MONITORING AGEING OF BITUMINOUS BINDERS

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ABSTRACT

The failure of the rolling thin film oven test (RTFOT) protocol to simulate the short-term ageing (STA) of *in situ* asphalt binder accurately for different binder types, can be attributed to the significantly different mixing, transport and compaction temperatures used for different asphalt mixes. The RTFOT procedure can be modified to accurately predict the STA of binders for a specific road construction scenario. The modification of the procedure constitutes the first step in the establishment of a modified protocol for a binder type/class. The method used for monitoring the ageing of binders should be applicable to all binder types, considering that the properties of modified binders often have opposing or juxtaposed ageing effects which result in irregular changes in the measured property with ageing. This paper evaluates a method of rheologically following the ageing of both modified and unmodified binders, based on a single temperature/frequency point. Ultimately data from a number of contract sites would need to be collated; repeatability and accuracy established for the proposed method, before a final protocol is determined.

1. INTRODUCTION

The rheological and chemical natures of road binders continuously change during asphalt production and throughout the service life of the pavement. This process is referred to as ageing. The effect of ageing on the chemistry and rheology of bitumen is well documented (Lu and Isacsson, 2002; Mastrofini and Scarsella, 2000).

In order to predict asphalt mix performance with ageing, both short-term and long-term ageing needs to be simulated. The current industry practise internationally uses the rolling thin film oven test (RTFOT) procedure to simulate hot-mix asphalt (HMA) plant and placement ageing for road binders, i.e. short-term ageing (STA). The RTFOT residue is then aged in a pressure ageing vessel (PAV) to simulate the in-service ageing of the binder over a 5 – 10 year period i.e. long term ageing (LTA). It was the initial intention of these accelerated thermal ageing methods to use the Arrhenius relation to bring about accelerated ageing. This relation is based on the temperature dependence of the rates of individual ageing reactions which ideally should be proportional to exp($-E_a$/RT), with E_a being the Arrhenius activation energy, R being the ideal gas constant, and T being the absolute temperature.

The rheological properties of the short-term aged binder are used in predictive equations to predict asphalt mix performance directly after construction (Witczak and Fonseca, 1996; Andrei *et al.*, 1999; Christensen *et al.*, 2003).

The RTFOT procedure assumes a similar ageing temperature and time for all mixes prior to field compaction. O'Connell *et al.* (2011) demonstrated that the RTFOT protocol cannot accommodate the wide mixing, transport and compaction temperatures used in South

African asphalt mixes. The authors monitored the ageing of unmodified binders in the Rolling Thin Film Oven, using an empirical property (i.e. softening point), but found that the Superpave Performance Graded (PG) rutting parameter was more suitable for a modified binder. Lu and Isacsson (2002) measured the susceptibility of binders to ageing using an ageing index, defined as the ratio of a chemical or a rheological parameter before and after ageing. They found the ageing susceptibility of bitumens varies when different ageing indices were used, suggesting inconsistent chemical and rheological changes during ageing. This is possibly due to diffusion-limited oxidation in some binder types (related to test temperature and sample geometry) and/or different kinds of chemical reactions occurring within a single binder (oxidation, degradation, etc). These factors result in deviations from the Arrhenius behaviour which could cause misleading accelerated thermal ageing predictions.

This paper aims to demonstrate that the heterogeneous nature of modified binders results in different rheological changes during ageing. This investigation explores the use of a single frequency and temperature to follow the ageing of binders, taking into account that modified binders exhibit complex ageing. The two properties monitored were complex modulus (G*) and phase angle (δ). The temperature and frequency used for monitoring ageing was varied depending on the binder type.

2. EXPERIMENTAL

The binders analysed in this investigation were: a 40/50pen grade bitumen, a styrene-butadiene-styrene (SBS) modified binder and a crumb rubber modified (CRM) bitumen.

Ageing of the binders was done using:

- The standard Rolling Thin-Film Oven test according to ASTM D 2872: Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test).
- The Pressure Ageing Vessel test in accordance with AASHTO R28-02: Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel.

The effects of ageing, RTFOT and PAV, were monitored by change in physical properties of the binder before and after ageing, namely:

- Softening point data: softening point determination was done as stipulated in ASTM D36: Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus).
- Dynamic shear rheometer (DSR) data: the DSR model employed was an Anton Paar Physica Smartpave Plus using a Peltier system with a parallel plate measuring configuration. Oscillatory testing initially involved carrying out strain sweeps to obtain the linear viscoelastic range then running frequency sweeps while measuring complex moduli (G*) and phase angle (δ).

Ageing monitoring for the CRM binder involved testing the recovered soluble binder. The solvent-soluble fraction of the CRM binder was recovered using an internal CSIR test method, BE-TM-BINDER-1-2006:

- BE-TM-BINDER-1-2006 combines selected parts of ASTM D1856 (1995) “Test Method for Recovery of Asphalt from Solution by Abson Method” as supplied by ASTM International.
- BE-TM-BINDER-1-2006 uses AR benzene, instead of AR trichloroethylene (TCE) as the solvent for binder recovery.

