluble, toluene soluble, and methylene chloride-methanol soluble asphaltene subfractions. Each of the six fractions passed through a 500 nm wavelength optical detector and an evaporative light scattering detector (ELSD). The 500 nm optical detector is sensitive to the concentration of brown-colored pericondensed ring structures, and the ELSD provides near gravimetric detection for all six SAR-AD fractions. SAR-AD is proving superior to standard SARA and Iatroscan methods in monitoring composition changes associated with aging and modification.

2.6 Dynamic shear rheometry (DSR)

The dynamic shear rheometer (DSR) is used to characterize the viscous and elastic behavior of bitumen. This characterization is also used in the Superpave PG bitumen specification for limited temperature and frequency cases. DSR testing is performed on a small amount of bitumen sample sandwiched between two parallel circular plates. The lower plate is fixed in place and the upper plate rotates the sample back and forth over a range of frequencies. This may be done at multiple isothermal temperatures to produce a master curve describing the full temperature and frequency-dependent behavior of the material.

The DSR measures a specimen's complex shear modulus (G^*) and phase angle (δ). The complex shear modulus can be considered to be the sample's total resistance to deformation when repeatedly sheared, and the phase angle is the lag between the applied shear stress and the resulting shear strain. The larger the phase angle, the more viscous the material, with purely elastic material having a phase angle of 0 degrees and purely viscous material having a phase angle of 90 degrees.

Rheological changes were obtained by running isotherms on a Malvern dynamic shear rheometer (DSR) fitted with 4 mm plates, using the method developed by Sui et al. [17]. The isotherms typically ranged from -30 to 30°C, with a few more highly aged samples including a 45°C isotherm. Machine compliance corrections were employed, as they become more significant with stiff material – this happens when large plates and low temperatures are used. Master curves were fit with the Christensen-Anderson (CA) model [18]. The shift function employed is a quadratic fit of an Arrhenius plot.

This 4mm-DSR method is under consideration in the USA for possible use in complement or replacement to the Bending Beam Rheometer for low temperature rheological evaluation and specification of bituminous binders.

3. RESULTS AND DISCUSSION

3.1 FTIR Spectral Changes with Oxidation

To evaluate sulfoxide and carbonyl changes, the time-zero spectrum was subtracted from the other aging time samples, providing a net-change spectrum. These net-change spectra indicated a change in the PPA or the appearance of new oxidation products near and interfering with the sulfoxide region. However, both bitumen pairs show qualitatively a reduction in sulfoxide formation rates that are somewhat balanced by an increase in carbonyl formation rates. The largest differences occur early in the oxidation process.

Oxidation effects in bitumens 1 and 2 are plainly seen in IR at wave numbers 1035 (sulfoxide) and 1700 (carbonyl). The net-change spectra for the sulfoxide region of bitumen 1 are shown in Figure 1. The net-change spectra for the carbonyl region are shown in Figure 2.

