

### **Rheological properties of phase-incompatible bituminous binders**

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#### Abstract

The North American bitumen specification system, SuperPave™, is the newest and the most elaborate specification system for bituminous binders. The system was developed and validated for straight-run refinery-produced bitumens and it has been implemented in the United States and Canada throughout the 1990s. Since then, there has been increased use of modified grades, Recycled Asphalt Pavement and artificial “softeners” such as recycled engine oil bottoms, aromatic or paraffinic oils, bio-based oils, etc. Not all these compositional changes manifested in adequate bitumen long-term performance in the field. It was demonstrated that the current SuperPave™ system cannot prevent acceptance of some of the lower quality materials. There has been a significant effort in the US and Canada to improve the SuperPave™ system to address these challenges, more specifically to prevent premature binder aging and pavement cracking. Current paper is showing how excessive oxidative aging and physical hardening susceptibility together with loss of cohesion in inadequately modified binders relates to phase compatibility and how this can be reliably manifested in measurement of rheological phase angle in Dynamic Shear Rheometer (DSR). It is shown that the DSR test performed on the Pressure Aging Vessel (PAV) residue can be simply modified to exclude phase incompatible binders from passing the specification. The discussion of evolution of SuperPave™ specification system in North America is important from the European perspective too as Europe is heading towards a rheology-based specification system in the near future.

## 1. INTRODUCTION

In the last few decades, economic pressures in the paving and refining industries have been driving changes to bitumen composition. In the U.S.A., reclaimed asphalt pavement (RAP) usage has averaged at around 20% wt. of the total asphalt laid. To compensate for aged and harder RAP-containing bitumen, softer virgin bitumen, previously not used or available in a given climatic region, is now needed. Similarly, there is an increasing need from the paving industry for modified bitumen that also requires softer bitumen grades as feedstock. The considerable amount of softer bitumen needed by the market has to be manufactured economically. The economic preference of the refining industry is to send lighter lube molecules to disposition channels with higher financial uplift, rather than sending them to the bitumen pool. Together with logistical limitations related to additional softer grade manufacturing, these factors result in a significant shortage of accessible and high quality straight-run bitumen in the market today.

The bitumen and paving industries are attempting to secure suitable and economic softer grades by blending 'softeners' into available refinery-produced feedstocks. Materials used as softeners range from refinery-produced paraffinic/aromatic oils, extracts and cracked oils or residues, to recycled engine oil bottoms (REOB), pyrolysis products and bio-oils. Some softeners are carefully engineered and have a proven track record and maximum dosage recommendations, while others are used simply to satisfy current bitumen specifications, without much consideration of bitumen composition and durability. The latter cases might result in premature pavement failures, as demonstrated in a number of studies and road trials [1,2]. Consequently, these failures have motivated road owners to restrict acceptance criteria. The challenge is that the root cause of these failures is often not well understood and the impact of altering specifications is not fully considered.

The current bitumen specification in North America, SuperPave™, AASHTO (American Association of State Highway and Transportation Officials) M320, was developed in the late 1980s and early 1990s. SuperPave™ introduced many scientific advancements that were thoroughly validated in the field. However, the validation was performed only on typical bitumen available at that time in North America: almost entirely refinery-produced grades. The change in rheology and chemical composition introduced now-a-days by the addition of softeners to the bitumen was not vetted by the SuperPave™ specification. Therefore, it is not surprising that SuperPave™ is no longer able to differentiate between well- and poor-performing bitumen. These modified materials behave differently in laboratory aging and rheological testing, and prediction of their field performance might be difficult by current methods.

### 1.1. Research objective

In the current work the ability of the SuperPave™ specification tests to identify phase instable or incompatible bitumen is studied, and a simple and practical adjustment to SuperPave™ specification limits to properly screen these inferior binders is proposed.

## 2. ASPHALT PHASE COMPATIBILITY

Asphalt consists of tens of thousands of different molecules ranging from non-polar fully saturated linear alkanes to highly polar polycyclic aromatics substituted with heteroatoms [3,4]. Therefore it is necessary to understand asphalt as a continuum of molecules with a gradual transition in polarity, molecular weight and functionality. For practical reasons, asphalt has traditionally been separated, by means of chromatography, into four basic groups. Those groups, in order of increasing polarity, are saturates, aromatics, resins and asphaltenes; however, there is no sharp transition among the molecular types comprising each group. For examples, a molecule can be a precipitated out either in resin and/or asphaltene groups depending on the separation conditions (solvent/precipitant, dilution, temperature, etc.), and its interactions with other molecules [5,6,7,8].

The nature of molecular interactions, in particular those between asphaltenes and resins, as well as the overall structure and phase stability of bitumen systems, are still not fully understood [9]. Interactions between asphaltene molecules and/or resin molecules are crucial for maintaining phase stability and preventing further aggregation into bigger agglomerates. Such agglomeration would eventually lead to instability, and potentially phase separation [10,11,12,13]. The formation and stability of molecular aggregates, such as micelles or dispersed solids, in bitumen is dictated by the relative free energies of such structures with regard to the continuous phase. The binding of molecules is always entropically unfavourable because it reduces the molecular degrees of freedom [14]. As such, the enthalpy change associated with the formation of aggregate structures must be negative [10,15], since only processes with an overall negative change in Gibb's energy are spontaneous. Molecular associations thus become more probable with decreasing temperature, as the entropic term in the total Gibb's energy scales with temperature. However, at low temperatures the increasing viscosity of the continuous phase impedes molecular diffusion and, therefore, molecular association. Aggregates or micelles might further associate into more complex structures [16]. In the case of a medium with sufficient solvating power, phase separation does not set in and internal structures (networks) may form through the aggregation of asphaltenes [17].