Short-term aged binder was recovered from HMA samples manufactured in the laboratory. Asphalt samples were subjected to laboratory STA (four hours in an oven at compaction temperature prior to sample compaction) in order to simulate field ageing.

3. RESULTS

3.1 Ageing of 40/50pen grade bitumen

The two rheological properties, complex modulus (G*) and phase angle (δ), can characterise bitumen at various temperatures and frequencies, and this can be done for various conditions of ageing.

Figures 1 and 2 show G* and δ plotted against frequency (respectively) for an unmodified 40/50pen grade bitumen unaged, after RTFOT Treatment and after PAV ageing.

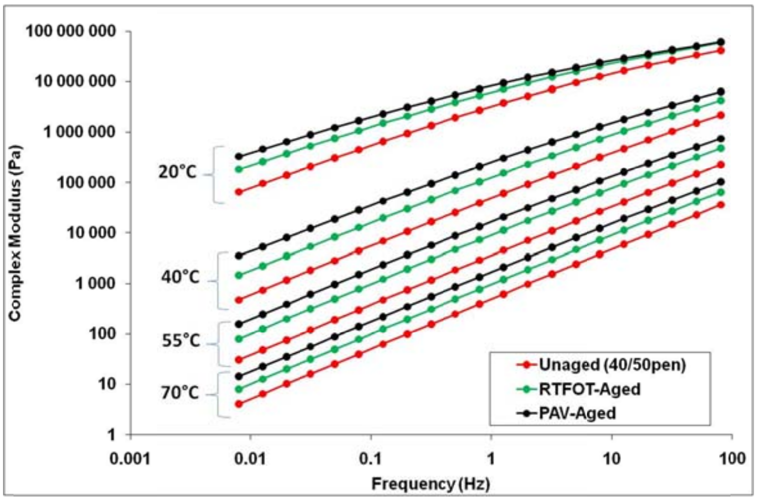


Figure 1: Complex Modulus vs. Frequency of the 40/50pen grade bitumen with ageing.

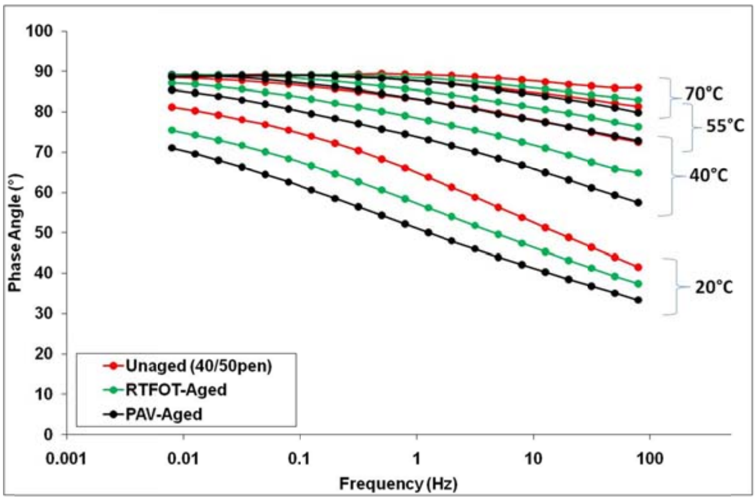


Figure 2: Phase Angle vs. Frequency of the 40/50pen grade bitumen with ageing.

The results show that the ageing of unmodified binders results in an increase in stiffness and a reduction in phase angle. The increase in stiffness is more notable at 40˚C and at the lower frequencies. Reduction in phase angle occurs due to oxidative hardening of the binder with ageing; and this was more notable at lower temperatures and mid to high frequencies.

3.1.1 *Single frequency-temperature monitoring*

Based on the increase in stiffness and decrease in phase angle illustrated in Figures 1 and 2, the authors perceived that the single frequency / temperature that would best serve to illustrate the greatest combined increase / decrease in stiffness / phase angle could be taken as 2 Hz / 20 ˚C. Although, graphically, a frequency of 0.1 Hz may have served even better, 2 Hz was chosen because of the improved repeatability / reproducibility obtained at this frequency value.

Figures 3 and 4 contains plots of the 40/50pen grade bitumen unaged, RTFOT-aged and PAV-aged in terms of G* and δ at a frequency/temperature of 2Hz/20°C, with the x-axis reversed for Figure 4.

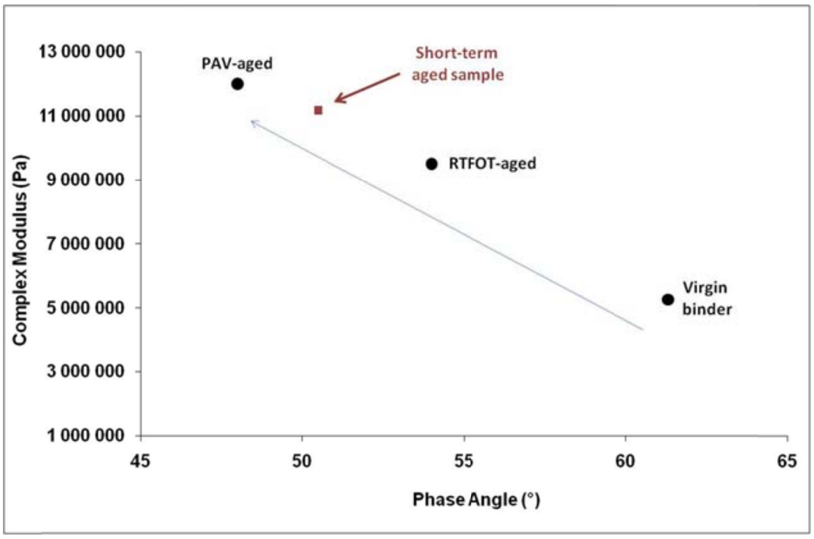


Figure 3: G* vs. δ at 2Hz / 20°C for a virgin, RTFO-aged and PAV-aged 40/50pen grade binder sample.