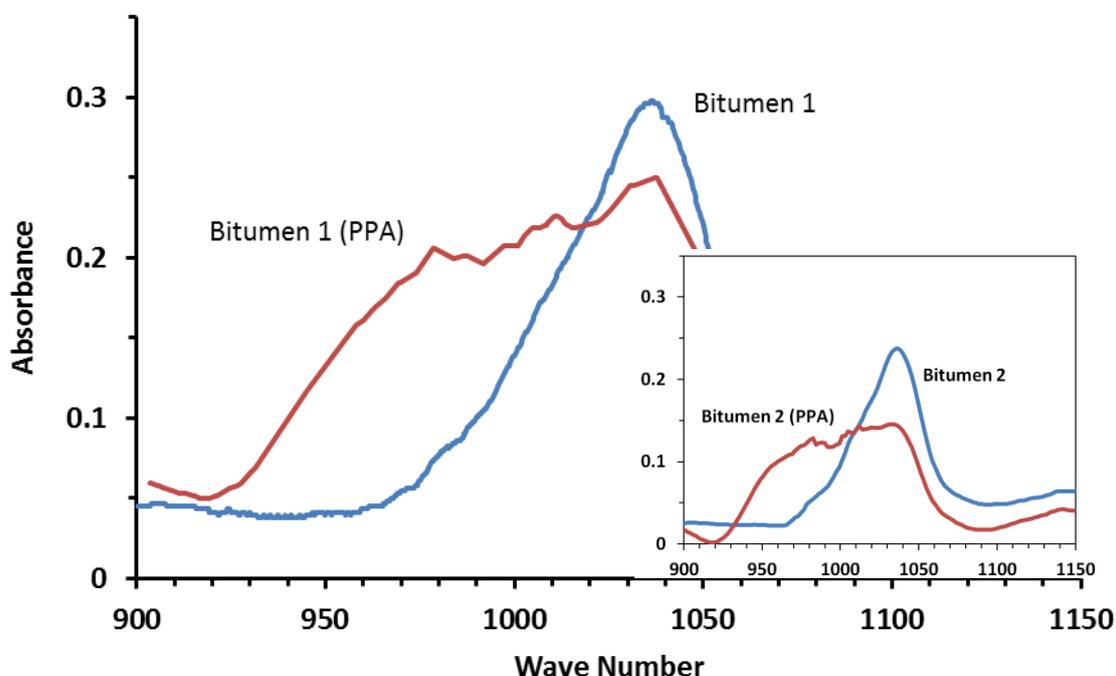


Figure 1. Difference spectra for aged (70°C, 8 wks) bitumens in sulfoxide region.

For this Bitumen 1 pair, the 1035 wave number region suggests possibly less sulfoxide oxidation and a new absorbance below 1035 (not seen in neat bitumen). The 1700 wave number region shown in Figure 2 suggests no significant change in chemistry or rate for carbonyl formation for Bitumen 1 after the general rise in baseline is accounted for.

The Bitumen 2 pair behaves similarly, there is a minor reduction in sulfoxide production rate when the baseline shift is considered, and a small increase in the carbonyl formation rate, even after consideration of the baseline shift. In both bitumen there are unique oxidation products forming in the PPA-modified samples with a broad response around 970 wave numbers.

To verify that the peak near wave number 970 is from PPA, a thin film of PPA was exposed in the laboratory and infrared spectra were gathered periodically for about 11 hours. In this period an increase in the PPA absorption spectra in this region was observed, indicating that the 970 peak is not related to bitumen interaction with PPA.

