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Relationship between Asphalt Compatibility, Flow Properties, and Oxidative Aging

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Abstract: Studies involving nine SHRP asphalts, RTFO/PAV aged at 80℃ for 144 hours, 240 hours, and 480 hours, were conducted to investigate changes in asphalt composition as they relate to flow properties of asphalt binders after oxidative aging according to a colloidal suspension model of asphalt and a phenomenological rate law of oxidation. Unaged and aged asphalt samples were subjected to both chemical/compositional and rheological analysis. The unaged and aged samples were separated into four fractions according to Corbett separation (ASTM D4124-09) to investigate changes in asphalt composition resulting from the aging process. To investigate changes in rheological properties due to laboratory aging the Christensen-Anderson-Marasteanu (CAM) model was modified to generate aging master curves. The parameters generated from aging master curves were found to correlate with material compatibility as measured by asphaltene content in accordance with our colloidal suspension model and phenomenological rate law of oxidation.

***Key words**: Asphalt compatibility; Model; Oxidative aging; Reaction mechanism; Rheology.*

Introduction

Embrittlement of asphalt pavements is related to changes in the flow properties of the binder [1]. Changes in the binder flow properties are brought about in part by changes in material composition due to formation of oxidation products. Formation of oxidation products, in turn, results in the subsequent depletion of solvent phase material which changes the binder flow behavior.

It has been recognized for a long time that asphalt oxidation directly contributes to the embrittlement and eventual failure of pavements due to age hardening of the binder [2, 3]. It is generally accepted that the kinetics of asphalt oxidation resembles a two-stage or dual reaction mechanism, [2-4]. Petersen and Harnsberger [2, 3] showed that a two stage oxidation process is observed when asphalts are aged at constant oxygen pressures at temperatures between 60℃ and 130℃ for time periods of simulated aging as long as 1600 hours. Compositional changes in the material are characterized in terms of changes in chemical properties, as for example the increase in carbonyl and sulfoxide functionalities as determined by infrared spectrophotometry. Petersen and Harnsberger [2, 3] also observed that as asphalts age in the presence of O2-(300 psi), during the “first” early stage of the aging process (or so called “initial spurt”), the rate law defining the production of both carbonyl and sulfoxide moieties resembles, and subsequently could be modeled in terms of a first-order rate law (or fast reaction rate), while at the “second” later stage the rate law defining the production of carbonyl has been approximated by a zero-order reaction rate (or constant reaction rate) law.

Domke et al. [4] conducted laboratory oxidation experiments of asphalts which differed by crude source, while also considering the effects of changing the oxygen pressure (i.e., 0.2-atm to 20-atm) in their experiments. They too observed the dual reaction mechanism reported by Petersen and Harnsberger [2, 3] while also observing that oxygen pressure influences the rate of carbonyl production.

Petersen and Harnsberger [2, 3] and Domke et al. [4] have both suggested that the variability in age hardening susceptibility of binders, when determined for sets of asphalts derived from different crude sources, is somehow related to an asphalt's molecular compatibility. Each or these investigators reported that asphalts which were known to contain higher natural abundance of asphaltenes (i.e., incompatible asphalts) showed slower increases in carbonyl functionality, but disproportionately greater changes in dynamic shear modulus, where the reverse trend was observed for (compatible) asphalts which contained much lower natural abundance of asphaltenes (i.e., greater carbonyl increases were associated with smaller increases in dynamic shear modulus).

A detailed reaction mechanism of asphalt oxidation, defined in terms of the consumption of specific chemical reactants, is still uncertain, but it is generally accepted that naphthene aromatic and polar aromatic fractions (resins) of asphalt are readily consumed during the oxidation process [5]. Researchers, in the meantime, have relied on the determination of the rate of production of carbonyl (i.e., ketones and carboxylic acid) and sulfoxides, usually determined by infrared spectroscopy, to predict changes in the physical/rheological properties of asphalt upon oxidation [2-7]. Liu et al. [5, 6] and Juristyarini et al. [7] studied the effects of aging time, temperature and oxygen pressure of whole asphalts and Corbett selective Adsorption/Desorption (SARA) fractions (ASTM D4124-86) by an accelerated aging technique (pressure aging vessel) and observed the general rate laws for viscosity increase and the production rate of carbonyl,

$$r = \frac{\mathrm{d}(\ln \eta)}{\mathrm{d}t_{age}} = \left(\frac{\mathrm{d}(\ln \eta)}{\mathrm{d}c_A}\right)\left(\frac{\mathrm{d}c_A}{\mathrm{d}c_{CA}}\right)\left(\frac{\mathrm{d}c_{CA}}{\mathrm{d}t_{age}}\right) \tag{1}$$

and

$$r_{CA} = Ap^{\alpha} e^{-E_a/RT} \tag{2}$$

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In these two expressions η is the low shear rate limiting dynamic complex viscosity (measured at 60℃), C_C and C_{CA} define the concentrations of asphaltene (i.e., usually defined as n-heptane insolubles) and carbonyl species, respectively, p is pressure, α is the pressure reaction order, E_a and A are the activation energy to carbonyl production and pre-exponential factor, respectively, and R and T are the gas constant and absolute temperature, respectively. These researchers observed carbonyl production in both naphthene aromatic and polar aromatic fractions somewhat similar to carbonyl production in whole asphalts, but also observed that E_a and α values differed for different asphalts and asphalt fractions suggesting multiple reaction mechanisms. Asphaltenes, when present in mixtures or in whole asphalts in higher concentrations were observed to act as a catalyst.