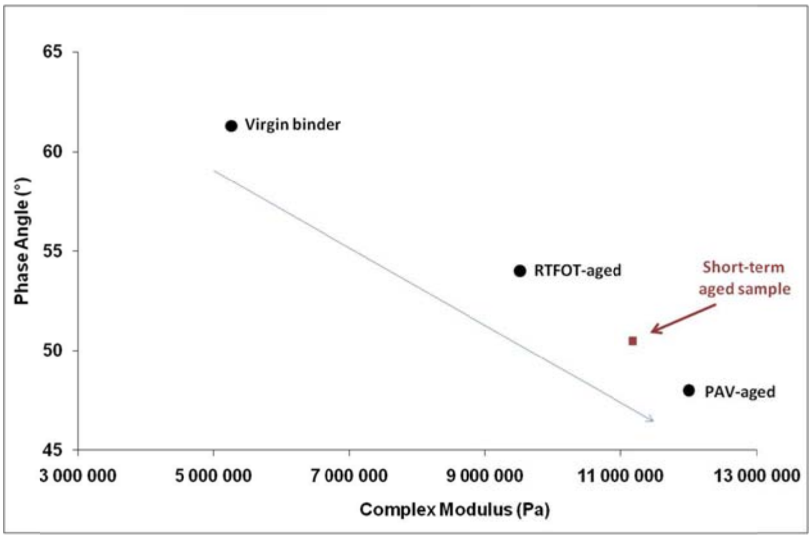


Figure 4: δ vs. G* at 2Hz / 20°C for a virgin, RTFO-aged and PAV-aged 40/50pen grade binder sample.

Figure 3 illustrates that where the phase angle is plotted on the x-axis; there is a natural progression from virgin- to RTFOT-aged to STA- to PAV-aged binder as the phase angle decreases from right to left on the x-axis. Similarly, Figure 4 illustrates that where the complex modulus is plotted on the x-axis, there is natural progression from virgin- to

RTFOT- to STA- to PAV- binder as the complex modulus increases from left to right on the x-axis. Figures 3 and 4 serve to demonstrate that at the single frequency / temperature point of 2 Hz / 20˚C it is possible to plot both complex modulus and phase angle against extended RTFOT time to determine the time required to simulate STA conditions.

3.1.2 *Softening point monitoring*

Figure 5 shows the oxidative stiffening of 40/50pen grade bitumen with extended RTFOT ageing. The ageing of the binder has been monitored by an empirical property, softening point. This can be correlated with the STA or field ageing of the *in situ* binder after placement of the asphalt surfacing.

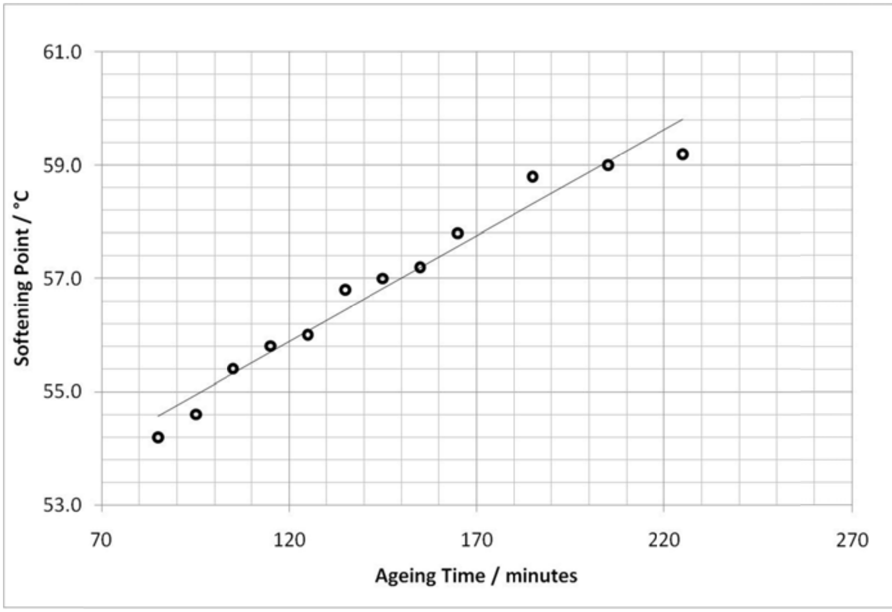


Figure 5: Softening point data for aged 40/50pen grade binder (O'Connell *et al.*, 2011).

