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Analysis of thermal, rheological, and colloidal compatiblity of bitumen modified with engineered bio-based rejuvenators and rheology modifiers

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Abstract

Increasing incorporation of highly aged bituminous material into pavements on one hand, and the potential deterioration of the quality of soft bitumen has accentuated the need to engineer the properties of bitumen with various “rheology modification” and the properties of high-recycled mixtures with “Rejuvenation” technology. While it is understood that any modified formulation will need to adhere to high standards of compatibility and long term stability and durability, consensus on the definition of “Rejuvenation” and the associated mechanisms does not exist. The present study utilizes chemical fractionation, thermal analysis, and thermo-rheological analysis for to evaluate the impact of an engineered bio-based additive from a chemically modified vegetable-oil source. Chemical fractionation was performed using an “Iatroscan” and used to derive colloidal stability indices. The viscoelastic response was analyzed via thermo-rheological parameters such as ΔTc, derived from 4-mm Dynamic Shear Rhoemeter master curve modeling and Bending Beam Rheometry. The glass transition properties were measured using a Differential Scanning Calorimeter (DSC). A selection of virgin and reclaimed bitumen at various levels of aging from across Europe, South America, and North America were utilized to develop a database to investigate relationships between measures of bitumen compatibility, colloidal stability, and thermal and visco-elastic properties. The trends were further assessed in the context of the impact of bio-based rheology modification and rejuvenation. The results show clear relationships can be established across rheological, thermal, compositional properties, and used to show more consistent measures of bitumen compatibility, especially with progression of aging as a result of the modification. Such trends present opportunities to utilize emerging compatibility parameters in bitumen modification and mixture rejuvenation specification.

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Relating Thermal and Rheological Analysis to Phase Compatibility of Bitumen Modified with Rejuvenating and Softening Recycling Agents

Abstract

Increasing incorporation of highly aged bituminous material into pavements on one hand, and the potential deterioration of the quality of soft bitumen has accentuated the need to engineer the properties of bitumen with various "rheology modification" and the properties of high-recycled mixtures with "Rejuvenation" technology. While it is understood that any modified formulation will need to adhere to high standards of compatibility and long term stability and durability, consensus on the definition of "Rejuvenation" and the associated mechanisms does not exist.

The present study utilizes thermal analysis and thermo-rheological analysis to evaluate the impact of two recycling agents, and attempts to tie the results to "rejuvenating" vs. "softening" categorization. The viscoelastic response was analyzed via thermo-rheological parameters such as ΔT_c, derived from 4-mm Dynamic Shear Rhoemeter master curve modeling and Bending Beam Rheometry. The glass transition properties were measured using a Differential Scanning Calorimeter (DSC).

Two bitumen sources, one known for high phase compatibility and quality, and the other generally associated with lower compatibility, were selected to investigate relationships between measures of bitumen compatibility, thermal analysis spectra and visco-elastic properties at various aging levels. The trends were assessed in the context of the impact of bio-based softener in comparison to a biobased recycling agent. The results show that relationships can be established across rheological, thermal, compositional properties, and used to show more consistent measures of bitumen compatibility, especially with progression of aging as a result of the modification. Such trends present promising opportunities to utilize emerging compatibility parameters in bitumen modification and mixture rejuvenation specification, however further work is necessary to better understand the causal mechanisms involved.

1. INTRODUCTION

Many additives have been investigated as potential recycling agents, often utilizing different types of categorization methods based on the source or manufacturing process [1, 2, 3, 4]. Furthermore, researchers have increasingly employed terms such as "Rejuvenation" vs. "Softening" in recent years, often without a clear and quantifiable definition of the differences between the two categories. It has been the authors' observation that many seem to accept that something beyond decrease of modulus should be expected from a "true" rejuvenator, with "compatibilization" and "aging-resistance" often cited as the potential differentiating mechanism. As stakeholders begin the process of creating new specifications for complex binders and rejuvenators, the gap in reliable and non-circumstantial measures of compatibility between recycling agents and aged bitumen are becoming an increasingly evident.

Tabatabaee and Kurth proposed a functional categorization of recycling agents based on the bitumen fraction most affected by the additive and the expected mechanism of effect upon addition to aged bitumen, based on which the following categories were proposed [5, 6, 7]:

- "Soluble Softener", which supplement the "solvent" phase of the bitumen colloidal structure by being most compatible with the low polarity naphthenic aromatic fraction of the bitumen. Such additives reduce the viscosity and modulus of the overall bitumen through lowering the viscosity of the continuous solvent phase, but may have little effect on the intermolecular agglomeration and self-assembly of the polar micelles.
- "Compatibilizers", which have affinity for multiple fractions in the bitumen and may be derived through careful engineering of the source material, whether Petroleum- or bio-based. In addition to reduction in viscosity, these additives are hypothesized to result in a reduction in high molecular weight micelle agglomerations through disruption of the intermolecular associations and molecular self-assembly, similar to the postulated effect of the bitumen "resin" phase.
- "(Phase-) Incompatible Softeners", which often exhibit low compatibility with the low polarity naphthenic aromatic and polar fractions, especially at lower temperatures. This category may include some paraffinic and saturated material with high crystalline fractions. It was speculated that although dispersion of such lower viscosity additives in the bitumen may still achieve a reduction in overall bitumen modulus, increasing the dosages of "insoluble softeners" in bitumen may lead to colloidal instability and the long term durability and phase stability may be compromised [8, 5].