In this paper we hypothesize that asphalt oxidation influences the flow properties of the material towards a state of embrittlement of the binder, and that this change in flow properties is innately tied to the production of polar species. Studies were undertaken to investigate the compositional and rheological properties of neat and oxidatively aged asphalts in an attempt to predict differences in the rates of material embrittlement based on asphalt compositional changes derived in terms of a phenomenological first order rate law of asphalt flow behavior. This flow behavior is governed by colloidal interactions of the asphaltene phase with the remaining asphalt continuous phase.

Experiment

Experimental Approach

Studies discussed in the present communication were undertaken to try to relate changes in asphalt composition to changes in asphalt rheological behavior due to oxidation based on adopting a colloidal model of asphalt as reported in Roberson et al. [8]. To accomplish this goal, SHRP asphalts were selected for investigation given the wealth of compositional and rheological data previously reported for these materials [8-10]. This wealth of background data provides for the development of extensive correlations which may be utilized to relate changes in compositional properties to changes in rheological behavior in order to gain a better understanding of how asphalt binder composition drives rheological behavior, especially after oxidative aging. Here, specifically, we wanted to understand how changes in colloidal stability, otherwise referred to asphalt molecular compatibility, relate to corresponding changes in asphalt binder rheology due to oxidative aging. Experimental testing in the present studies included development of oxidation master curves derived from rheological testing and characterization of changes in asphalt composition (e.g., changes in chemical functionality and chemical classes or chromatographic fractions) as a function of oxidation. Some of the data reported here is derived from the literature and other data is derived from newly developed test methods which are thought to better characterize asphalt compositional changes.

The concentration of carbonyl compound was determined using a Perkin-Elmer 983G infrared spectrometer. The infrared spectrum of a bitumen sample was obtained by dissolving 50 mg of asphalt in 1 mL of carbon disulfide, placing the sample in a sodium chloride cell with a 0.1-cm path length, and recording the spectrum, using solvent compensation, from 4000 to 600 cm^{-1}. The amount of the carbonyl-containing compounds, centered at 1700 cm^{-1}, was estimated using a peak-height method. The detail information about carbonyl measurement and calculation can be found in the references [11, 12].

Asphalt Selection and Laboratory Aging

Nine asphalts studied during the Strategic Highway Research Program (SHRP) [13] were selected for this research. They are: AAA-1, AAB-1, AAC-1, AAD-1, AAF-1, AAG-1, AAK-1, AAM-1, and ABD. The chemical/compositional and physical/rheological properties of these nine asphalt binders can be found in Roberson et al. [8], Branthaver et al. [9] and Anderson et al. [10].

The asphalts were first aged using the standard procedure of the rolling thin film oven (RTFO) test (AASHTO T240). The RTFO-aged asphalts were then further aged using the PAV test (AASHTO PP1) at a temperature of 80℃ for different durations of 144, 240, and 480 hours.

All of the unaged and aged samples were subjected to chemical and rheological analyses. The rheological properties of the aged and unaged samples were determined using an Ares rheometer.

Asphalt Fractionation

Materials were fractionated by SARA (Saturates, Aromatics, Resins, Asphaltenes) chromatography [14]. In this procedure a precipitating solvent, isooctane (HPLC grade 2,2,4-trimethyl pentane), was combined with asphalt in a 50:1 (i.e., volume: mass) ratio. Sample asphalt plus solvent were combined in 2-L wide mouth Erlenmeyer flasks, stirred on a hotplate with refluxing for 30-min, then set aside overnight. Filtration of the asphaltenes was conducted the following day using a 1-L 10-15μm fritted glass funnel fitted to a 2-L suction flask. Filter cakes of asphaltenes were washed with an additional 1000-mL of solvent and dried in a nitrogen purged vacuum oven at 80℃. Maltenes were recovered from the eluate by roto-evaporation and dried to constant weight on an oil bath at 120℃.