3.1.3 *Rutting parameter failure temperature monitoring*

Figure 6 shows the oxidative stiffening of 40/50pen grade bitumen with extended RTFOT ageing. The ageing of the binder has been monitored by an advanced parameter, namely the failure temperature of the rutting resistance factor (G*/sin δ), i.e. the temperature where |G*|/sin δ = 2.20kPa. This can be correlated with the STA or field ageing of the *in situ* binder after placement of the asphalt surfacing.

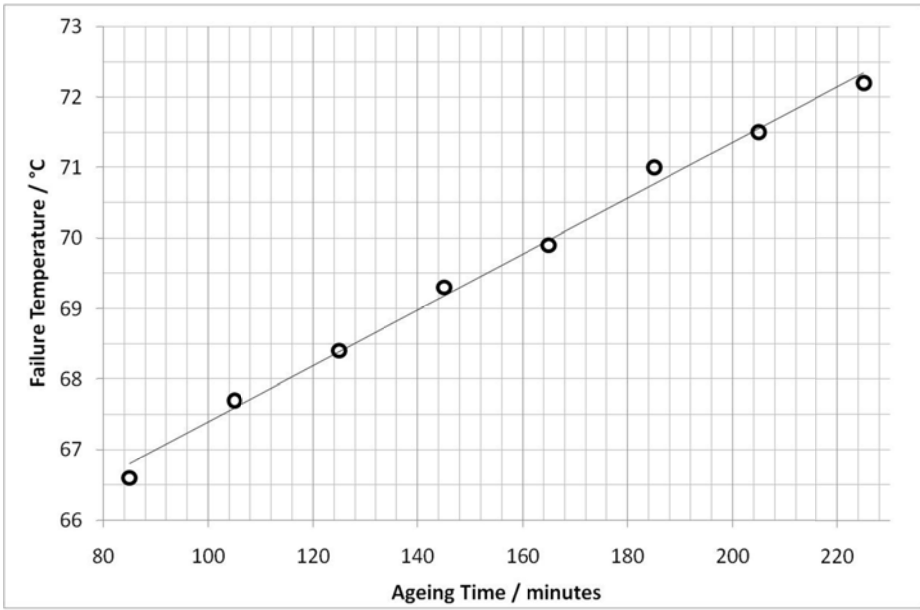


Figure 6: Failure temperature where |G*|/sin δ = 2.20kPa against ageing time for 40/50pen grade binder (O'Connell *et al.,* 2011).

3.2 <u>Ageing of SBS modified binder</u>

The effect of ageing on modified binders is not as simple rheologically and chemically as with unmodified bitumen. The ageing of modified binders can be monitored through master curves or with the use of the rutting parameter. The former can be laborious and the latter can result in a non-linear relationship during the ageing of modified binders.

Lu and Isacsson (1998) found that ageing indices can be misleading for SBS modified binders because they are highly influenced by the temperature and frequency of evaluation. The argument of using the rutting parameter to monitor ageing is whether it will always give a linear relationship, given that the two components (bitumen and SBS) of these binders have opposing ageing effects on binder rheology.

The rheological profile of modified binders is more clearly illustrated using a black diagram. Figure 7 shows the black diagram of an SBS modified binder when unaged and after RTFOT- and PAV-ageing. The binder behaves like a binary system. The SBS modifier imparts increased complex moduli with reduced phase angles at higher temperatures. At lower temperatures, the properties of the bitumen phase predominate. The effect of ageing is dependent on the temperature. At higher temperatures, ageing results in the partial loss of the proportional elastic contribution from the SBS modifier. At lower temperatures, ageing causes decreased phase angle and increased complex moduli as a result of oxidation of the dominant bitumen phase, as observed for unmodified binders.