Asphaltenes are responsible for most of the weak intramolecular interactions that govern asphalt rheological properties. These interactions help determine their solvency state, *i.e.*, whether they are solubilized or precipitated, and are a critical parameter when physical properties of a bitumen are considered. It is therefore important to understand bitumen as a

continuum of molecular types with molecules that have the tendency to precipitate (asphaltenes) and molecules which can prevent (solvent – resins, aromatics) or accelerate precipitation (precipitant – saturates). Gaestel [18] proposed a simple ratio: (asphaltenes + saturates) / (resins + aromatics), termed the colloidal instability index, to describe asphaltene solvency in bitumen. Many different analytical techniques have been utilized to study bitumen phase compatibility. Brûlé [19] studied bitumen phase stability via gel permeation chromatography (GPC) and differential scanning calorimetry (DSC), and related the observations to bulk bitumen viscoelasticity and thin-film rheology. Miknis [20] utilized nuclear magnetic resonance (NMR) spectroscopy to study the state of asphaltene precipitation in maltenes. Pauli [21] studied various phases within bitumen, including a crystalline wax phase, by atomic force microscopy (AFM), and pioneered many solutions on both the experimental and theoretical front in this area. Mangiafico [22] utilized the colloidal instability index in modeling of rheological properties of virgin and reclaimed bitumen blends. A very comprehensive review on bitumen phase compatibility and solubility can be found in the review paper by Polacco [23]. Although the review predominantly focuses on phase behavior of bitumen–polymer blends, it contains a detailed review of many concepts related to bitumen phase compatibility.

### 3. EXPERIMENTAL DATASETS

Three sets of experimental data were used in this study:

1) Experimental mastercurves of dynamic material functions obtained and re-analyzed with different objective from Kriz 2012 [24].

2) ExxonMobil Asphalt Assay Database (EMAAD) contains specification properties of a great variety of bitumen that were prepared by laboratory vacuum distillation of crude oils sourced globally. The purpose of this dataset is to demonstrate general relationships of properties obtained for straight-run and unmodified bitumen. Not all properties were available for all samples; the maximum possible number of properties were used in correlations and outliers were not removed. Charts presented in this study contain 522 individual datapoints/samples. These data were collected according to relevant ASTM, EN and AASHTO standards by Imperial Oil Limited Asphalt Laboratory, Sarnia, Ontario, Canada.

3) An experimental dataset was created containing properties obtained for 37 laboratory blended bitumen. The individual blends were prepared by adding asphaltenes and saturates to destabilize the system and induce phase separation. Asphaltenes, except A50, were prepared using a pilot deasphalting unit to varying deasphalted lube yields. Bitumen B1 was a feedstock for Asphaltenes A75 and A65, bitumen B2 was a feedstock for asphaltenes A25, and A50 was a commercial sample from a refinery deasphalting unit whose feed bitumen was of different chemical composition from B1 and B2. The number associated with the asphaltene sample name represents the lube yield from the associated deasphalting process. The higher the lube yield, the higher the polarity of the separated asphaltenes. This increase in polarity is demonstrated by increased n-Heptane Insoluble (NHI) content (Table 1). The saturates used were paraffinic heavy and very-heavy vacuum gas oils. Oils O2 and O3 are from the same refinery vacuum distillation unit (VDU) and their chemical composition is similar. O1 is from a different VDU, and its composition differs from O2 and O3. Oil viscosity is listed in Table 2. Two of the straight-run bitumens also were used in blends and their properties are presented in Table 3. Blends of two to three components were prepared at prescribed ratios. Some samples were air-blown to varying degrees of oxidation to further induce phase instability. It is important to note that all samples in this dataset passed DSR parameter  $|G^*| \sin \delta$  maximum limit of 5000 kPa at their respective intermediate PG temperature. Details of the experimental blends are in Table 4.

**Table 1. Asphaltene properties**

<i>Property</i>	<i>Method</i>	<i>75% Lube yield</i>	<i>65% Lube yield</i>	<i>50% Lube yield</i>	<i>25% Lube yield</i>
Acronym		A75	A65	A50	A25
Softening Point, °C	ASTM D36	155.8	128.4	106.6	54.8
NHI, %wt.	ASTM D3279	45.7	29.0	28.3	8.9

**Table 2. Heavy vacuum gas oil properties**

<i>Property</i>	<i>Method</i>	<i>Oil 1</i>	<i>Oil 2</i>	<i>Oil 3</i>
Acronym		O1	O2	O3
Viscosity at 60 °C, Pa.s	ASTM D2171	0.101	0.071	0.023

**Table 3. Straight run bitumen properties**

		<i>Bitumen 1</i>	<i>Bitumen 2</i>
Acronym		B1	B2
Softening Point, °C	ASTM D36	52.6	40
Penetration at 25 °C, dmm	ASTM D5	47	162

**Table 4. Experimental bitumen blend ratios**

Sample	<i>Oils</i>			<i>Asphaltenes</i>		<i>Bitumens</i>		High PG	Low PG	Intermediate PG	
	O1	O2	O3	A75	A65	A50	A25				B1
1			0.41		0.59				64	-22	25
2	0.44				0.56				64	-22	25
3		0.44		0.56					64	-10	31
4			0.49	0.51					64	-16	28
5	0.52			0.48					64	-16	28
6			0.51	0.49					64	-16	28
7	0.54			0.46					58	-16	25
8			0.47	0.53					70	-10	34
9	0.48			0.52					70	-10	34
10	0.05						0.95		64	-22	25
11			0.04				0.96		64	-22	25
12	0.07						0.93		58	-22	22
13		0.06					0.94		58	-22	22
14			0.07				0.93		58	-22	22
15	0.12					0.22	0.66		64	-16	28
16	0.06					0.57	0.37		64	-16	28
17	0.09					0.37	0.54		58	-22	22
18						0.78		0.22	64	-16	28
19				0.13				0.87	70	-16	31
20						0.57		0.43	64	-22	25
21				0.09				0.91	64	-22	25
22						0.37		0.63	58	-22	22
23				0.05				0.95	58	-22	22
24									70	-22	28
25			0.378			0.622		1	58	-16	25
26		0.33				0.67			58	-16	25
27			0.515	0.485					58	-16	25
28*			0.517	0.483					64	-10	31
29		0.462		0.538					58	-16	25
30*		0.462		0.538					64	-4	34
31			0.423		0.577				64	-22	25
32*			0.423		0.577				64	-16	28
33		0.375			0.625				58	-22	22
34*		0.375			0.625				64	-16	28
35*			0.378			0.622			64	-16	28
36*		0.33				0.67			64	-16	28
37**		0.42		0.58					70	-10	34