Corbett (or SARA) separations [15] were carried out by dissolving 1-g of isooctane-type maltenes in 10 mL of HPLC grade n-heptane and injecting the solution onto a 70-cm long, 1.5-cm diameter glass LC-column filled with approximately 110-g of CG-20 chromatographic grade activated alumina. Fractions (i.e., saturates-aromatics-then resins) were eluted by introducing the following solvents onto the column; 50-ml n-heptane, 100-mL of toluene, 75-mL of methanol/toluene (50:50 by vol.), and 150-mL trichloroethylene (TCE). Saturates were collected prior to elution of a fluorescent band migrating up the column. Naphthenic aromatics characterized by the fluorescent band were collected prior to a dark band migrating up the column below the fluorescent band. TCE was finally introduced to strip the column of any remaining “dark band” material defined as the polar aromatics fraction. Fractions were recovered by roto-evaporation and dried to constant weight.

Results and Discussion

Table 1. Physical and Compositional Properties Determined for 20 SHRP Asphalts.

Asphalt	[a] η	[a] η_{nC_7}	$\eta_r = (\eta/\eta_{nC7})^{-0.4}$	[b] x_{isoC8}	K
AAG-1	248900	82460	0.64	0.10	3.3
AAM-1	364400	101800	0.60	0.11	3.3
AAC-1	90100	10520	0.42	0.16	3.3
AAV-1	46700	5334	0.42	0.16	3.3
AAX-1	275900	24057	0.38	0.17	3.3
AAJ-1	201100	15251	0.36	0.18	3.3
AAF-1	381700	25000	0.34	0.19	3.3
AAN-1	122700	3720	0.25	0.21	3.3
AAA-1	37020	804	0.22	0.22	3.3
AAB-1	118600	3020	0.23	0.22	3.3
AAH-1	159500	1804	0.17	0.24	3.3
AAQ-1	302130	3243	0.16	0.24	3.3
AAK-1	251700	1620	0.13	0.25	3.3
AAE	184500	530	0.10	0.26	3.3
AAS-1	164100	734	0.11	0.24	3.3
AAD-1	57280	329	0.13	0.27	3.3
AAW-1	288700	8962	0.25	0.25	3
AAL-1	43145	739	0.20	0.27	3
AAT-1	702180	6030	0.15	0.28	3
AAP-1	42243	5753	0.45	0.21	2.6

[a] Branthaver et al. [9], [b] Robertson et al. [8]

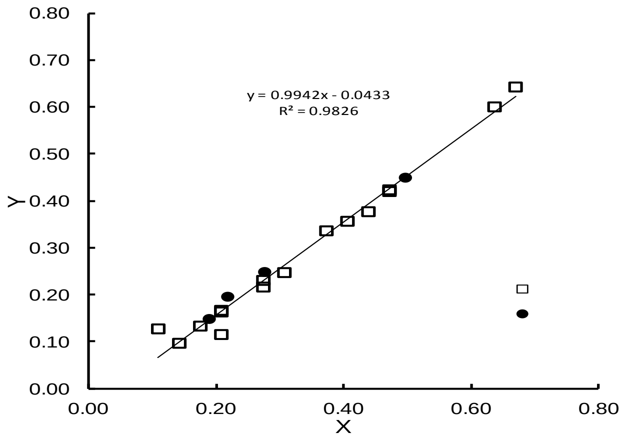

Fig. 1. Correlation of Relative Viscosity Function, $Y \equiv (\eta/\eta_{nC_7})^{-1/2.5}$ to Iso-octane Insoluable Asphaltene Mass Fraction, $X \equiv (1 - Kx_{isoC_8})$, Determined for 20 SHRP Asphalts.

Asphalt Composition and Viscoelasticity

Asphalts derived from different crude sources have been successfully modeled as colloidal suspensions. The Pal-Rhodes model, which describes the flow properties of concentrated micro-emulsions, has specifically served as a model for quantifying heavy oil and asphalt viscosity as a function of material composition [16-21]. By adopting this model, asphalts may be classified as either exhibiting gel-type (less compatible) or sol-type (more compatible) [22] characteristics in terms of their flow properties. With “more” compatible asphalts, the material fraction referred to as “dispersed-phase” asphaltenes is generally lower in natural abundance and well dispersed or peptized by the maltene solvent “continuous” phase. Compatible asphalts also exhibit more of Newtonian-like flow properties, and are generally more ductile than less compatible asphalts. Conversely, “less” compatible asphalts exhibit more of elastic behavior, have a higher natural abundance of asphaltene, and are less ductile (or more brittle) than more compatible asphalts.

Several researchers [17-20] have considered the Pal-Rhodes model [17], which builds upon Einstein's colloid theory of dilute suspensions [23], to accommodate for highly concentrated suspensions required to model asphalt flow properties. Bullard et al. [24] have recently applied differential effective-medium theory (D-EMT) to derive solutions to the Pal-Rhodes model. In D-EMT, the properties of a composite material (the effective medium) are shown to be directly related to the relative amounts of the starting fractions. In this case, the effective viscosity, η, of an asphalt is modeled in terms of the viscosity of the solvent phase maltenes, η_0, and the mass fraction of suspended phase asphaltenes, *X*. The final conserved solution to the Pal-Rhodes model is generally expressed by

$$\eta = \eta_0 (1 - Kx)^{-2.5} \tag{3}$$

where *K* is a solvation factor and may be assumed to be shear rate and temperature dependent [17-20].