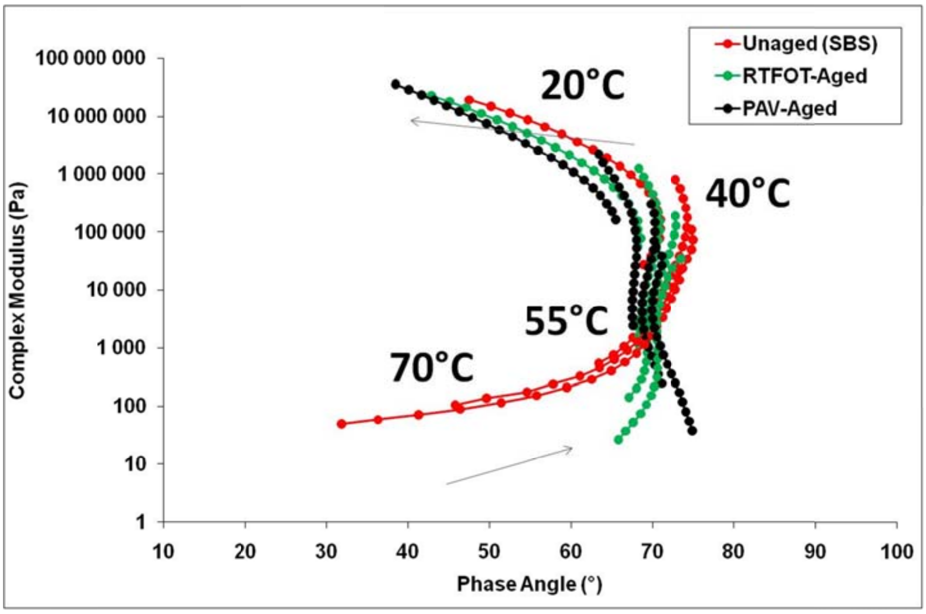


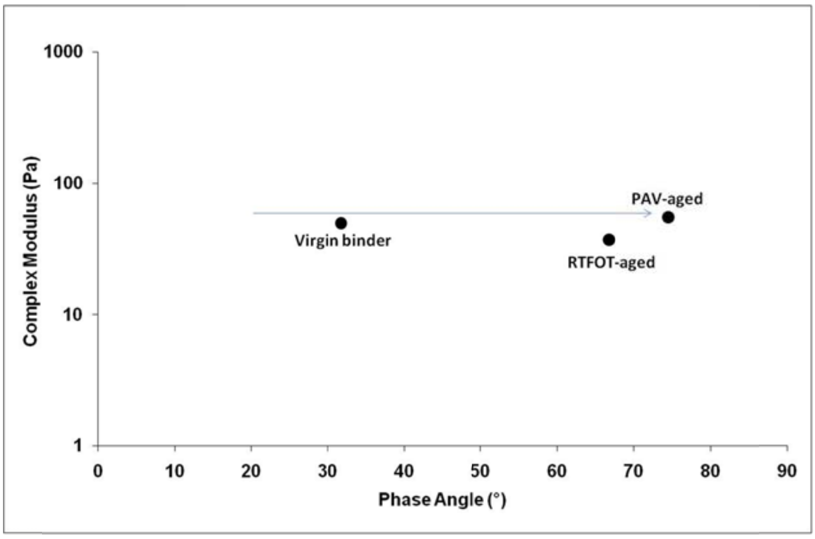
Figure 7: Black diagram of an SBS-modified binder with ageing (Mturi and O'Connell, 2011) [Arrows show the direction of ageing].

3.2.1. *Single frequency-temperature monitoring*

Due to the complexity in rheology profiles of SBS modified binders, the point of monitoring has to be chosen with care. Ageing should be monitored at a frequency / temperature where the rheology of the binder is predominantly controlled by that of a single component, to minimise the opposing effects of the two competing components. Standard unmodified binders that are often used as the base bitumen for SBS modified binders are Newtonian towards 70°C. This implies that the elastic component of SBS modified binders is solely that of the polymer at around 70°C.

Moreover, ageing should also be monitored at that frequency / temperature where the differences between the various states of ageing are clear and visible. As depicted in Figure 7, this would occur at 70˚C and at lowest frequency. The authors chose the ideal point of monitoring the ageing for these binders at a low frequency of 0.0126Hz and at a temperature of 70°C.

Figures 8 and 9 presents plots of the SBS modified binder in terms of G* and δ at a frequency/temperature of 0.0126Hz/70°C for the unaged, RTFOT-aged and PAV-aged SBS-modified binder, with the x-axis reversed for Figure 9.



(b)

Figure 8: Plot G* (log-scale) vs. δ at 0.0126Hz / 70°C for a virgin, RTFO-aged and PAV-aged SBS-modified binder sample.

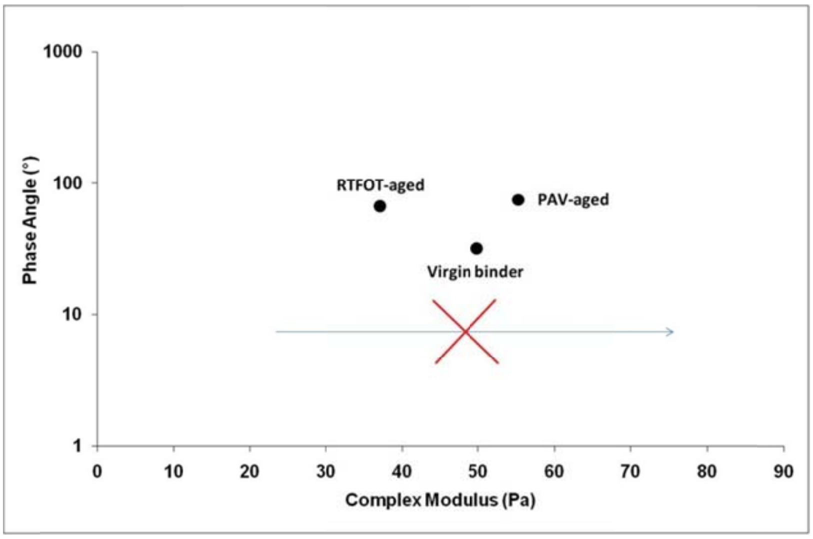


Figure 9: Plot of δ (log-scale) vs. G* at 0.0126Hz / 70°C for a virgin, RTFO-aged and PAV-aged SBS-modified binder sample.