However a practical measure or index of established direct evidential correlation asphaltene association, compatibilization, and sol/gel morphology continues to be elusive. The potential possibility of using continuum rheological parameters such as ΔTc (defined as the difference in critical temperature for the creep stiffness (S) and relaxation rate (m value) passing values from bending beam rheometer (BBR) test), and indices from Black space plots and mastercurve shape parameters for assessing binder-additive compatibilities is attractive. However, such

measures have often only been indirectly related to analytically quantified measures of compatibility, and direct relationship to field performance is often based on limited historical datasets. For example, the commonly used ΔTc parameter which was first defined by Anderson et al. [9], and the associated limiting value of -5°C, were developed based on correlations between bitumen ductility values below 5 cm at 15°C, and associated pavements that experienced block-cracking in the states of Ohio and Pennsylvania in the 1980s [9, 10].

An analysis of a large database bitumen from across Europe and North America was used to establish the quality of the general relationships between the Colloidal Instability Index (CII) and ΔTc, as shown in Figure 1. Smaller values of CII have been taken to indicate a higher stability and better dispersion of the micelle fractions in the bitumen. The CII was calculated as the ratio of the sum of the asphaltene (N-Heptane insolubles, following ASTM D3279) and saturates fractions, to the sum of the aromatic and resin fractions (the "solvent" phase). The fractionation of the N-Heptane soluble fractions (the "maltenes") was performed using an Iatroscan Thin Layer Chromatography methodology following IP-469. The correlation is relatively poor and scattered, as bitumen with equal CII are shown to have ΔTc that varies by 5-10°C, and bitumen with equal ΔTc can have CII varying by more than ±50% of the average CII. This behaviour indicates the potential limitation of using such a relationship as the basis of support for using either parameter as a measure of bitumen compatibility.

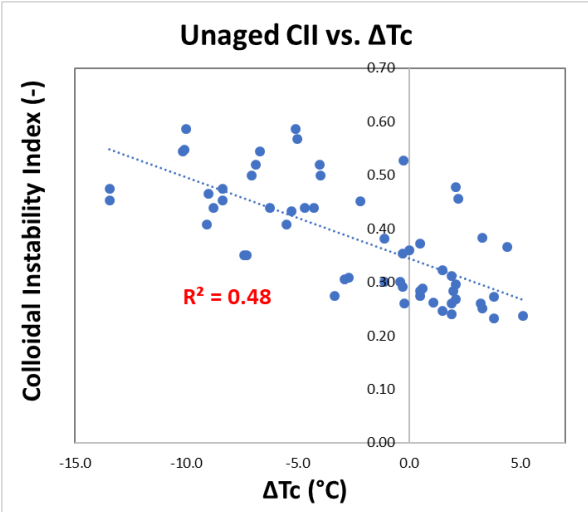


Figure 1 Loose relationship between colloidal instability index, and ΔTc

Previous work has shown that aging and increase in asphaltene content shifts the glass transition temperature (Tg) toward higher temperatures, thus increasing the susceptibility of the bitumen to cracking and durability issues due to ductile to brittle transition behaviour. It has been shown that certain rejuvenators can significantly shift the Tg towards lower temperatures [5]. An opportunity exists in linking the difference in impact of suspected "rejuvenators" and "softeners" on with the morphology of the glass transition region of the aged bitumen, and further establishing a more direct connection to bitumen phase compatibility. Establishment of such a framework will allow further assessment of relationships with practical measures and indices such as theΔTc, and other continuum rheological measures, and potentially providing a simpler means for "rejuvenator" vs. "softener" differentiation.

2. METHODOLOGY

The initial performance grades (PG) for the base bitumen were measured following standard AASHTO M320 methodology using a TA DHR2 Dynamic Shear Rheometer, and a ATS BBR# Bending Beam Rheometer.

Multiple levels of additional aging was carried out on the bitumen using an ATS PAV-3 Pressure Aging Vessel (PAV), with each level consisting of 20hrs of conditioning at 2.1 MPa of pressurized air at 100°C. For the multiple aging analysis the performance grade, mastercurve, and Black space parameters were measured on a TA AR-2000EX Dynamic Shear Rheometer using a 4-mm spindle for the intermediate and low temperatures following a ASTM D7175, and a standard 25mm spindle for the high temperature PG. The Christensen-Anderson model [11], was used to fit the isotherms to a master curve using a minimization technique to determine the shift factors and derive the mastercurve shape parameters, as shown below in equation [1].

$$G^* = G_g^* \left(1 + \left(\frac{\omega}{\omega_c}\right)^{log2/R}\right)^{R/log2} \qquad [1]$$

In which:

- G^* is the complex modulus in Pa at frequency ω in Hz;
- G^*_g is the glassy modulus asymptote variable;
- ω_c is the cross-over frequency;
- R is the Rheological Index or "R-Value".

A Perkin Elmer 8000 model Differential Scanning Calorimeter (DSC) was used to measure the glass transition range of aged and rejuvenated bitumen using a Step Scan method. A StepScan test method on a Perkin Elmer DSC is approximately analogous to the "Modulated" test method commonly used for bitumen using a TA DSC. The heating rates, rest rates, and increment periods were selected as to be comparable to test conditions previously developed by by Kriz et al. [12]:

1. Hold for 1 minute at 150°C to erase thermal history
2. Cool from 150°C to -100°C at a rate of 20°C/min
3. Hold for 5 minutes at -100°C to achieve equilibration
4. StepScan from -100°C to 100°C in 2°C intervals consisting of a 4°C/min heating ramp followed by 30 seconds of temperature hold. The Stepscan analysis can be used for similar as that of a modulated DSC run to separate the thermally reversible and irreversible response from the heat capacity (Cp) calculation. All analysis performed and presented in this paper were done on the reversible Cp spectra.

Analysis of the DSC data required the development of a protocol for reduction and smoothing of the initial dataset. The Stepscan collected approximately 30,000 datapoints over the 200°C span. The data was first uniformly reduced to 1000 data points (~1 point per every 0.2°C). A smoothing was then performed using a moving average over 75 data points. Transition temperatures were determined as the local maxima on the derivative of the heat capacity derivative spectra.