Dynamic shear rheology measurements of low shear rate (0.1 rad/s) dynamic viscosities of whole asphalts and n-heptane soluble maltenes at ambient temperature reported by Robertson et al. [8] and Branthaver et al. [9] relate flow properties of asphalt to its composition. Table 1 lists rheological and compositional properties determined for 20 SHRP asphalts; dynamic viscosity of neat asphalt, η (Pa*s, @ T = 25℃, ω = 0.1 rad/s), dynamic viscosity of n-heptane soluble maltenes, $\eta_n C_7$ (Pa*s, @ 25℃, ω = 0.1 rad/s), and mass fractions of isooctane insoluble asphaltenes, $x \equiv x_a \approx x_{isoC_8}$. Expressing Eq. (3) as a linear function,

$$\left(\frac{\eta}{\eta_0}\right)^{\frac{-1}{2.5}} = (1 - Kx_a) \tag{4}$$

given the following conditions for *K*, where it is observed that

$$K = \begin{cases} 3.3, & x \le 0.25 \\ < 3.3, & x > 0.25 \end{cases} \tag{5}$$

results in the plot depicted in Fig. 1. Data in Table 1 show, for the majority of asphalts, that asphaltene concentrations below approximately 25% correlate well with the expression in Eq. (4) for *K = 3.3*. Above this value in x_a, with the noted exception of asphalt AAP-1, and noting the margin of error for asphaltene content determination being about ±1.0 mass%, *K* is observed to be less than 3.3, thus, *K* is be considered an adjustable parameter for value in x_a greater than 0.25. Furthermore, additional limitations to this model have been considered, namely, the Pal-Rhodes model assumes spherical particle shapes by asphaltene agglomerates may assume other shapes, and in this particular case, given *K* = 3.3, x_a

can have a value no higher than $x_a = 1/k = 0.30$, thus, K is considered an adjustable parameter for value in x_a greater than 0.25.

Asphalt Composition and Oxidation

By taking a phenomenological approach to correlating asphalt compositional changes to changes in rheological behavior with oxidation, the rate of change in the flow property of an age hardened binder, as quantified by the change in dynamic viscosity as a function of aging time, $d\eta/dt_{age}$, may be shown to be directly related to the production of new polar species which tend to fractionate as asphaltenes via standard solvent gravimetric methods. This "new" asphaltene material is likely produced at the expense of the consumption of species originally present in the material fraction of asphalt referred to as the maltenes. A phenomenological rate law may be defined for the reaction

$$x_m^0 + x_a^0 + O_2 \xrightarrow{k} x_m^- + x_a^0 + x_a^+ \qquad (7)$$

by

$$r = \frac{d}{dt_{age}}\left(\eta^{-0.4}\right) \propto \frac{d}{dt_{age}}\left\{\left(\eta_0^{-0.4}\right)\left(1 - Kx_a^0\right)\right\}$$
$$= \eta_0^{-0.4}\left[K\left[t_{age}\right]\frac{d(x_a^+\left[t_{age}\right]}{dt_{age}} + x_a^+\frac{d\left(K\left[t_{age}\right]\right)}{dt_{age}} + x_a^0\frac{d\left(K\left[t_{age}\right]\right)}{dt_{age}}\right] \qquad (8)$$

given $x_m^0 + x_a^0 = x_m^- + x_a^0 + x_a^+ = 1$ and assuming $d\left(x_a^0\right)/dt_{age} = d\left(\eta_0^{-0.4}\right)/dt_{age} = 0$. Here x_m^0 and x_a^0 are the initial maltene and asphaltene mass fractions, respectively, and x_m^- and x_a^+ are the mass fractions of remaining maltene and "new" asphaltene material, respectively, after reaction with oxygen for a given amount of time, t_{age} at temperature, T. Next, assuming first-order kinetics as proposed by Petersen and Harnsberger [2, 3], the concentration in newly formed asphaltenes, as defined by the mass, x_a^+, fraction may be expressed by

$$x_a^+\left[t_{age}, T\right] = \left(1 - x_a^0\right)\left(1 - e^{-kt}\right) \qquad (9)$$

Drawing from Eqs. (7) to (9), the phenomenological rate expression for the change in asphalt viscosity with aging time may finally be expressed by

$$r = \frac{d}{dt_{age}}\left(\eta^{-0.4}\right)$$
$$= x_m^0\eta_0^{-0.4}\left[\left(1 - e^{-k(T)t} + x_a^0\right)\frac{d\left(K\left[t_{age}\right]\right)}{dt_{age}} - K\left[t_{age}\right]ke^{-k(T)t}\right] \qquad (10)$$

Here, the solvation factor is defined as a function of aging time, $K[t_{age}]$, while the rate constant, $k(T)$, is defined as a function of temperature.