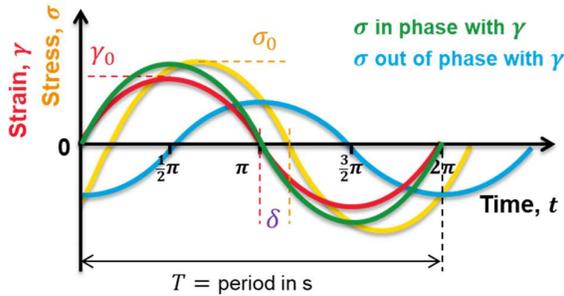
\*air-blown samples

\*\*oil was solvent-dewaxed prior to blending

#### 4. ALTERNATIVE TO CURRENT SUPERPAVE™ INTERMEDIATE TEMPERATURE PARAMETER

The North American SuperPave™ specification utilizes the dynamic shear rheometer (DSR) in determination of the intermediate temperature parameter  $|G^*| \sin \delta$ . For example, for PG 64-22, the intermediate temperature DSR test is performed at 25 °C on pressure aging vessel (PAV) residue. To pass the AASHTO M320 specification requires  $|G^*| \sin \delta \leq 5000$  kPa. The reasoning behind introducing a maximum limit for this parameter was to “control a shape of a mastercurve” and limit stiffness to prevent fatigue cracking susceptible binders passing the specification [25]. One could argue that if stiffness at intermediate temperature needed to be limited,  $|G^*|$  should have been limited and not  $|G^*| \sin \delta$  as it is explained further. The relationship between stress and strain in a dynamic oscillatory experiment, and the definitions of complex, storage and loss moduli and phase angle, are represented graphically in Figure 1. It is apparent that the intermediate temperature parameter  $|G^*| \sin \delta$  is identical to the loss modulus,  $G''$ . From a simple graphical representation (Figure 2) of the complex modulus in a complex plane, it is apparent that setting a maximum limit on  $G''$  favours low-phase angle bitumens over high-phase angle bitumens. If one considers, as in Figure 2, two bitumens with the same magnitude of the complex modulus, their peak stress would be identical at a given peak strain. Thus, lower

phase angle bitumen would yield more elastic response to deformation, a higher relative portion of energy would be stored, and faster stress accumulation would be observed during repeated deformation.



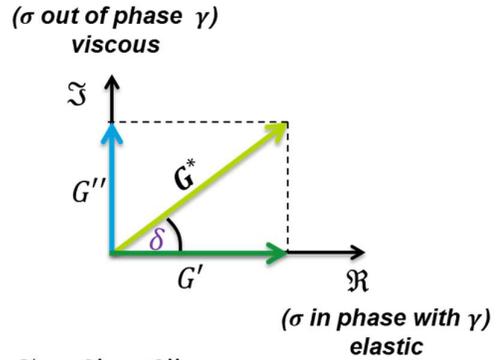
$$\omega = \frac{2\pi}{T} = 2\pi f \text{ (analogous to } \dot{\gamma}\text{)}$$

$$\sigma = \sigma_0 \sin(\omega t + \delta)$$

$$\sigma = \underbrace{\sigma_0 \cos \delta \sin \omega t}_{\sigma \text{ in phase with } \gamma} + \underbrace{\sigma_0 \sin \delta \cos \omega t}_{\sigma \text{ out of phase with } \gamma}$$

$$\sigma = \gamma_0 \left[ \underbrace{\left(\frac{\sigma_0}{\gamma_0}\right) \cos \delta}_{G'} \sin \omega t + \underbrace{\left(\frac{\sigma_0}{\gamma_0}\right) \sin \delta}_{G''} \cos \omega t \right]$$

### Representation in Complex Plane



$$G^* = G' + iG''$$

$$|G^*| = \sqrt{G'^2 + G''^2} = \frac{\sigma_0}{\gamma_0}$$

$$\tan \delta = G''/G'$$

symbol	modulus	energy	response
$G'$	storage	stored	elastic
$G''$	loss	dissipated	viscous

Figure 1. Graphical representation of dynamic material functions, where  $|G^*|$ ,  $G'$ , and  $G''$  are the complex, storage and loss moduli, respectively,  $|G^*|$  is the magnitude of the complex modulus,  $\gamma$  is the shear strain,  $\sigma$  is the shear stress,  $\delta$  is the phase angle, subscript 0 denotes “peak”,  $\omega$  is the angular velocity,  $f$  is the frequency, and  $\dot{\gamma}$  is the strain rate.