Figure 8 illustrates that where the phase angle is plotted on the x-axis; there is a natural progression from virgin- to RTFOT-aged to STA- to PAV-aged binder as the phase angle decreases from right to left on the x-axis. However, Figure 9 illustrates that where the complex modulus is plotted on the x axis, there is no natural progression from virgin- to RTFOT-aged to STA- to PAV-aged binder as the complex modulus increases from left to right on the x-axis. Figures 8 and 9 serve to demonstrate that at the single frequency / temperature point of 0.0126 Hz / 70˚C it may be possible to plot phase angle against extended RTFOT time to determine the time required to simulate STA conditions, but there appears to be no relationship between G* and ageing time.

A plot of phase angle vs. ageing time in Figure 10 was developed to determine the extended RTFOT-ageing time required to simulate the average short-term ageing of the SBS-modified binder samples. This was found to be 205±20 minutes or about 2.5 times the current ageing time specified in ASTM D2872. This agrees well with the ageing time determined by O'Connell *et al.* (2011) when using the rutting parameter.

Figure 10: Phase angle, δ (at 0.0126Hz / 70°C) vs. ageing time for an SBS modified binder sample.

3.2.2. *Softening point monitoring*

Figure 11 depicts softening point data with RTFOT time and illustrates how the two components (bitumen and SBS) of these binders have opposing ageing effects on binder rheology

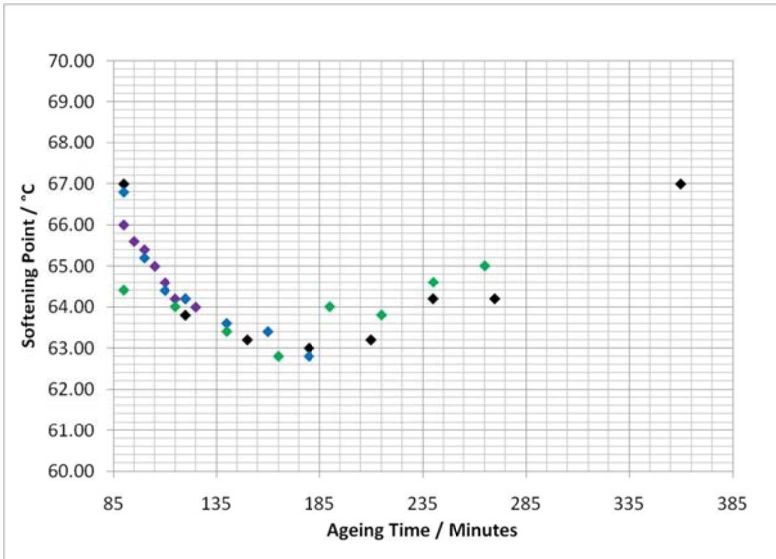


Figure 11: Softening point data for aged SBS-modified binder – separate colours represent four different data sets obtained on separate occasions (O'Connell *et al.*, 2011)

3.2.3 *Rutting parameter failure temperature monitoring*

O'Connell *et al.* (2011) showed that the ageing of an SBS modified binder can be monitored with the rutting parameter to predict short-term ageing behaviour (see Figure 12), as opposed to an empirical property such as the softening point. The authors determined that an SBS modified binder sample needed to be RTFOT-aged for 200 ± 5 minutes to simulate the average PG failure temperature of short-term aged samples.

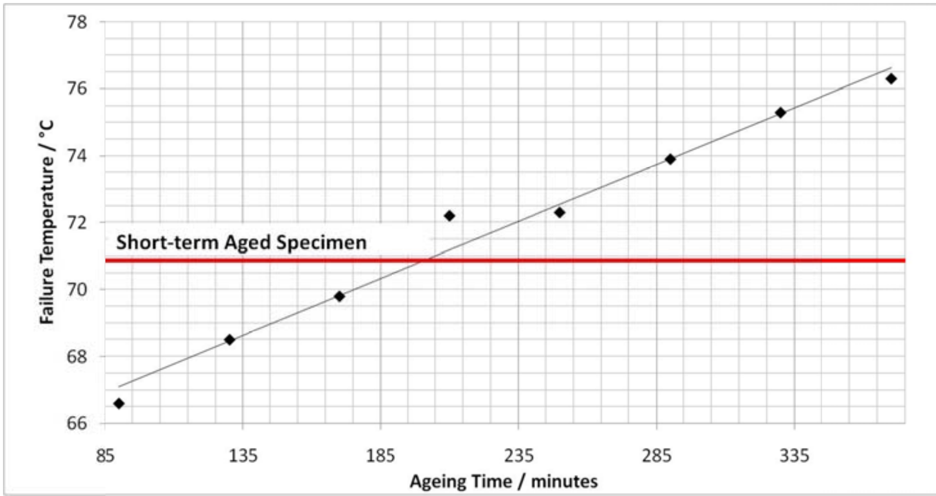


Figure 12: Failure temperature where |G*|/sin δ < 2.20kPa against ageing time for the SBS-modified binder (O'Connell *et al.*, 2011).