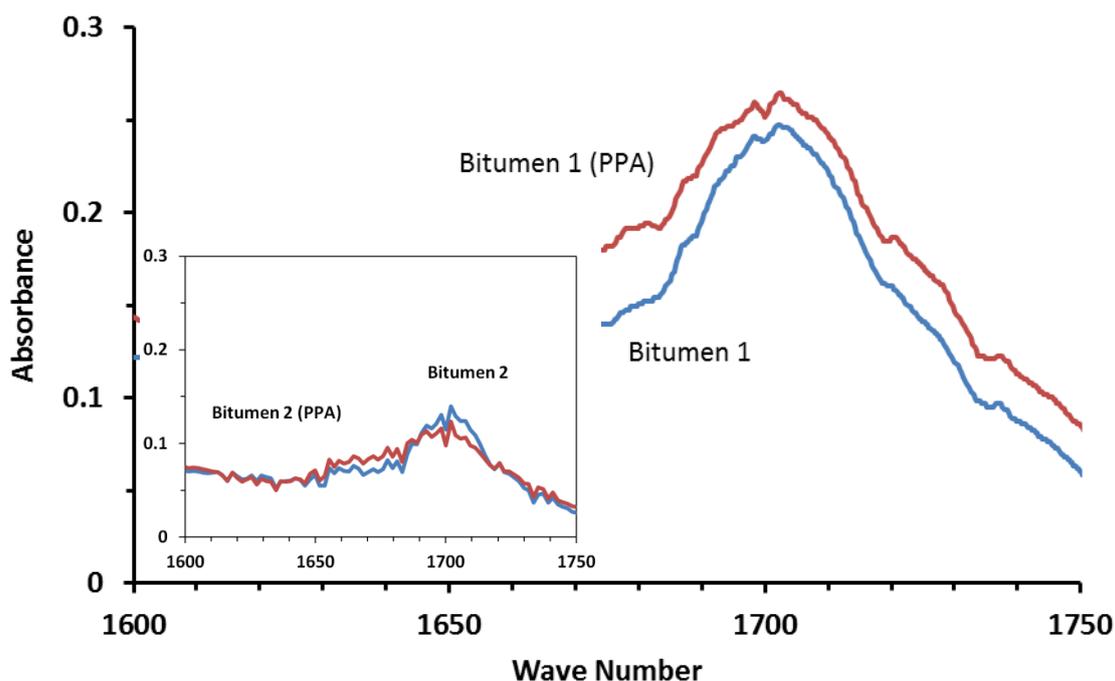


Figure 2. Difference spectra for aged (70°C, 8 wks) bitumens in the carbonyl region.

3.2 Diffusion Effect

For pure compounds, the diffusivity is inversely proportional to viscosity, so it is reasonable to expect the more viscous PPA-treated bitumen to have slower oxygen diffusion in thick samples. However, in a material that behaves more as a suspension, the absence of evidence for lower diffusion rates in PPA-treated bitumen would strongly suggest that the PPA interacts with the suspended phase and not with the suspending (liquid) continuous phase (maltenes). Oxygen transport would favor the less viscous suspending phase.

For the Bitumen 1 pair, the PPA-treated material appears to have a higher diffusivity than the untreated material. This would only be true if the PPA influence is on the suspension structure. There may be a migration of polar molecules in the suspending phase to the suspension, decreasing the viscosity (and increasing the diffusivity) of the suspending phase, but having substantial enough effect on the suspension to increase the viscosity of the whole system. This is consistent with the widening of performance grade limits in PPA treated bitumen (typically 1 grade per 0.5% PPA), since the mobile phases control rheology at low temperature. For the Bitumen 2 pair, the PPA-modified material has a lower diffusivity than the untreated bitumen. This diffusion study demonstrates that PPA does influence diffusivity, but that original bitumen properties must determine the direction of the influence.

3.3 Oxidation Kinetics

The WRI oxidation kinetics model was applied to the data collected for the neat and PPA treated bitumen through the 8 week aging process. An example of the model fit to the Bitumen 1 data is shown in Figure 3. The rate limiting step, prior to carbonyl and sulfoxide formation, is identical and mechanism changes that affect observed oxide production amounts occur after this step. The fit parameters for the model are identical for all four materials, except for the time-zero offsets (Table 1). Hence, the rate limiting step is not affected. These rate curves are the sum of the oxides, so the results infer that only the proportions of oxides change in the PPA treated samples, but the overall amount of oxygen uptake is the same. A likely explanation is that the PPA sterically interferes with radical collision with aliphatic side chain sulfides, allowing more of the radicals to reach the benzyl carbons near the aromatic cores. Both of these reaction sequence steps are much faster than the rate limiting step.