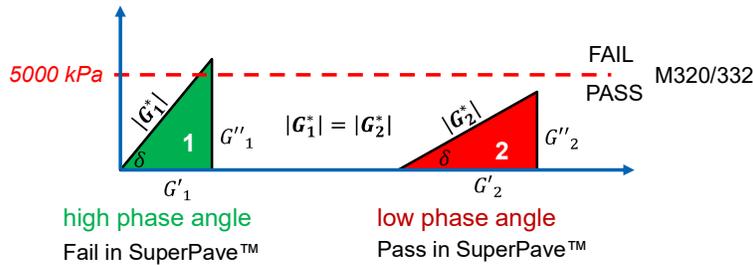


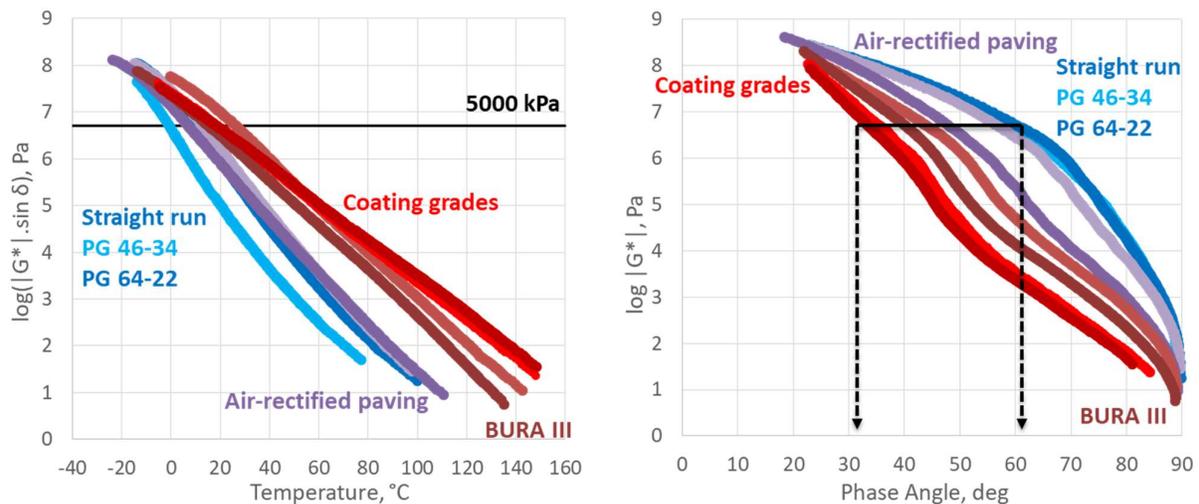
Figure 2. Comparison between high- and low-phase angle bitumen in the complex plane with the current intermediate SuperPave™ specification indicated.

To find a more suitable parameter distinguishing binders at intermediate temperature with respect to cracking susceptibility, mastercurves of dynamic material functions from the author’s previous study [24] were re-analyzed with a different objective. The results are presented in Figure 3. The binders in that study ranged from straight-run paving bitumen to severely oxidized roofing shingle coating grades. As it is apparent, the  $|G^*| \sin \delta$  parameter does not sufficiently distinguish among the rheologically diverse samples, and cannot correctly rank them from neat to the most oxidized one. However, presenting the same data in black space clearly shows the difference between straight-run and oxidized samples, and correctly ranks them in order of oxidation severity. Pauli et al. [26] made the same observation and was able to demonstrate a very good correlation between isothermal phase angle (especially at 50 °C) and test-pavement cracking severity and also showed the close linkage between phase angle and severity of oxidative aging in the field. The ability of the phase angle to correctly rank binders is critically important. As severity of oxidation increases, the ability of the binder to relax stresses significantly decreases. Faster stress accumulation eventually leads to cracking as the strength of binders does not significantly change with oxidation. Please refer to Kriz 2012 [24] for additional details on the chemical changes that occur during oxidation and their impact on stress relaxation. Another advantage of the black diagram is that it is indifferent to sample viscosity, and in fact nearly identical curve is obtained for binders of the same

chemical origin. Specifically, the two straight-run binders (blue curves in Figure 3) are distilled from the same crude oil, and their black diagrams are nearly identical, despite one being PG 46-34 (~360 dmm penetration) and the other being PG 64-22 (~85 dmm penetration). Black diagrams are thus extremely useful in studying the extent of oxidative aging, as well as changes in chemical composition over a wide range of samples. It is in fact a fingerprint of bitumen chemical composition and phase stability. Phase angle at constant modulus thus can be considered as a useful intermediate temperature parameter. This is represented graphically in Figure 3 Right.

There are several advantages of using a minimum phase angle limit at a constant modulus as a new specification parameter over the  $|G^*| \sin \delta$  as the Superpave™ intermediate temperature parameter:

1. Phase angle represents correct science as it correctly ranks samples based on their ability to relax stresses.
2. Phase angle is insensitive to the grade of asphalt. The same limit and test can be used for any grade of bitumen. The cumbersome and somewhat arbitrary practice of intermediate PG temperature determination can be abandoned.
3. Phase angle can easily be determined from existing data; AASHTO T 315 has prescribed that  $|G^*|$  and phase angle to be reported independently since the SuperPave™ inception in 1990s. Phase angle at a given modulus can be determined by simple interpolation.
4. Phase angle is highly repeatable measurement. Current AASHTO determination of precision estimates for phase angle is: (1s/d2s)  $0.09^\circ/0.25^\circ$  and  $0.76^\circ/2.11^\circ$  for single operator and multiple laboratories, respectively. If we consider a typical phase angle at intermediate temperature to be  $45^\circ$ , then  $2.11^\circ$  represents approx. 4.7%. This is nearly 10 times lower variability than for the  $|G^*| \sin \delta$  parameter where AASHTO T315 reports 40.2% for d2s% for multi-laboratory precision.



**Figure 3. Left: Mastercurve of the current Superpave™ intermediate temperature specification parameter. Ranking from straight-run (not oxidized) to severely oxidized roofing coating grade (softening point  $>100^\circ\text{C}$ ) not captured by  $|G^*| \sin \delta$ . Specification limit of 5000 kPa indicated on the chart. Right: Black diagram correctly ranks samples from straight-run to severely oxidized, arrows indicate a range of phase angles these samples cover at 5000 kPa constant  $|G^*|$ . Data adapted from Kriz [24].**

## 5. RELATIONSHIP BETWEEN PHASE ANGLE AND PHASE COMPATIBILITY

### 5.1. Distribution of specification grades in this study

Superpave™ and penetration-softening point specification grade distributions for the binders examined in this study are presented in Figure 4 and Figure 5. It is apparent that both sets cover an extremely wide range of grades, spanning well beyond the typical grades used in the paving industry. The binders also cover a very wide range of chemical compositions and rheological properties. The variability in chemical and rheological properties of the samples together with very large number of individual samples in the datasets increase a confidence in validity of the herewith presented analysis and conclusions.