3. MATERIAL

Table 1 shows that the two bitumen sources used were relatively similar in terms of overall grade properties. The overall material matrix is shown in Table 2. The recycling agents were added to the 2xPAV aged bitumen (simulating use of recycling agent on RAP).

Table 1 Bitumen Properties

Bitumen Properties	AC#1	AC#2
Bitumen Source	North-Central USA	West Coast USA
Penetration (dmm)	51	46
Softening Point (°C)	50.9	54.5
Performance Grade	PG 64-22	PG 64-16
Continuous Performance Grade	PG 66-24.8	PG 68-19.6
ΔTc at 20hrs PAV Aging (°C)	-0.2	-4.7
ΔTc at 40hrs PAV Aging (°C)	-4.5	-8.6

Table 2 Material Matrix

Parameter	Description
Base Bitumen	A known "good" bitumen (AC#1), and a suspected "incompatible" bitumen (AC#2)
Recycling Agents	A chemically engineered bio-based oil (additive 1), and a commodity regular vegetable oil (additive 2)
Aging Levels	Neat, RTFO, 1xPAV, 2xPAV, 3xPAV, 4xPAV, 5xPAV

Two additives were used as recycling agents in this study, one was a regular vegetable oil (a refined, bleached, and deodorized triglyceride)and the other was a chemically modified triglyceride-based additive specifically manufactured for rejuvenation applications. The selected additives have very similar impact on the Penetration at 25°C (i.e. ~20-25% increase per 1% additive) and Softening point (i.e. ~-2 Δ°C/1%) parameters at equal dosage. Therefore the bitumen at a similar 5% by weight level for either additive, resulting in an approximately 10°C reduction in softening point..

In absence of formal definitions separating "rejuvenators" and "softeners", full conformance the criteria shown in Table 3 were used to as the basis of the labelling. The criteria was selected through consideration of the aforementioned mechanisms for recycling agent [5, 6, 7], and consideration of aging, stability and physical properties inspired by ASTM D4552 for Hot Mix Recycling Agents. Recognizing that ASTM D4552 was created for petroleum-based recycling agents, the criteria presented in Table 3 were updated and expanded to not discriminate based material source, while in the case of aging, it was expanded to cover long term aging in addition to short term aging as is

currently covered by the standard. The present study will compare the performance of the two additives in terms of impact on bitumen performance and compatibility, results of which will be used to support the selected designations.

Table 3 Recycling Agent Properties (passing criteria in Green, failing in Red)

Bitumen Properties	Additive 1 (Hereafter labelled as "Rej1")	Additive 2 (Hereafter labelled as "Sftnr1")	Potential Criteria
General Description	Chemically Modified Vegetable Oil-based	Commodity Regular Vegetable Oil	N/A
Visual Appearance	Dark Brown Colour, Liquid, Homogenous	Light Yellow Colour, Liquid, Homogeneous	Liquid and homogeneous at ambient conditions (no phase separation)
Density (20°C), g/cm^3	~0.93	~0.91	0.90-1.10 (~±10% of bitumen to prevent storage separation)
Open Cup Flashpoint	>290°C	>290°C	Meet bitumen minimum requirements (i.e. >240°C)
Viscosity at 60°C (Brookfield, #18)	29.25 cP	16.25 cP	N/A
Viscosity Ratio (After TFO[1])	1.05	2.2	< 3.0 (similar to bitumen and ASTM D4552)
Viscosity Ratio (After PAV[2])	1.07	31.8	< 3.0 (limit needs verification)
Viscosity Ratio (TFO 5-days at 85°C[3])	1.0	50.5	< 3.0 (limit needs verification)
TFO Mass Loss, %	> 0.2%	>0.2%	< 1.0% (similar to bitumen, to prevent excessive volatiles)
Fraction Separating with the "Resin" Fraction[4]	~35%	~0%	> 30% Resin Content (limit needs verification)
Fraction Separating with the "Saturate" Fraction[4]	~0%	~0%	< 30% Saturate content in accordance to ASTM D4552

[1] In accordance to ASTM D1754, conditioned for 5.5hrs at 163°C in a force-draft oven.
[2] In accordance to ASTM D6521, conditioned for 20hrs at 100°C at an air pressure of 2.1 MPa.
[3] In accordance to ASTM D1754, modified for conditioning for 5-days at 85°C in a force-draft oven.
[4] In accordance to IP-469, in which the "saturate" fraction is separated through n-Pentane elution, "aromatics" by a Chloroform-Toluene blend (90:10 by volume) elution, and the remainder designated as the polar aromatic (resin) fraction.

4. RESULTS AND DISCUSSION

A review of existing literature and a the correlations between ΔTc and CII for a large database of bitumen highlighted the need for an independent measure of bitumen compatibility that can be used as a means to validate or support the utilization of either parameter, or help determine new practical parameters to be used for such means. The present study was designed under the hypothesis that thermal analysis can be utilized as a more direct measure of bitumen compatibility. Therefore two bitumen of relatively similar grades but perceived differences in quality were aged and treated with two recycling agents and further conditioned through extended aging. The resulting bitumen is first rheologically characterized by constructing a mastercurve and consideration of the associated shape parameters, and performance grade. This is followed by a thermal analysis of the bitumen and finally establishment of relationships between various thermal analysis parameters and rheological measures.

Figure 2(a) and (b) show the mastercurves constructed for either bitumen. Immediately some differentiation between the impact of aging can be observed between the two bitumen types: for AC#1 (the "good" bitumen) the subsequent 3xPAV aging did not dramatically alter the relative rheological performance of the various bitumen, resulting in a relatively similar shift towards high |G*| and lower reduced frequency values. However for AC#2 (the "poor" bitumen), the neat binder and the binder treated with the "softener" showed a much more significant shift towards the higher |G*| and lower reduced frequencies compared to the AC#2 binder treated with the "rejuvenator". This trend is more clearly quantified in Figure 2(c) and (d) in which the "R" value is plotted against the cross-over frequency.