Asphaltene production at the expense of naphthene aromatic and resin fraction materials may be demonstrated by chromatographically separating both neat and aged asphalt materials, and comparing the resulting distributions of material mass fractions. Table 2 lists mass percentages of SARA fractions determined for two asphalts employing a modified ASTM method D4124 [14]. The materials represented here are two SHRP asphalt, both of which were PAV aged for 144-hr at 100℃. For both asphalts, asphaltene content almost doubles under these aging conditions. Furthermore similar proportions of either polar aromatic or naphthene aromatic materials, on average, 4.5% and 16.5%, respectively, are consumed to produce, on average, 21% new asphaltene. Saturates concentrations appear to be unaffected by the oxidation process. Additional studies of this nature are presently being conducted for the remaining SHRP asphalt considered in this study.

Table 2. Mass Percentages of SARA Fractions Derived from Neat and Aged (100℃ PAV for 144 hr) Materials. Note: Δ%(Asphalt) = [%(Aged) - %(Neat)].

Asphalt	% Asphaltene	% Polar Aromatics	% Naphthene Aromatics	% Saturates
AAB-1	20	42	26	10
AAK-1	24	42	23	8
AAB-1, Aged	38	27	21	11
AAK-1, Aged	47	24	19	8
Δ(AAB-1)	+18	-15	-5	+1
Δ(AAK-1)	+23	-18	-4	0

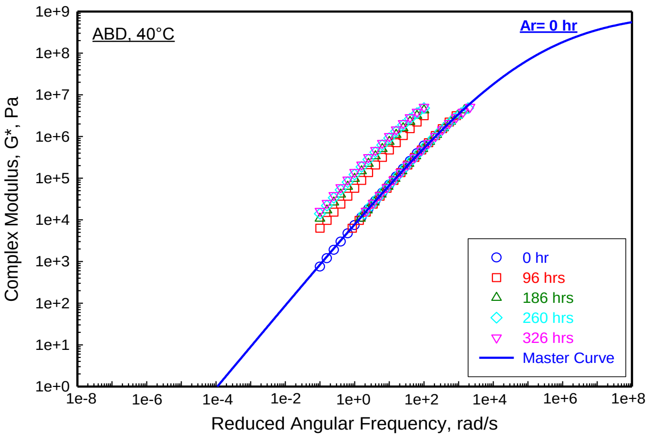

Fig. 2. Complex Modulus as a Function of Frequency with Respect to Aging Times for Asphalt ABD and Its Corresponding Master Curve at 40℃.

Flow Properties and Oxidation

The Christensen-Andersen-Marasteanu (CAM) model developed during SHRP [13] for constructing time-temperature master curves was modified to model oxidation master curve data of SHRP asphalts. Fig. 2 shows complex modulus as a function of frequency with respect to aging times for asphalt ABD and its corresponding master curve at 40℃. As depicted in Fig. 2, the complex modulus increases as the aging time increases at a given frequency. This phenomenon is similar to the temperature dependency of asphalt binder, where the complex modulus increases as the temperature decreases. The master curves plotted for asphalts prepared using different aging times indicate that there is a similar parallel shift (if the material exhibits rheologically simple flow behavior) between the modulus curves at various aging times. So the same principle of time-temperature superposition was applied for the aging-time master curves. The data translation is carried out by using shift factors which express the dependence of the material rheological behavior on the aging time. This approach simplifies the problem of estimating rheological properties for loading times and aging times outside the range of laboratory measurements. The generalized power law model, shown below, is employed to generate the oxidation master curves [13, 25-29]; Note that the model proposed here is not suitable for some highly aged or polymer modified asphalts that exhibit rheologically complex behavior.

$$G^*(\omega,t)=G_g^*\left[1+\left(\frac{\omega_c}{\omega'}\right)^k\right]^{1/k} \tag{11}$$

where G^* is the complex modulus, t is aging time, G_g^* is a complex glassy modulus, ω_c is the location parameter of frequency, k is a dimensionless shape parameter, and ω' is a reduced frequency defined as $\omega'=a_T(t)\cdot\omega$ where $a_T(t)$ is an aging shift factor. Here an aging shift factor shifts the complex modulus and phase angle at a given aging time to a reference aging time (zero aging time in this case) to form a single aging master curve. The values in these shift factors can be considered to be modulus (stiffness) changes with respect to the modulus at the reference aging time, which gives an indication of how the properties of a material change with aging time, expressed by

$$a_T(t)=\frac{\omega_c}{\omega}\left[1-\left(\frac{G^*(\omega,t)}{G_g^*}\right)^k\right]^{-1/k} \tag{12}$$

An age hardening susceptibility parameter is determined by comparing the aging shift factor to the production of new asphaltene measured in terms of infrared absorbance of carbonyl functionality, A_{CA}, expressed by the differential

$$\frac{dA_{CA}}{dt_{age}}\propto\frac{dx_a^+}{dt_{age}} \tag{13}$$

The age hardening susceptibility is thus expressed by the slope in aging shift factor relative to carbonyl absorbance

$$HS = a_T(t) / A_{CA} \tag{14}$$

Fig. 3 shows the relationships between aging shift factors and carbonyl content for eight SHRP asphalts after PAV aging. Each of these plots show a linear relationship between the aging shift factor and the carbonyl content, (R-square values 0.96 to 0.99). The slopes of the lines represent changes in rheological properties with respect to chemical property changes which develop due to aging, and thus define the hardening susceptibility of asphalt.