3.3 *Crumb Rubber Modified (CRM) Bitumen*

Figure 13 shows the black diagram of a CRM binder. Upon ageing, the binder loses its elastic response at higher temperatures and exhibits a decrease in phase angles at lower temperatures. The oxidative ageing increase in G* of the bitumen phase at lower temperatures is juxtaposed against S-S bond scission, leading to unpredictable changes in G*.

The rheological monitoring of binder ageing for CRM bitumen is complicated since the *in situ* binder within the asphalt cannot be recovered as a single fraction. The benzene insoluble rubber crumbs separate out of the binder during solvent recovery. Once the separated rubber crumbs and solvent-soluble portions are recombined, they do not reproduce the same binder as it occurs *in situ* inside the asphalt. The only practical way of monitoring ageing of CRM binders is through the recovered solvent-soluble binder: a mixture of base binder, extender oil and benzene soluble polymer fractions of the crumb rubber.

Figure 14 shows black diagrams of the solvent-soluble binder from the CRM bitumen blend. The ageing observed is due to oxidative hardening of the base bitumen and the increasing amalgamation of de-linked polymers with the solvent soluble binder (Mturi and O'Connell, 2011).

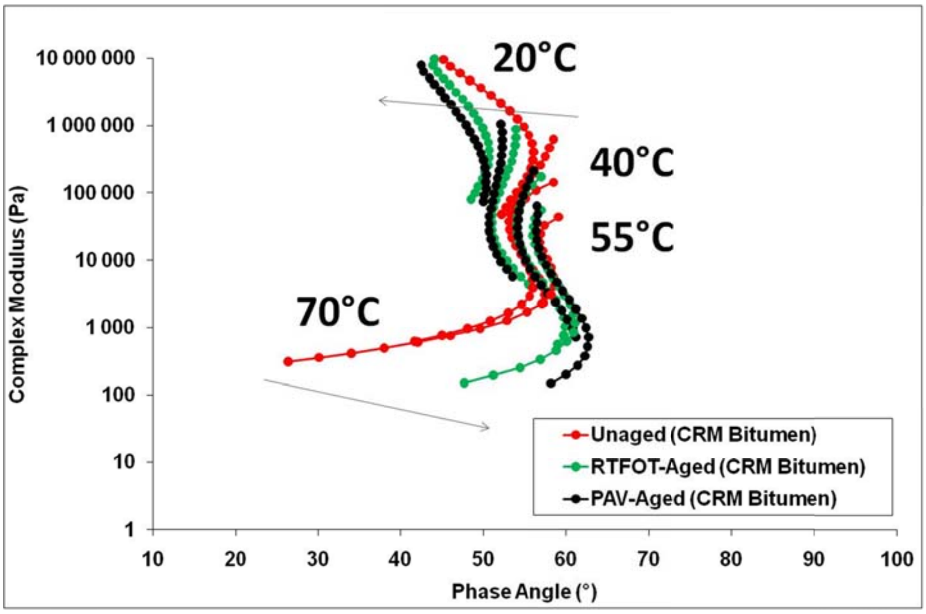


Figure 13: Black diagram of CRM bitumen binder with ageing (Mturi and O'Connell, 2011) [Arrows show the direction of ageing].

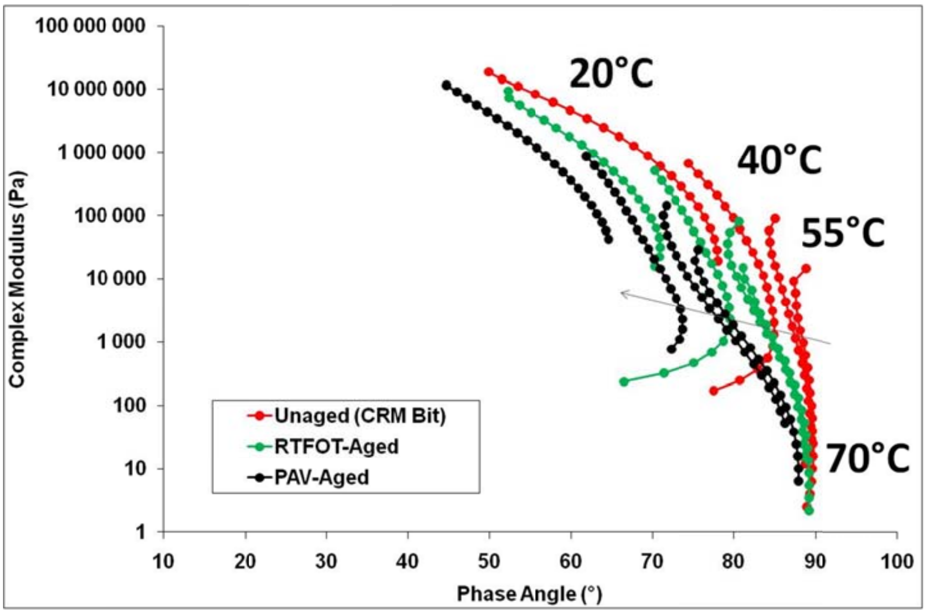


Figure 14: Black diagram of solvent-soluble recovered binder from CRM bitumen at various stages of ageing (Mturi and O'Connell, 2011) [Arrow shows the direction of ageing].