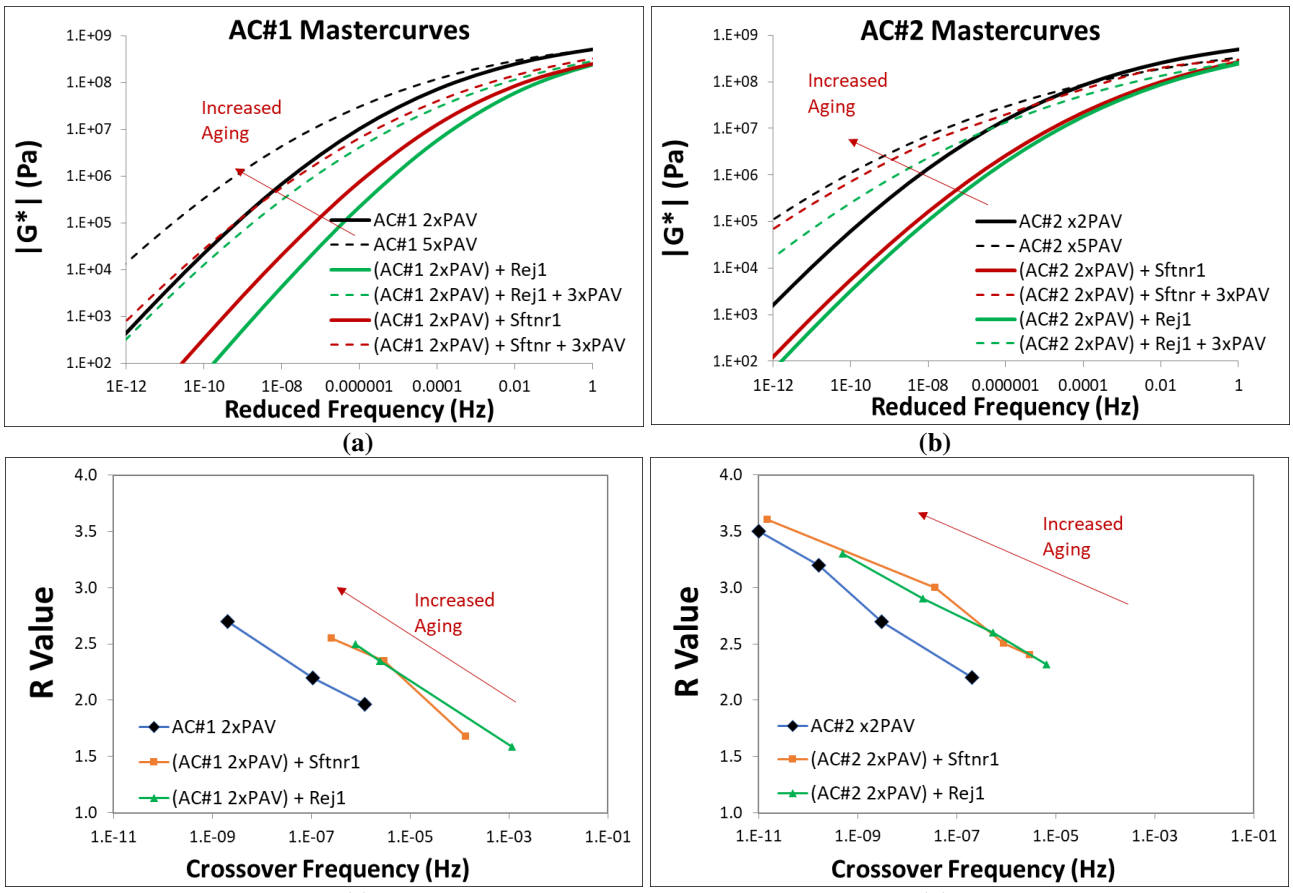


Figure 2 (a) and (b): Mastercurve analysis for bitumen AC#1 and AC#2; (c) impact of further aging on the neat and treated AC#1 bitumen (data points from right to left are: initial aging (2xPAV), initial+2xPAV, and initial + 3xPAV) (d) impact of further aging on the neat and treated AC#2 bitumen (data points from right to left are: initial aging (2xPAV), initial+1xPAV, initial+2xPAV, and initial + 3xPAV).

The low temperature performance grades were controlled by the relaxation parameter (m-value) in all cases. Figure 3(a) and (b) show the impact of further aging on the neat and treated bitumen. A few observations are made: for both AC#1 and AC#2, the grade is initially improved more with the "Softener" than the "rejuvenator", prior to any additional aging. However as aging is applied the trend changes, until after 3xPAV aging the "rejuvenator" retains a better grade for AC#1. In the case of AC#2 the trend is more dramatic, showing a loss of the majority of the "softener" impact after extended aging. A similar behaviour is observed in terms of the ΔTc parameter in Figure 4(a) and (b). These results agree with the trend of rheological parameters previously shown in Figure 2.