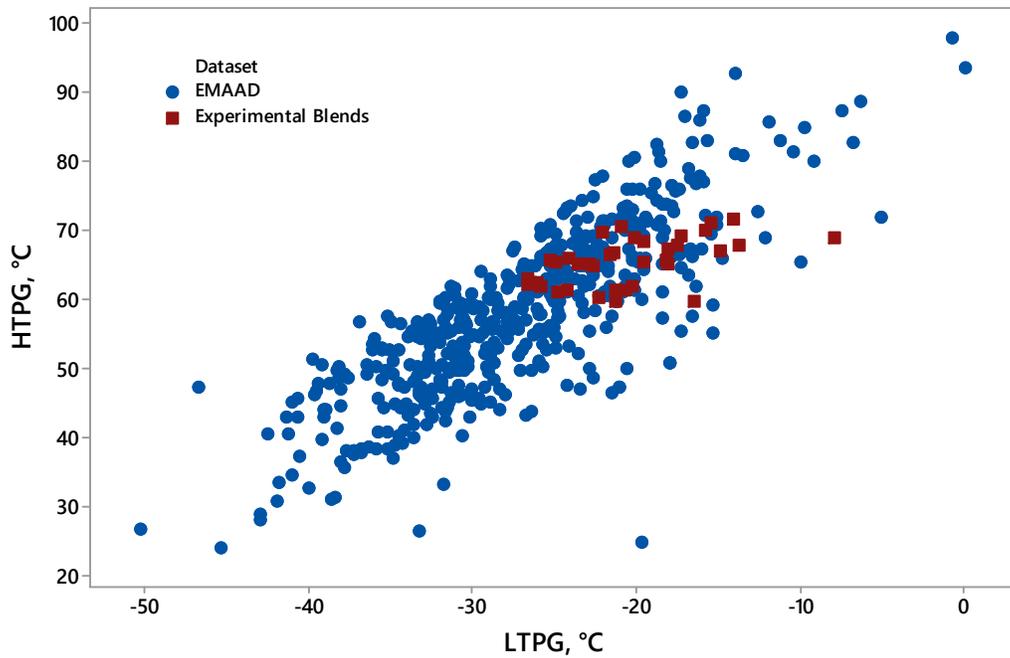


Figure 4. Distribution of PG properties of the two datasets.

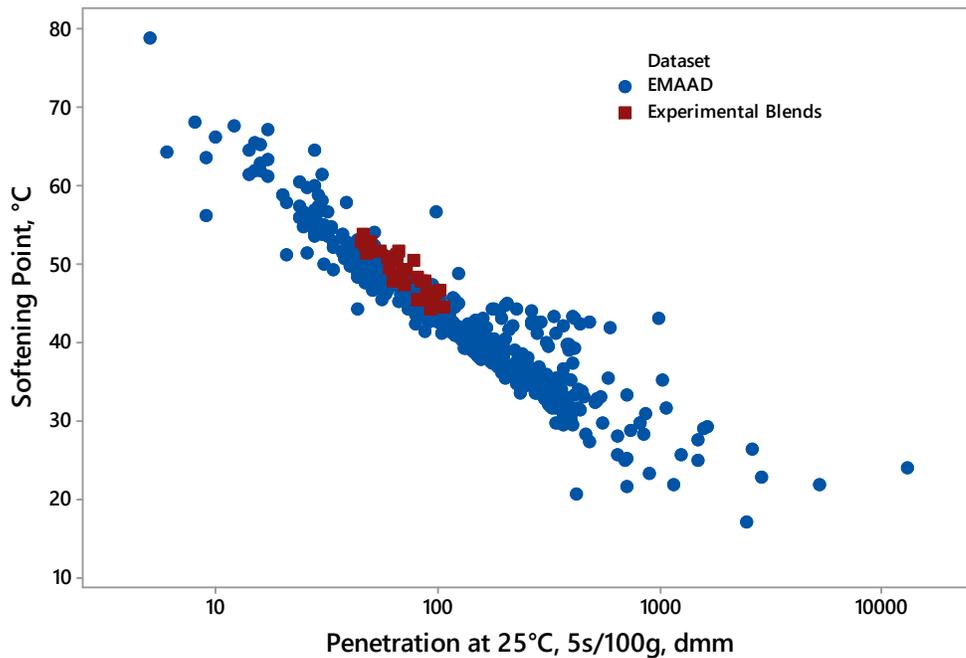


Figure 5. Distribution of properties of the two datasets in softening point – penetration system. Penetration values over 400 dmm were extrapolated from measurements at lower temperatures.

### 5.2. Relationship between phase angle and phase stability/compatibility

As noted earlier, phase compatibility can be simply described by the colloidal instability index. Adding asphaltenes and/or saturates to the system will eventually lead to phase instability and separation, forming a rigid phase interface. Moreover, saturates, especially n-paraffins, can form a crystalline phase within the binder matrix, forming yet another interface. These processes thus form a matrix of rigid interfaces that increases the elastic response of the sample. Stress dissipation

over the interfaces would be impeded. To validate this hypothesis, the phase angle was determined at a constant magnitude of complex modulus of 8967 kPa<sup>1</sup> for all samples in the EMAAD and experimental libraries. Subsequently the phase angle was plotted versus a property termed “accumulated solids” which is calculated as the weight percentage of crystallizable wax by DSC [27], times 2.5, plus the weight percentage of n-Heptane insoluble asphaltenes (Figure 6). A very reasonable correlation was observed for the 522 samples in EMAAD, confirming that phase angle is very sensitive to phase interfaces that would generally increase with increasing fraction of asphaltenes and crystallizable saturates. The same observation was made for the experimental blends (Figure 7).