3.3.1 *Single frequency-temperature monitoring*

Figure 14 shows great rheological differences at mid-temperatures (40°C, 55°C) and mid-frequencies for the recovered binder of the virgin, RTFOT-aged and PAV-aged CRM bitumen. Consequently, G* and δ were monitored at a frequency/temperature point of 2Hz/40°C for these recovered binders as shown in Figure 15. The plot shows that the average short-term aged sample seems to have aged significantly more than the RTFOT-aged sample but slightly lesser than the PAV-aged sample. This means there is potential in using a single frequency and temperature to monitor and quantify the ageing of CRM binders at the in-service temperatures. The current national specifications do not ask for any sort of ageing for CRM bitumen.

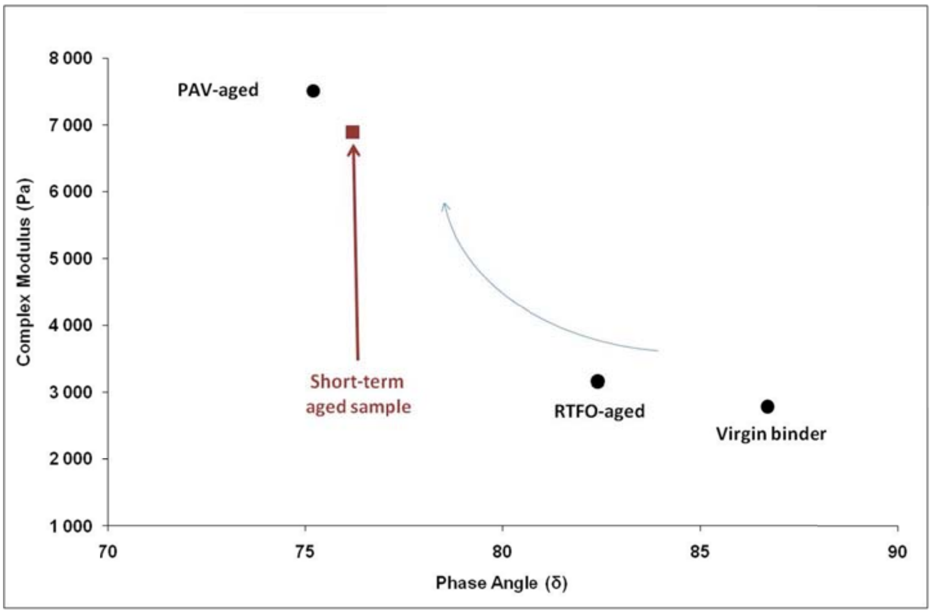


Figure 15: G* vs. δ at 2Hz / 55°C for a virgin, RTFO-aged, STA and PAV-aged solvent-soluble binder recovered from CRM bitumen blends.

4. CONCLUSION

The standard RTFOT method does not simulate short term ageing of South African binders during HMA manufacture, transport, laying and compaction. The actual short-term ageing of the *in situ* binder within asphalt will vary from contract to contract; the monitoring of binder ageing per contract scenario is therefore required. The data can eventually be gathered to enable the industry to develop a better method to predict binder ageing on a contract-to-contract basis. Ageing therefore needs to be properly monitored in order to avoid producing misleading data because not all measured properties change uniformly during the ageing of modified binders. This paper has demonstrated that a single temperature/frequency point can be used to monitor the ageing of both modified and unmodified binders. It is a more accurate means of monitoring ageing for modified binders with opposing or juxtaposed ageing effects.

REFERENCES

Andrei, D, Witczak, MW, and Mirza, MW, 1999. Development of a Revised Predictive Model for the Dynamic (Complex) Modulus of Asphalt Mixtures. "Interim Team Technical Report", Department of Civil Engineering, University of Maryland, College Park, MD.

Christensen, DW, Pellinen, T and Bonaquist, RF, 2003. Hirsch model for estimating the modulus of asphalt concrete. Asphalt Paving Technology, 72 p.97-121.

Lu, X, and Isacsson, U, 1998. Chemical and rheological evaluation of ageing properties of SBS polymer modified bitumens. Fuel. 77:9-10 p.961-972.

Lu, X, and Isacsson, U, 2002. Effect of ageing on bitumen chemistry and rheology, Construction and Building Materials 16 p.15-22.

Mastrofini, D, and Scarsella, M, 2000. The application of rheology to the evaluation of bitumen ageing. Fuel, 79 1005-1015.

Mturi, G, and O'Connell, J, 2011, Rheological analysis of crumb rubber modified binder. Proceedings of the 30th Southern African Transport Conference, Pretoria, South Africa.

O'Connell, JS, Mturi, G, and Maina, J, 2011, Adjusting the standard rolling thin film oven procedure to improve the prediction of short term ageing. Proceedings of the 10th Conference on Asphalt Pavements for Southern Africa, Drakensburg, South Africa.

Witczak, MW, and Fonseca, OA, 1996, Revised predictive model for dynamic (complex) modulus of asphalt mixtures. Transportation Research Record 1540, Transportation Research Board, Washington, D.C.

KEY WORDS
Rolling Thin Film Oven Test, Ageing, Rheology, Single Frequency and Temperature