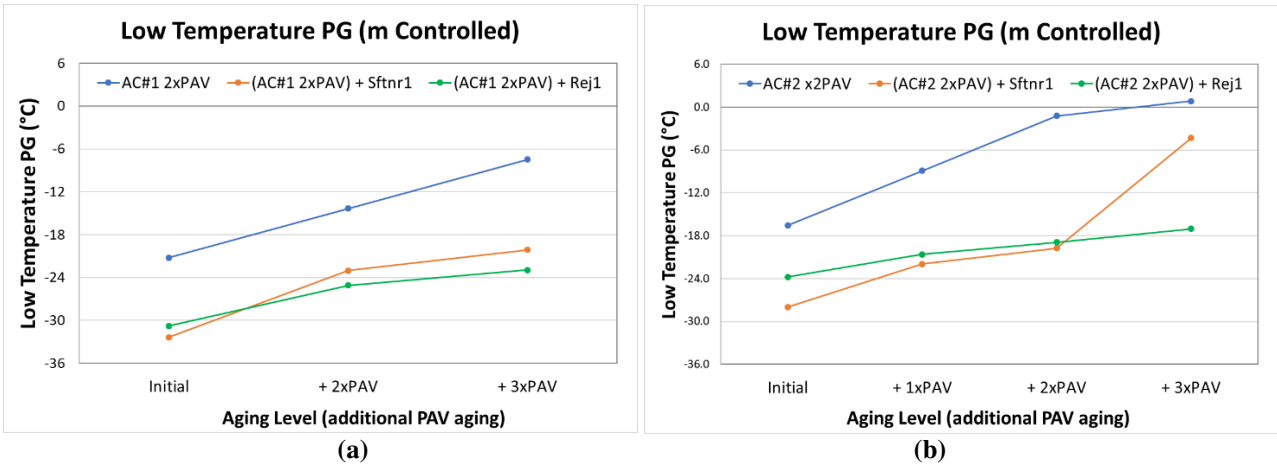
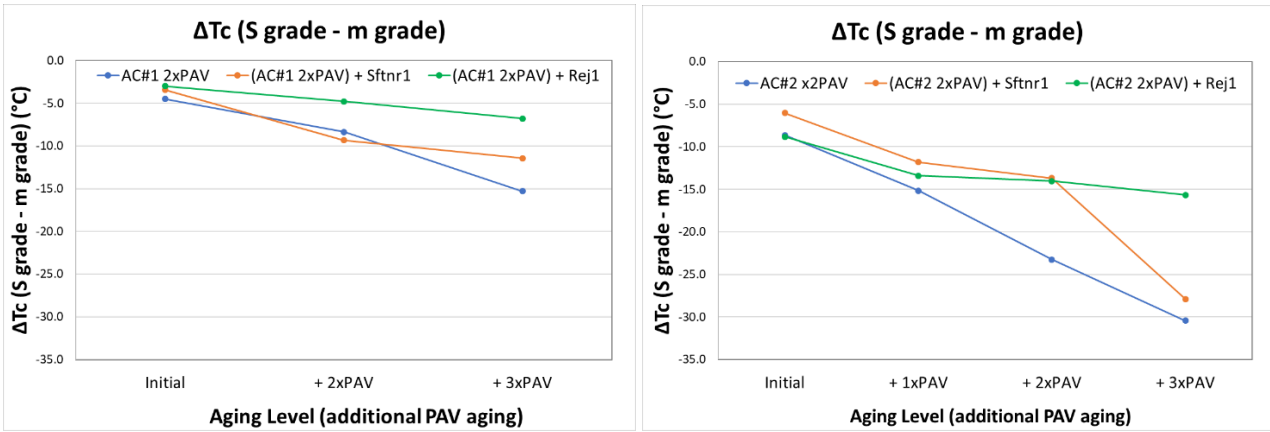


Figure 3 Low temperature PG (controleld by m-value) for AC#1 (a) and AC#2 (b). A significant loss of relaxation grade is observed in the AC#2 treated with the "softener" after 3xPAV.



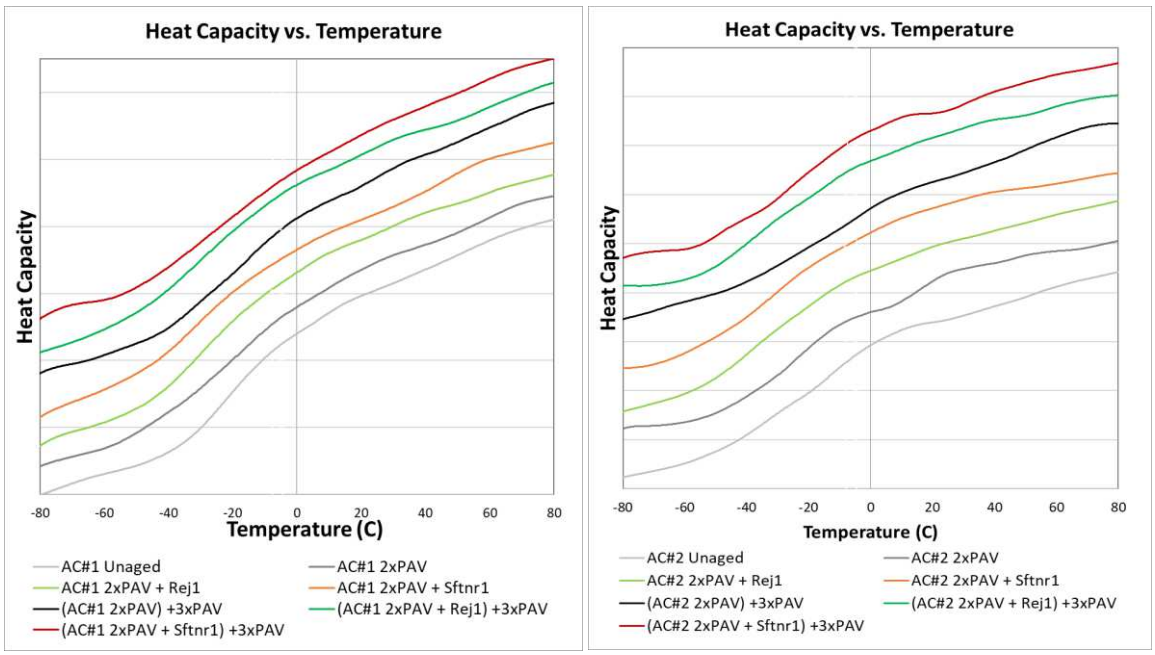
(a) **(b)**

Figure 4 ΔTc parameters for AC#1 (a) and AC#2 (b). A significant loss decrease in ΔTc is observed in the AC#2 bitumen treated with the "softener" after 3xPAV conditioning.