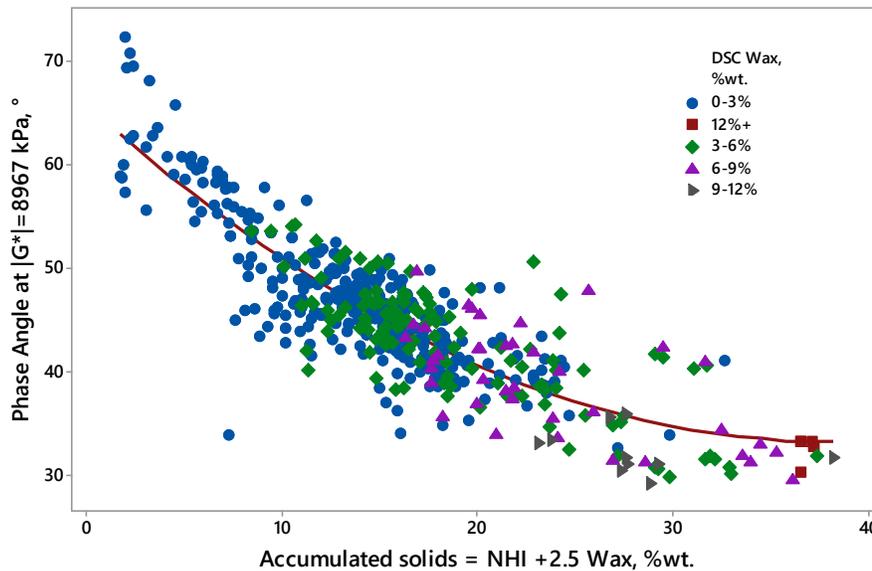


Figure 6: Phase angle versus asphaltenes and wax content. EMAAD data,  $R^2=75.6\%$  quadratic fit.

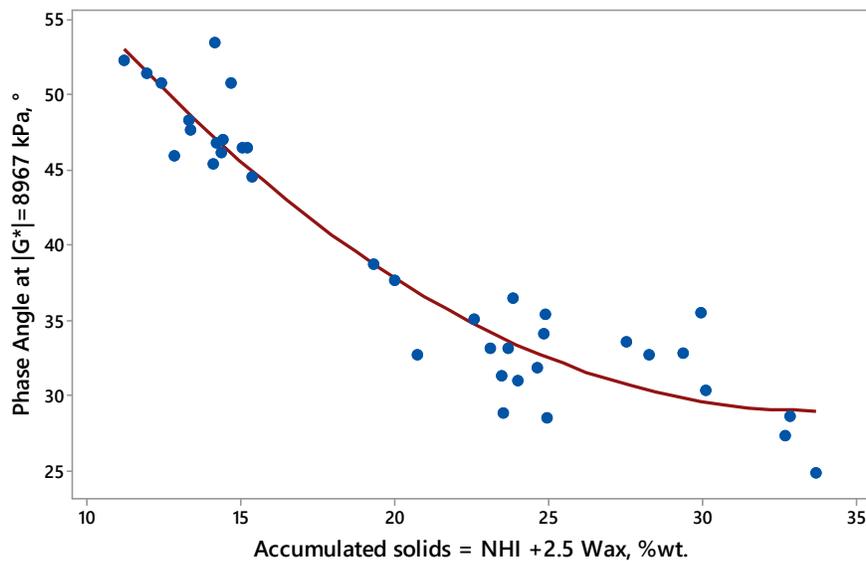
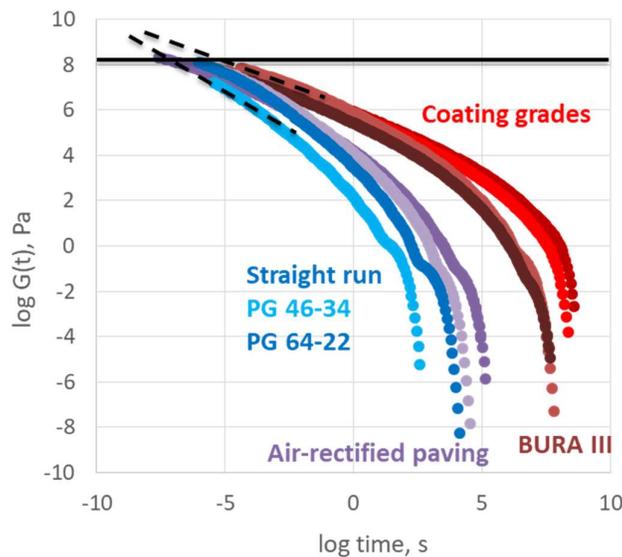


Figure 7: Phase angle versus asphaltenes and wax content. Experimental blends data,  $R^2=90.2\%$  quadratic fit.

<sup>1</sup> The value originated from a recent proposal to AASHTO to increase  $|G^*| \sin \delta$  limit to 6000 kPa in AASHTO M320 and M332 specification for binders having a phase angle  $42^\circ$  or higher to allow high quality ductile binders in the specification. By using trigonometry and expression presented in Figure 1,  $|G^*|$  equals 8967 kPa for  $G''=6000$  kPa and  $\delta=42^\circ$ .

### 5.3. Relationship between Phase Angle and Low Temperature Properties

In the Superpave™ specification, the time dependent flexural creep stiffness function,  $S(t)$ , is evaluated at 60 s deformation time for magnitude (stiffness) and slope ( $m$ -value) to determine the low temperature performance grade. For a perfectly elastic solid, or a viscoelastic solid in equilibrium,  $S(t)$  can be calculated from the relaxation modulus,  $G(t)$ , under certain conditions [28]. However, partly glassy systems far from equilibrium, which most bitumen after one hour conditioning at low PG temperature are, do not fully satisfy these conditions. Accurate calculation of  $S(t)$  from  $G(t)$  is thus non-trivial. Nevertheless, both functions will assume the same functional shape. By utilizing the data from Kriz 2012 [24], relaxation moduli were calculated and are presented in Figure 8. It is apparent that at very short times, which are analogous to low temperatures, the slope of the curve decreases with the severity of sample oxidation. Therefore, at the same relaxation modulus (or flexural creep stiffness), the time derivative (slope) represents the relaxation rate, and it decreases with oxidation severity. The chemical compositional reasons for reduced relaxation rate are discussed in detail here [24]. The same can be demonstrated in SuperPave™ specification testing. The difference between the temperature where BBR flexural creep stiffness is 300 MPa and  $m$ -value (slope) is 0.300 has been studied and it is referred to as  $\Delta T_c$  critical, or  $\Delta T_c$ , parameter [29,30]. The advantage of  $\Delta T_c$  is that it can be easily determined from a standard bending beam rheometer (BBR) test.