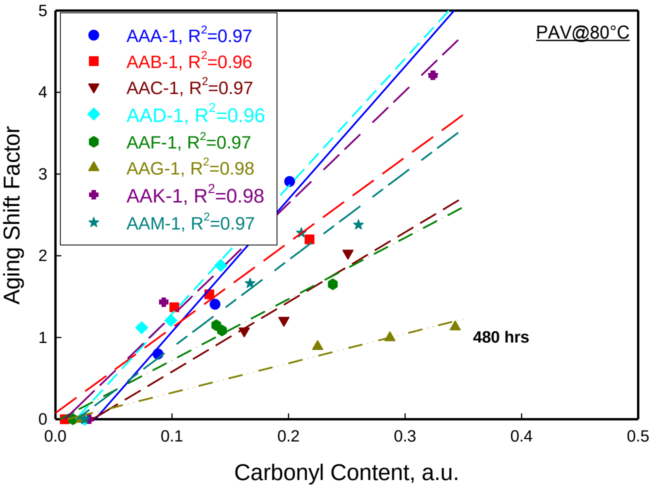

Fig. 3. Relationship between Aging Shift Factor and Carbonyl Content for Different Asphalts.

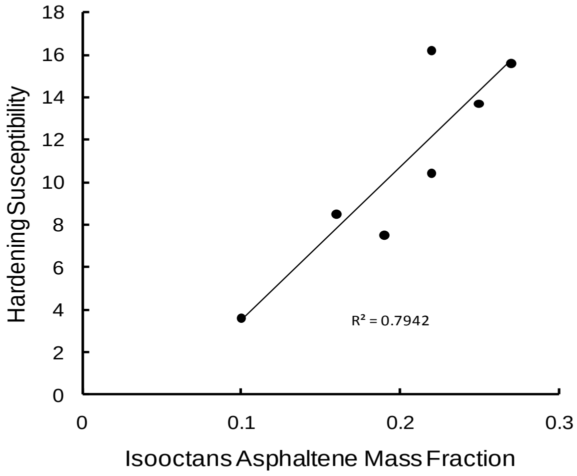

Fig. 4. Hardening Susceptibility Parameter determined for 8 SHRP Asphalts Plotted versus Isooctane Asphaltene Content.

Petersen and Harnsberger [2, 3] have suggested that the variability in an age hardening susceptibility slope, when determined for sets of asphalts derived from different crude sources, is related to differences in molecular compatibility [2] for asphalts which differ in terms of crude source. The rate function developed in expression 10 suggests that the rate of change in viscosity should then be a function of aging time and new asphaltene concentration, but should also be a function of the initial asphaltene concentration, X_a^0, as per

$$\begin{aligned} r &= \frac{d}{dt_{age}}\left(\eta^{-0.4}\right) \\ &= \left(1-X_a^0\right)\eta_0^{-0.4}\left[\left(\left(1-e^{-k(T)t}\right)++X_a^0\right)\frac{d\left(K\left[t_{age}\right]\right)}{dt_{age}}-K\left[t_{age}\right]ke^{-k(T)t}\right] \end{aligned} \tag{15}$$

Thus, trends were sought which related the hardening susceptibility parameter (i.e., the slope of the change in viscosity or modulus to the change in carbonyl absorbance and thus new asphaltene content) with measures of compatibility, in this case initial asphaltene content, X_a^0 [30]. Fig. 4 depicts a plot of the hardening susceptibility as it relates to isooctane asphaltene content (data listed in Table 3).

Table 3. Hardening Susceptibility, ($HS = a(t)/A_{CA}$), and Isooctane Asphaltene Mass Fraction Content.