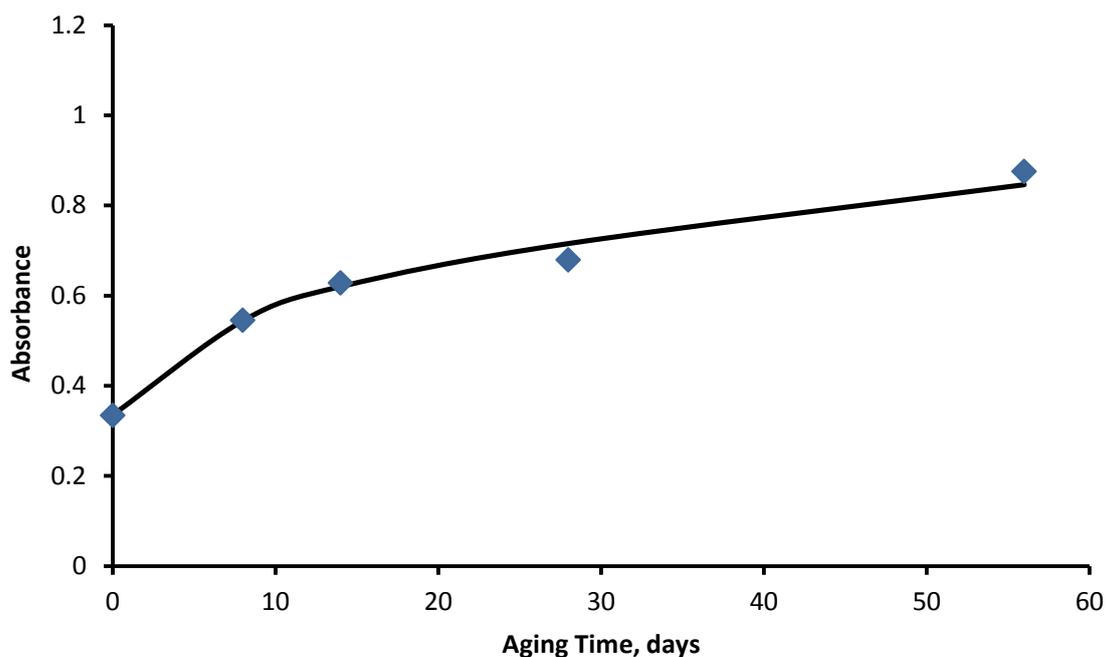


Figure 3. Aging model fit to oxide sums for Bitumen 1.

Table 1. Fit parameters for kinetic model fits for all samples.

Model Parameter	Bitumen 1	Bitumen 1 (PPA)	Bitumen 2	Bitumen 2 (PPA)
k_1	0.136	0.136	0.136	0.136
$C_{fast,0}$	0.294	0.294	0.294	0.294
P_0	0.335	0.710	0.352	0.731
k_2	0.015	0.015	0.015	0.015
R^2	0.986	0.994	0.979	0.970

3.4 Changes in generic composition by SAR-AD analyses

The results of the SAR-AD analyses of the control bitumen, modified bitumen, and 8-week aged samples are summarized in Table 2. The response changes with aging for ELSD (evaporative light scattering detector) are very similar for the two bitumen studied, with and without PPA modification. The ELSD detector can be thought of as a mass proportional detector. PPA addition increases asphaltenes, decreases resins and aromatics, with small changes to saturates. The low polarity fraction of the asphaltenes (Cyclohexane), however, does decrease; the most polar fraction (Methylene chloride:Methanol) remains essentially the same, with most of the increase in mid-range polarity material (Toluene fraction). For both bitumens, the toluene and cyclohexane asphaltenes increase at the expense of aromatics and resins. However, in this case there is some difference in how PPA affects large ring structures (500 nm detector). Bitumen 1 has a larger shift of these materials from the aromatics fraction to the toluene-soluble asphaltene fraction than Bitumen 2.

Long-term aging with PPA modified bitumen produces less ELS aromatics, less resins, and slightly more cyclohexane and toluene-soluble asphaltenes than aging without PPA modification. There is little difference between Bitumen 1 and Bitumen 2. Although more subtle, the same trend is seen with the 500 nm detector.

Table 2. SAR-AD results for all materials.

<u>Sample</u>	<u>Detector</u>	<u>Saturates</u>	<u>Aromatics</u>	<u>Resins</u>	<u>CyC₆</u>	<u>Toluene</u>	<u>CH₂CL₂: MeOH</u>	<u>Total Asphaltenes</u>
Bitumen 1 (PPA)	ELS	21.5	44.5	7.0	7.8	19.0	0.3	27.0
	500nm		9.9	7.4	24.1	55.3	3.4	
Bitumen 1 (PPA) Aged	ELS	19.6	30.3	13.7	6.4	28.5	1.5	36.3
	500nm		4.7	7.5	18.0	61.8	8.0	
Bitumen 1	ELS	23.0	49.9	12.3	3.7	11.0	0.1	14.8
	500nm		14.0	16.8	24.3	42.9	2.0	
Bitumen 1 Aged	ELS	18.2	34.2	23.0	2.6	21.2	0.8	24.6
	500nm		8.3	13.1	15.9	57.9	4.8	
Bitumen 2 (PPA)	ELS	20.0	43.2	7.1	8.9	20.6	0.3	29.8
	500nm		11.4	6.1	24.1	54.8	3.6	
Bitumen 2 (PPA) Aged	ELS	16.6	29.1	13.8	6.5	32.2	1.8	40.5
	500nm		4.0	6.4	17.0	64.0	8.7	
Bitumen 2	ELS	22.3	46.5	13.0	4.3	13.8	0.1	18.2
	500nm		11.9	14.7	23.9	47.0	2.5	
Bitumen 2 Aged	ELS	18.3	33.6	18.6	3.5	25.2	0.9	29.6
	500nm		6.0	10.9	16.5	61.3	5.4	

3.5 DSR

Rheological changes due to oxidation are perhaps the most important metrics for pavement design. Standard master curves were generated by free shifting, as well as the cross-over moduli and frequencies noted at 25 °C reference temperature. Cross-over denotes master curve parameters at a phase angle of 45° at a given reference temperature. Also, the Arrhenius shift function activation energies were determined.