**Figure 8: Relaxation Modulus. Slope indicated, lowers with severity of oxidation.**

Relatively good correlations were obtained between (equi-stiffness) phase angle and  $\Delta T_c$  for both datasets (Figure 9 and Figure 10). Even better correlation likely would be observed if the BBR conditioning time were longer than 1 h. Bitumen, and especially phase instable bitumen, is far from equilibrium at low temperature. Due to very high viscosity and low molecular mobility, the evolution of the material to its equilibrium structure is a very lengthy process [31]. Analogically, at intermediate temperature the time-dependent structure is much closer to equilibrium. Furthermore, the phase angle (or more precisely its tangent) is a ratio between the storage and loss moduli and it is thus less sensitive to time-dependent evolution of the structure (isothermal hardening). Therefore, the intermediate temperature phase angle measurement is far more reliable, even after short conditioning time, than measurement of  $|G^*| \sin \delta$ .

The relatively good correlation observed here confirms that the phase angle and  $\Delta T_c$  are both related to the relaxation rate. A decrease in  $\Delta T_c$  or phase angle is related to increasing phase instability – samples with high fractions of NHI and wax have lower  $\Delta T_c$  and equi-stiffness phase angle.

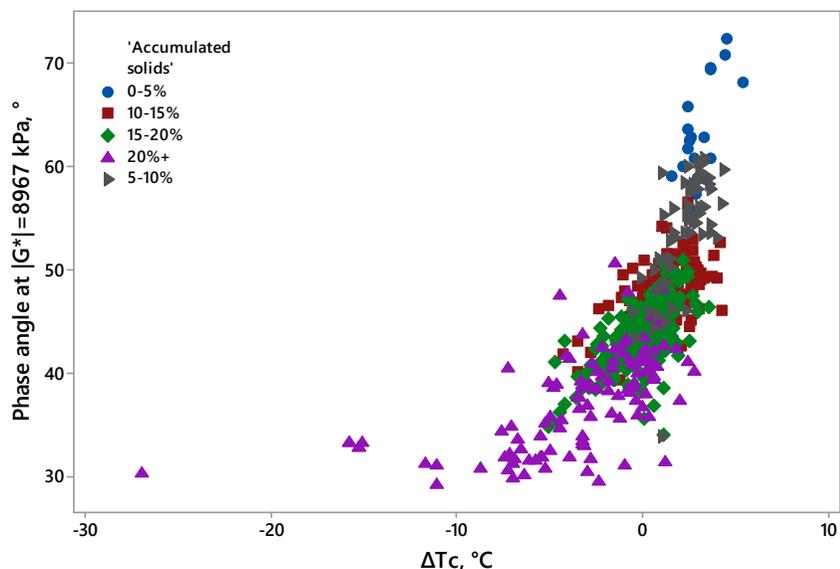


Figure 9: Phase angle of materials from EMAAD database with varying amounts of accumulated solids as a function of  $\Delta T_c$ .

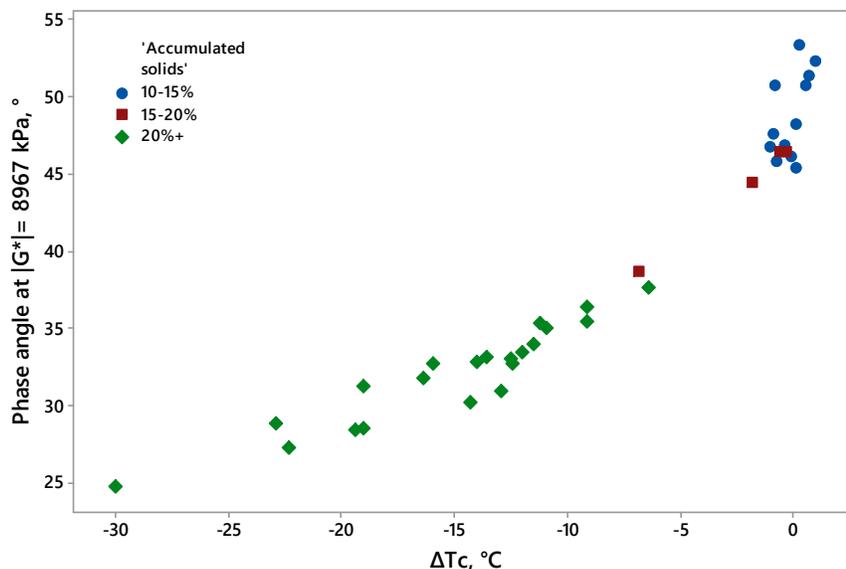


Figure 10. Phase angle of experimental blends with varying amounts of accumulated solids as a function of  $\Delta T_c$ .