The final component consisted of thermal analysis of the bitumen samples using a DSC, using the methodology described earlier. Figure 5 shows the reversible Cp curves for both binders at the various treatment and aging levels. A qualitative visual assessment shows a clear major transition, along with a number of minor transitions. The additional transitions are more distinct for AC#2, shown in Figure 5(b). The impact is better shown by plotting the derivative of the heat capacity, as shown in Figure 6.

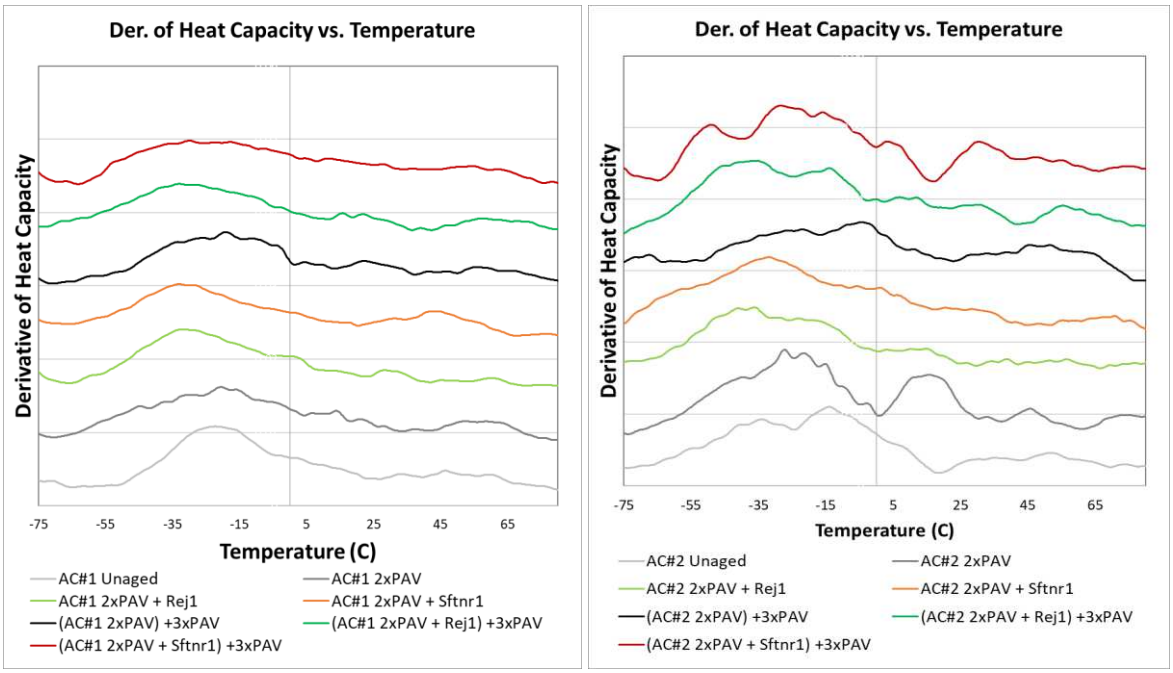
The heat capacity derivative curve for AC#2 shows a clear split in the major transition. As discussed earlier, this behaviour has been associated with bitumen phase incompatibility by Kriz et al. [12], providing additional support for the designation of AC#2 as a "poor" or "incompatible" bitumen in this study. It must be mentioned that although every effort was made to standardize the analysis process, a degree of judgement is needed to determine onset and end of each transition, especially for AC#2. The analysis resulted in the definition of three transitions for AC#1 and AC#2. The thirst transition was relatively weak for AC#1, and it suspected that the third transition may only be partially captured for some AC#2 samples within the analysed temperature range. Table 4 provides a summary of the DSC analysis, along with the rheological and grade data collected and used for analysis.

Figure 7 shows the results of comparison of the bitumen rheological and performance grade with the thermal analysis parameters. The first transition is believed to be the glassy transition based on the temperature range and the impact of aging generally increasing the value. It was observed that the first transition did not directly correlate well with any measure in this study. The nature of the 2nd and third transitions are less clear and first glance. However, the 2nd transition correlated well with the crossover temperature, suggesting a close relationship to the viscous to elastic transition behaviour. Catiuga and Lommerts [13] have suggested that the higher temperature transition in bitumen is related to the asphaltene association, with a higher transition temperature and stronger transition (larger ΔCp) suggesting a higher degree of association. Further testing is required in the present study to clearly determine which of the 2nd or 3rd transitions represent the asphaltene association transition. However, if it is confirmed that the 2nd transition is representative of the asphaltene association it may yield useful support for the utilization of viscoelastic crossover parameters in this regard, based on the relationship observed in Figure 7(a). The cross correlation between the crossover properties, R-value, and ΔTc, as has been observed in the literature, potentially enables the utilization of any of these parameters to represent the trend of the 2nd transition. The correlation of the second transition with ΔTc is shown in Figure 7(a).



(a) **(b)**

Figure 5 Impact of aging on the reversible heat capacity curves for the AC#1 and AC#2 bitumen



(a) **(b)**

Figure 6 Derivative of the reversible heat capacity curves for the AC#1 and AC#2 bitumen (heat capacity was calculated by the DSC as the normaliztion of heat flow to sample mass. The curves have been shifted vertically for clarity of comparison.)

The temperature span between the first and second transitions correlated well with the temperature span between the crossover temperature and the rheologically derived "glass transition" (derived as the peak of the G" curve against temperature), as shown in Figure 7(c). This is conceptually intriguing, suggesting potential underlying causal relationships between the temperature spans. However, interestingly both the first transition from the DSC and the rheologically derived Tg failed to directly correlate with each other or any measure considered in this study. For the rheologically derived Tg this may be due to the difficulty of accurately determining the peak of the G" curve when the peak does not clearly occur within the test temperature range, resulting in unintuitive trends in some cases.