There appears to be a larger change in cross-over modulus values for the PPA treated materials (Figures 5 and 6), but the comparison of a soft bitumen at time zero to a stiffer bitumen at time zero is perhaps not appropriate, since the relationship of cross-over parameter changes to oxygen uptake (essentially the same for all samples) is log-linear, meaning the changes are more dramatic with stiffer bitumen (the function is exponential). Bitumen 1, 2 and their PPA pairs display slightly different changes in crossover modulus and frequencies, confirming the impact of the base bitumen.

A better comparison would be between the PPA modified bitumen and an unmodified bitumen with a similar stiffness in the intermediate temperature range, in order to more definitely quantify and sort out the respective effect of PPA modification and oxidation regarding these crossover parameters. This comparison was not possible within the scope of the study. Crossover parameters are important as they are assumed to relate to fatigue and healing properties.

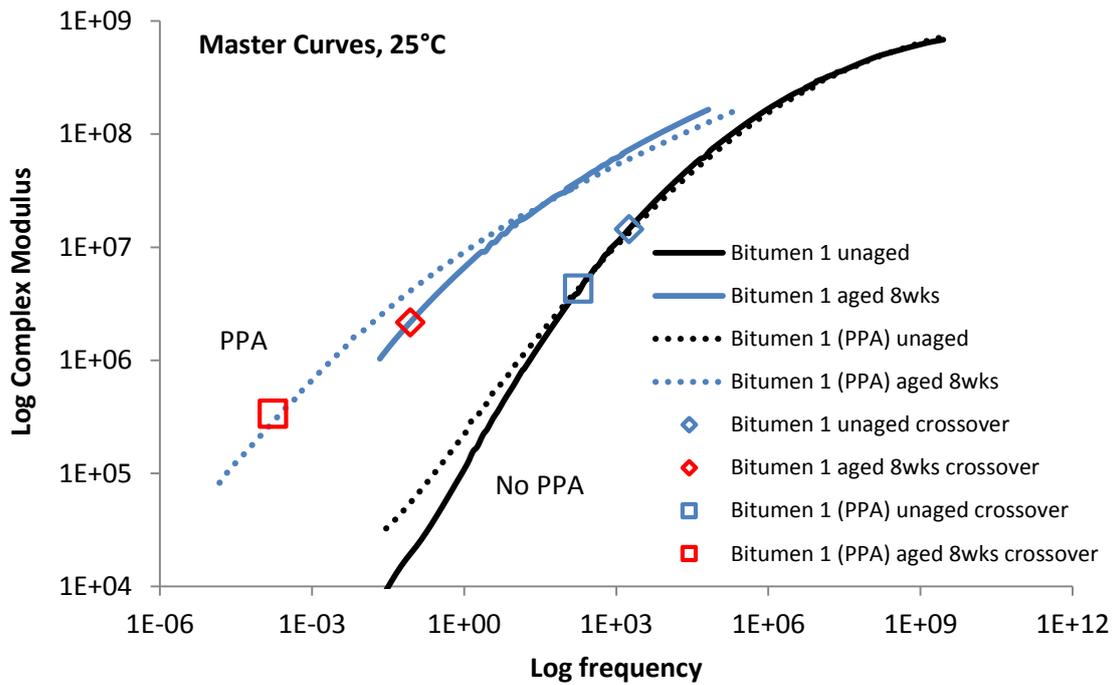


Figure 5. Master Curves (25° C) for Bitumen 1 and Bitumen 1 (PPA) with changes compared.