Sample	Hardening Susceptibility	^{a}Isooctane Asphaltene Mass Fraction
AAA-1	16.2	0.22
AAB-1	10.4	0.22
AAC-1	8.5	0.16
AAD-1	15.6	0.27
AAF-1	7.5	0.19
AAG-1	3.6	0.10
AAK-1	13.7	0.25
AAM-1	10.7	0.11

^{a}Reported in Robertson et al. [27]

Finally, the parameter, $K[t_{age}]$, in expression 15 is also shown to be a function of oxidation time based on the proposed phenomenological model. This parameter will then also be a function of increasing asphaltene content. The data listed in Table 1 tends to allude to this dependency given that neat asphalts with asphaltene contents above 25% correspond with K-values equal to 3 while lower asphaltene content asphalts correspond to K-values equal to 3.3 according to Eq. (5). Thus, as asphalts are oxidized asphaltene content will most likely increase above 25%, hence, the K-value is then expected to decrease as it does with neat asphalt of high asphaltene content. It is presently unknown experimentally whether oxidized asphalts will follow this trend, thus, additional studies are currently in progress to investigate the influence of aging time, and hence increasing asphaltene content, and/or depletion of polar aromatic and naphthenic content, on K-values as they pertain to modeling oxidation in terms of the colloidal suspension model of asphalt flow and oxidation proposed in the present communication.

Conclusions

Rheological and chemical/compositional properties of unaged and aged asphalt samples were considered in order to generate aging master curves based on a modified Christensen-Anderson-Marasteanu (CAM) model. The parameters generated from these aging master curves were further correlated with measures of asphalt compatibility, namely initial asphaltene content. The results indicate that the aging shift factors generated from master curves correlate well with initial asphaltene content according to a phenomenological first-order rate law derived by assuming that asphalt flow properties behave in accordance with a colloidal suspension description of asphalt. A yet unaccounted for parameter, the $K[t_{age}]$ solvation factor; also predicted by this model, will be the focal point of future investigations of this nature. Knowledge of how this parameter may vary as a function of oxidation, and hence increasing asphaltene content, should constitute a working model of changing asphalt flow properties as a function of aging. Additionally, master curves that account for rheologically complex flow behavior are also being considered.

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References

1. Mushrush, G.W. and Speight, J.G. (1995). *Petroleum Products: Instability and Incompatibility*, Taylor & Francis, Washington DC, USA.
2. Petersen, J.C. and Harnsberger, P.M. (1998). Asphalt Aging: Dual Oxidation Mechanism and Its Interrelationships with Asphalt Composition and Oxidative Age Hardening, *Transportation Research Board*, No. 1638, pp. 47-55.
3. Petersen, J.C., Harnsberger, P.M. and Robertson, R.E. (1996). Factors Affecting the Kinetics and Mechanisms of Asphalt Oxidation and the Relative Effects of Oxidation Products on Age Hardening, *American Chemical Society Division of Fuel Chemistry*, Preprints, 41(4), pp. 1232-1244. http://www.anl.gov/PCS/acsfuel/preprint%20archive/41_4_ORLANDO_08-96.htm
4. Domke, C.H., Davison, R.R. and Glover, C.J. (2000). Effect of Oxygen Pressure on Asphalt Oxidation Kinetics, *Industrial & Engineering Chemistry Research*, 39(3), pp. 592-598.
5. Liu, M.M., Lin, M.S., Chaffin, J.M., Davidson, R.R., Glover, C.J. and Bullin, J.A. (1998). Oxidation Kinetics of Asphalt Corbett Fractions and Compositional Dependence of Asphalt Oxidation, *Petroleum Science and Technology*, 16(7-8), pp. 827-850.
6. Liu, M., Lunsford, K.M., Davison, R.R., Glover, C.J. and Bullin, J.A. (1996). The Kinetics of Carbonyl Formation in Asphalt, *AIChE Journal*, 42(4), pp. 1069-1076.
7. Juristyarini, P., Davison, R.R. and Glover, C.J. (2003). Development of an Asphalt Aging Procedure to Assess Long-Term Binder Performance. Prepared for Presentation and Publication at the 82nd Annual Meeting of the Transportation Research Board, Washington DC, USA, January 2003.
8. Robertson, R.E., Branthaver, J.F., Harnsberger, P.M., Petersen, J.C., Dorrence, S.M., McKay, J.F., Turner, T.F., Pauli, A.T., Huang, S.-C., Huh, J.-D., Tauer, J.E., Thomas, K.P., Netzel, D.A., Miknis, F.P., Williams, T., Duvall, J.J., Barbour, F.A. and Wright, C. (2001). Fundamental Properties of Asphalts and Modified Asphalts, Volume I: Interpretive Report,

FHWA-RD-99-212, Federal Highway Administration, U.S. Department of Transportation, McLean, VA, USA.