#### 5.4. Relationship between Phase Angle and Oxidative Aging Susceptibility

Aging susceptibility can be well-tracked by the viscosity ratio – a ratio of the viscosity at 60°C before and after the rolling thin film oven test (RTFOT). Historically in the USA, and in various specification around the Globe today, the maximum limit for the viscosity ratio is typically set around three [3]. In other words, viscosity after RTFOT should not increase more than three times. A high viscosity ratio would mean the sample is too sensitive to oxidative aging and likely will deteriorate rapidly in the field. An interesting observation was made when the equi-viscous phase angle was plotted versus the viscosity ratio. Relatively good correlation was observed between the two parameters, with aging susceptibility increasing with lower phase angles (Figure 11). The reason could be simply because of increased NHI content (Figure 12). The asphaltene fraction is generally the most susceptible fraction to oxidation as those molecules contain the most reactive sites – polarized  $\pi$ -electrons due to high polarity bonds to electronegative heteroatoms and an electrophilic unsaturated hydrocarbon skeleton. The question remains whether phase incompatibility can somehow accelerate oxygen diffusion along interfaces or provide easier access of oxygen to more reactive polar molecules.

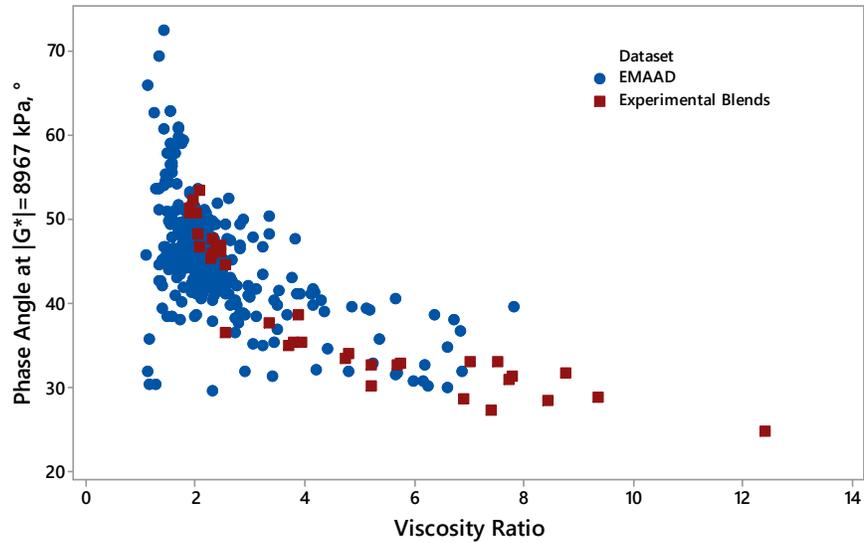


Figure 11: Equi-viscous phase angle versus viscosity ratio.

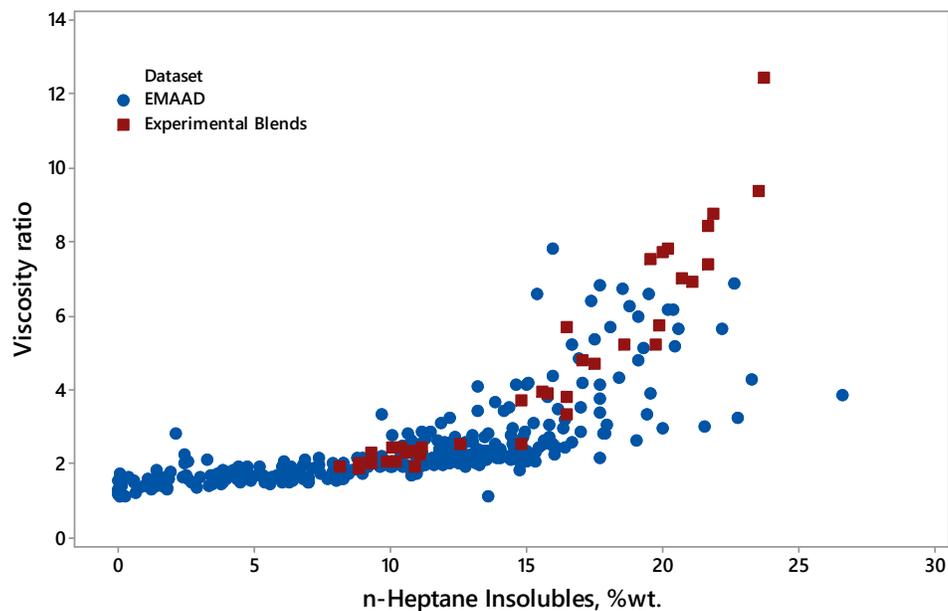


Figure 12: Viscosity ratio versus NHL.

## 6. CONCLUSIONS AND NEXT STEPS

The North American SuperPave™ specification was developed based on straight-run, refinery-produced bitumen. However, various global economic and logistical factors have led to today's bitumen being prepared with a variety of additives with a variety of chemical and rheological properties. These modified bitumen might behave and age differently than straight-run binders, and might not be properly screened by SuperPave™. In particular, the present work has shown that the current intermediate temperature parameter,  $|G^*| \sin \delta$ , fails to differentiate well-performing bitumen from those that exhibit poor-performance, and preferentially accepts bitumen with low phase angles. Therefore, it is proposed that phase angle at constant modulus be used as an alternative intermediate temperature parameter.

The phase angle was shown to correctly rank samples on the basis of their ability to relax stresses, and it is insensitive to the grade of asphalt being tested. Furthermore, phase angle is a highly reliable measurement with much lower variability than  $|G^*| \sin \delta$ , and can be determined easily from existing data. The phase angle was found to be well-correlated to the

accumulated solids (NHI + 2.5·Wax), and could be an indicator of colloidal instability. The phase angle also correlates relatively well to  $\Delta T_c$  and confirms the relationship between phase angle and relaxation. The phase angle also was found to have reasonable correlation to the viscosity ratio, indicating the applicability of phase angle to be used in the predication of oxidative aging susceptibility.

In general, the phase angle is a simple and important parameter which can be used to screen asphalts of poor phase stability, high aging rates and poor relaxation properties.

The present observations were made for straight-run and blended asphalts. The next steps should include analysis of bitumen prepared to contain components such as cracked stock, bio-oils, and oxidized materials. The aging and phase stability of these types of binders need to be better understood to prepare new specifications that screen bitumen for premature cracking and loss of cohesion.

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