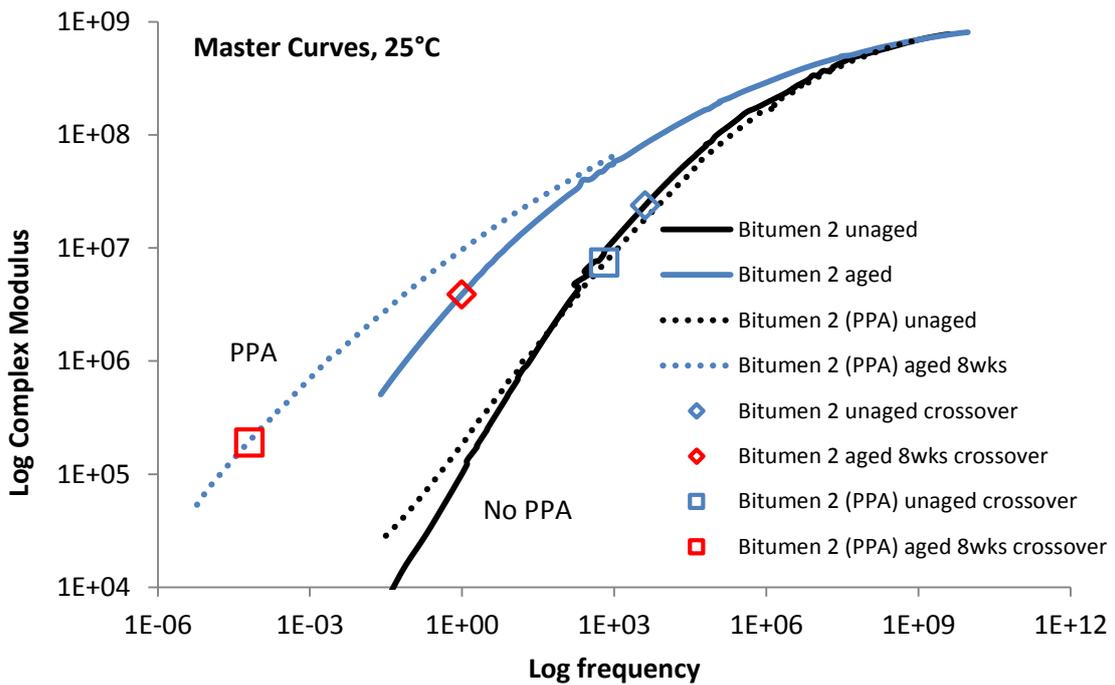


Figure 6. Master Curves (25° C) for Bitumen 2 and Bitumen 2 (PPA) with changes compared.

4. CONCLUSIONS

The results indicate some changes to the oxidation mechanism in bitumen treated with polyphosphoric acid. The formation of sulfoxide is slightly inhibited, with a corresponding slight increase in carbonyl under pavement oxidation conditions. While the competition between reactive sulfide and reactive benzyl carbons shifts slightly, the overall total amount of oxygen uptake is slightly less. Oxidation of PPA treated bitumen in this study, compared to the untreated bitumen, follows a similar course and is perhaps slightly slower under conditions found in pavement applications, not due to changes in chemical rate, but more likely diffusion rates. However, the SAR-AD fractions are changed by PPA addition, and the distribution of fraction after long-term aging is different for PPA modified bitumen. The results suggest the following answers to the research question posited at the onset of this study:

4.1 Research question 1: Does PPA change the intrinsic oxidation mechanism?

There is no change in the rate limiting step for oxygen uptake. Subsequent reaction steps are affected, with a change in the partitioning of sulfoxide and carbonyl products.

4.2 Research question 2: Does PPA change the mass transfer of oxygen and/or its solubility in the bitumen?

PPA did change the rate of oxygen diffusion in both bitumen examined, with indications of a higher rate in one, and a lower rate in the other. This complexity is likely due to source dependent effects related to PPA and viscosity changes of the mobile phase in the bitumen.

4.3 Research question 3: How does PPA affect the micro structure and resulting mechanic properties as bitumen oxidize?

Some implications are suggested by the data. Although not discussed here, SEC results indicate there is a dispersal effect when PPA is added. Spectral subtraction shows vibrational mode changes over time related to the PPA itself, but it is not completely clear whether these are caused by hydrolysis or the formation of other materials.

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