9. Branthaver, J.F., Petersen, J.C., Robertson, R.E., Duvall, J.J., Kim, S.S., Harnsberger, P.M., Mill, T., Ensley, E.K., Barbour, F.A. and Schabron, J.F. (1993). Binder Characterization and Evaluation. Vol. 2: Chemistry, *SHRP-A-368*, Strategic Highway Research Program, National Research Council, Washington, DC, USA, pp. 287-320.
10. Anderson, D.A., Christensen, D.W., Bahia, H.U., Dongre, R., Sharma, M.G., Antle, C.E. and Button, J. (1994). Binder Characterization and Evaluation, Volume 3: Physical Characterization, *SHRP-A-369*, Strategic Highway Research Program, National Research Council, Washington, DC., USA.
11. Petersen, J.C. (1986). Quantitative Functional Group Analysis of Asphalts Using Differential Infrared Spectrometry and Selective Chemical Reactions-Theory and Application, *Transportation Research Record*, No. 1096, pp. 1-11.
12. Petersen, J.C., Dorrence, S.M., Nazir, M., Plancher, H. and Barbour, F.A. (1981). Oxidation of Sulfur Compounds in Petroleum Residues: Reactivity-Structural Relationships, Preprints, *Division of Petroleum Chemistry*, American Chemical Society, 26(4), pp. 898-906.
13. Jones, D.R., IV. (1993). SHRP Materials Reference Library: Asphalt Cements: A Concise Data Compilation, *SHRP-A-645*, Strategic Highway Research Program, National Research Council, Washington, DC, USA.
14. ASTM D4124-0. (2010). Standard Test Methods for Separation of Asphalt into Four Fractions. Annual Book of ASTM Standards, Road and Paving Materials; Vehicle-Pavement Systems, Section 4, vol. 04.03. ASTM International, West Conshohocken, PA, USA, pp. 397-403.
15. Corbett, L.W. (1969). Composition of Asphalt based on Generic Fractionation, Using Solvent Deasphaltening, Elution-Adsorption Chromatography and Densimetric Characterization, *Analytical Chemistry*, 41, pp. 576–579.
16. Pal, R. and E. Rhodes. (1989). Viscosity/Concentration Relationships for Emulsions, *Journal of Rheology*, 33(7), pp. 1021-1045.
17. Sheu, E.Y. (2002). Petroleum Asphaltenes-Properties, Characterization, and Issues, Energy & Fuel, 16, pp. 74-82.
18. Sheu, E., DeTar, M. and D. Storm. (1991). Rheological Properties of Vacuum Residue Fractions in Organic Solvents, *Fuel*, 70, pp. 1151-1156.
19. Pauli, A.T. and Branthaver, J.F. (1998). Relationship between Asphaltenes, Heithaus Compatibility Parameters, and Asphalt Viscosity, *Petroleum Science and Technology*, 16(9&10), pp. 1125-1147.
20. Pauli, A.T. and Branthaver, J.F. (1999). Rheological and Compositional Definitions of Compatibility as They Relate to the Colloidal Model of Asphalt and Residua, American Chemical Society *Division of Petroleum Chemistry*, Preprints, 44, pp. 190-193.
21. Lesueur, D. (2009). The Colloidal Structure of Bitumen: Consequences on the Rheology and on the Mechanics of Bitumen Modification, *Advances in Colloidal and Interface Science*, 145, pp. 42-82.
22. Barth, E.J. (1962). *Asphalt Science and Technology*, Gordon and Breach Science Publishers, New York, NY, USA.
23. Einstein, A. (1906). Eine Neve Bestimmung der Moleküldimensionen, *Annalen der Physik*, 19, pp. 289-307 (in German).
24. Bullard, J.W., Pauli, A.T., Garboczi, E.J. and Martys, N.S. (2009). A Comparison of Viscosity-Concentration Relationships for Emulsions, *J. Colloid Interface Sci.*, 330(1), pp. 186-193.
25. Christensen, D.W., Jr. and Anderson, D.A. (1992). Interpretation of Dynamic Mechanical Test Data for Paving Grade Asphalt Cements. *Journal of the Association of Asphalt Paving Technologists*, 61, pp. 67-116.
26. Ferry, J.D. (1980). *Viscoelastic Properties of Polymers*, Third Edition, John Wiley & Sons, Inc., New York, NY, USA.
27. Zeng, M., Bahia, H., Zhai, H. and Turner, P. (2001). Rheological Modeling of Modified Asphalt Binders and Mixtures, *Journal of the Association of Asphalt Paving Technologists*, 70, pp. 403-441.
28. Marasteanu, M. and Anderson, D. (1999). Improved Model for Bitumen Rheological Characterization, *Eurobitume Workshop on Performance Related Properties for Bituminous Binders*, Paper No. 133, Luxembourg, May 1999.
29. Robertson, R.E., Thomas, K.P., Harnsberger, P.M., Miknis, F.P., Turner, T.F., Branthaver, J.F., Huang, S-C., Pauli, A.T., Netzel, D.A., Bomstad, T.M., Farrar, M.J., Sanchez, D., McKay, J.F. and McCann, M. (2006). “Fundamental Properties of Asphalts and Modified Asphalts II, Final Report, Volume I: Interpretive Report,” Federal Highway Administration, Contract No. DTFH61-99C-00022, Chapters 5-7 submitted for publication, March 2006.
30. Speight, J.G., Editor (1998). *Petroleum Chemistry and Refining*, Taylor & Francis, Washington DC, USA.