Figure 7(d) shows a relationship between the strength of the 3rd transition and the crossover temperature. The relationship is not very strong, but it suggests that third transition also potentially relates to polar associations within the bitumen. However, further work and a broader analysis temperature span is clearly needed to better understand the potential significance of the third transition.

Table 4 Summary of data used in this study (Legend below)

Bitumen Description	Grade Properties				DSR Mastercurve Parameters					DSC Thermal Analysis Results						
	S Grade	m Grade	IT PG	ΔTc	fc	R	Tg	Tc	Tc-g	T1	ΔCp1	T2	ΔCp2	T3	ΔCp3	ΔT2-1
AC#1 Unaged	-26.0	-25.7	17.4	-0.2	1.8E-03	1.2	-17.3	7.3	24.6	-23.3	0.41	5.5	0.11	47.0	0.19	28.8
AC#1 2xPAV	-25.7	-21.2	24.8	-4.5	1.0E-06	2.0	-19.4	23.7	43.1	-16.7	0.45	8.1	0.15	60.5	0.16	24.8
AC#1 4xPAV	-22.7	-14.3	35.3	-8.4	5.7E-08	2.3	-32.6	31.7	64.3							
AC#1 5xPAV	-22.8	-7.5	33.6	-15.3	1.7E-09	2.8	-18.3	37.9	56.2	-16.6	0.45	24.6	0.12	65.3	0.16	41.2
(AC#1 2xPAV) + Sftnr1	-35.8	-32.3	14.9	-3.4	1.4E-04	1.8	-25.3	15.1	40.4	-31.0	0.45	-0.5	0.11	24.1	0.17	30.5
(AC#1 2xPAV) + Sftnr1 + 2xPAV	-32.4	-23.0	22.6	-9.3	4.0E-06	2.3	-27.3	28.4	55.7							
(AC#1 2xPAV) + Sftnr + 3xPAV	-31.6	-20.1	28.2	-11.4	1.3E-07	2.6	-27.1	34.6	61.7	-31.0	0.49	18.3	0.13	59.2	0.14	49.3
(AC#1 2xPAV) + Rejl	-33.8	-30.8	15.4	-3.0	1.2E-03	1.7	-29.7	15.0	44.7	-30.3	0.45	-1.2	0.08	44.9	0.24	29.1
(AC#1 2xPAV) + Rejl + 2xPAV	-29.9	-25.1	22.7	-4.8	1.5E-06	2.3	-28.9	26.7	55.6							
(AC#1 2xPAV) + Rejl + 3xPAV	-29.8	-23.0	30.5	-6.8	6.1E-07	2.6	-22.1	33.1	55.2	-31.0	0.43	14.6	0.18	55.0	0.12	45.6
AC#2 Unaged										-33.9	0.28	-14.6	0.27	50.5	0.18	19.3
AC#2 x2PAV	-25.2	-16.6	28.8	-8.6	2.3E-07	2.1	-24.8	34.1	58.9	-27.0	0.47	15.2	0.17	44.3	0.08	42.2
AC#2 x3PAV	-24.1	-8.9	30.5	-15.2	3.3E-09	2.7	-17.0	43.3	60.3							
AC#2 x4PAV	-24.5	-1.2	35.5	-23.3	1.7E-10	3.0	-18.2	51.2	69.4							
AC#2 x5PAV	-29.6	0.8	39.5	-30.4	1.0E-11	3.5	-28.0	64.9	92.9	-4.2	0.47	45.1	0.23	74.0	0.00	49.3
(AC#2 2xPAV) + Sftnr1	-34.0	-28.0	18.9	-6.0	3.7E-06	2.4	-33.2	29.0	62.2	-36.1	0.57	14.1	0.10	37.3	0.12	50.2
(AC#2 2xPAV) + Sftnr1 + 1xPAV	-33.8	-22.0	20.5	-11.8	8.2E-07	2.5	-28.6	35.4	64.0							
(AC#2 2xPAV) + Sftnr1 + 2xPAV	-33.4	-19.7	25.0	-13.7	2.7E-08	3.0	-30.0	44.0	74.0							
(AC#2 2xPAV) + Sftnr + 3xPAV	-32.2	-4.3	33.0	-27.9	1.6E-11	3.5	-31.5	62.2	93.7	-35.7	0.59	29.8	0.09	54.1	0.10	65.5
(AC#2 2xPAV) + Rejl	-32.6	-23.8	18.1	-8.8	7.8E-06	2.2	-31.0	27.9	58.9	-31.7	0.62	20.2	0.08	69.4	0.08	51.9
(AC#2 2xPAV) + Rejl + 1xPAV	-34.0	-20.6	19.6	-13.4	5.0E-07	2.6	-35.8	36.7	72.5							
(AC#2 2xPAV) + Rejl + 2xPAV	-32.9	-18.9	25.3	-14.0	2.7E-08	2.8	-26.6	50.4	77.0							
(AC#2 2xPAV) + Rejl + 3xPAV	-32.7	-17.0	30.7	-15.7	5.0E-10	3.3	-23.3	63.3	86.6	-28.3	0.56	30.1	0.17	73.4	0.03	58.4

- "S Grade" and m Grade" are the AASHTO M320 passing temperatures for the low temperature PG corresponding to the S and m values.
- "IT PG" is the Intermediate Temperature Performance Grade
- DSR Mastercurve parameters (fc, R) are defined in Equation 1. DSR Tg is the peak of the G" at 1Hz vs. temperature curve. Tc is the temperature corresponding to a phase angle of 45° at 1 Hz. Tc-g is the difference between the DSR Tg and Tc.
- DSC Transitions (defined as the inflection point) are numbered in order of occurrence during heating, from low to high temperature.
- ΔT2-1 is the temperature difference between the second and first transitions.
- ΔCp is the strength of the transition, defined as the difference in heat capacity between the baselines before and after the transition.

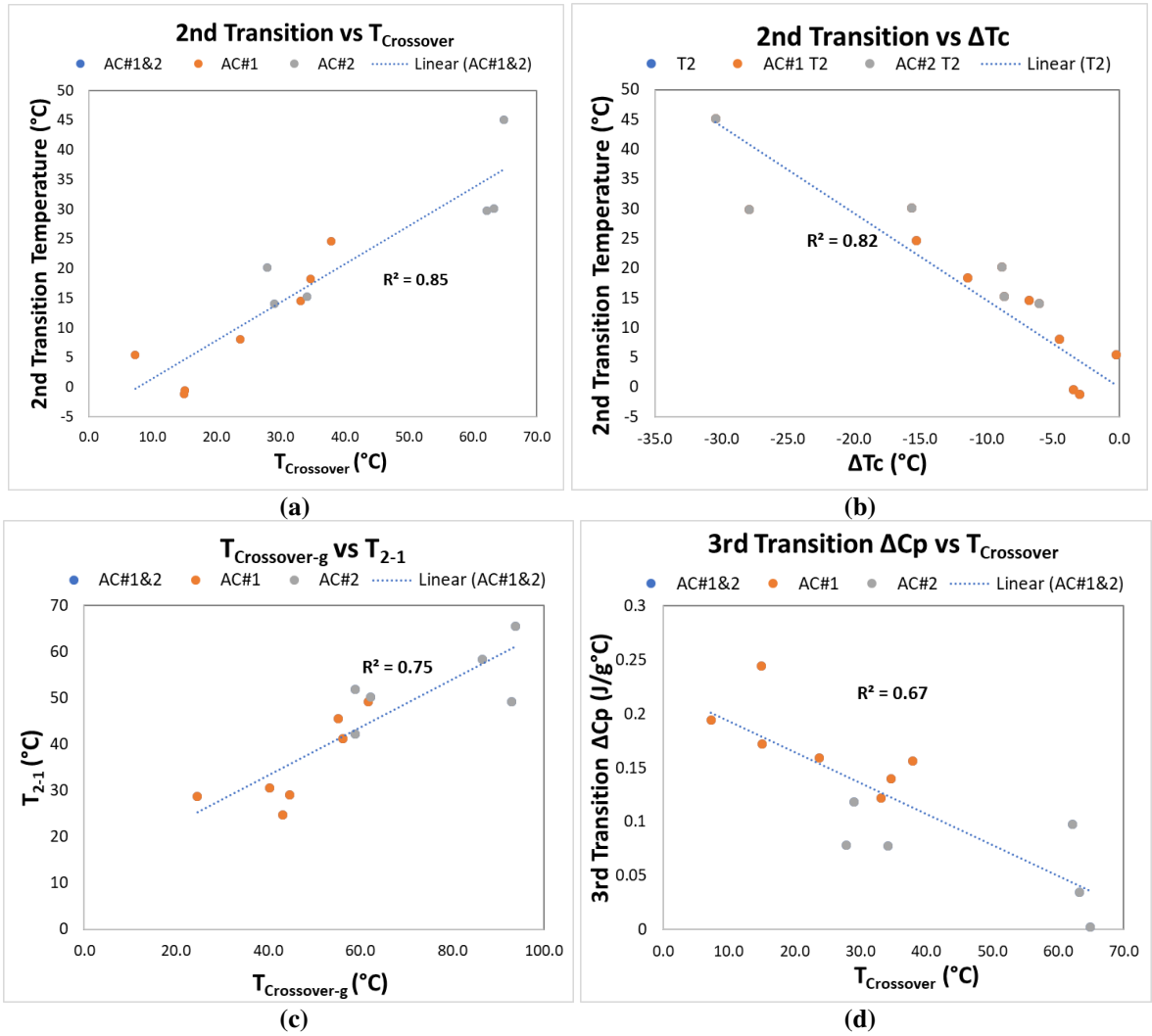


Figure 7 Establishment of relationships between rheological measures and DSC thermal analysis

5. CONCLUSIONS

A review of existing literature along with an analysis of an existing database of bitumen from across Europe and North demonstrated the limitation of using the CII and ΔTc parameters as a measure of bitumen compatibility without an independent measure of bitumen compatibility that can be used as a means to validate or support the utilization of either parameter, or help determine new practical parameters to be used for such means.

To this end, a smaller subset of material were selected for an in-depth comparison between The thermo-volumetric properties (i.e. transition behaviour), and the viscoelastic parameters. From the results the following main conclusions are derived:

- The difference between the impact of "rejuvenator" and "softener" recycling agents is most discernible in bitumen with poor compatibility.
- The differentiating impact of "rejuvenation" seems to manifests itself through retaining of performance after long term aging. However, 60 hours of PAV aging was required to observe clear differentiation.
- The differentiating impact of long term aging on the effect of the recycling agents seems to support the inclusion of the extended additive aging in recycling agent specifications focused on differentiating between "rejuvenators" and "softeners". However, more data is required in order to establish appropriate limits on the viscosity ratios.

Further research will focus on investigating the relationship between the CII and the DSC-derived transition behaviours. Although general trends were observed in this study, further work is necessary to fully validate and confirm the nature of the underlying mechanisms involved. Furthermore, the potential impact of physical hardening and isothermal conditioning on precipitating incompatibilities in bitumen treated with recycling agents will be investigated. Finally, additional bitumen sources will be considered in a broader temperature range in an attempt to better define the significance of the 2nd and 3rd transitions observed in the thermal analysis spectra, and the nature of possible relationship with polar associations within the bitumen.

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