AN OVERVIEW OF THE AGEING OF BITUMINOUS BINDERS

J O'CONNELL[1] and WJ VD M STEYN[2]

[1] CSIR Built Environment, P O Box 395, Pretoria, 0001 / Civil Engineering, University of Pretoria, Private Bag X20, Hatfield, 0028
2 Civil Engineering, University of Pretoria, Private Bag X20, Hatfield, 0028
1) Tel.: +27 12 841 2295 Email: JOConnell@csir.co.za
2) Tel.: +27 12 420 2171, Email: Wynand.Steyn@up.ac.za

ABSTRACT

The stiffness of an asphalt layer is an important characteristic affecting the performance of the layer. This stiffness is affected by temperature and time, as the bituminous component of the asphalt layer ages. As the stiffness increases, the distribution of traffic loads will be affected, as described in multi-layered linear elastic theory. In addition, the increasingly aged condition of the asphalt layer will allow cracking, as a mode of failure, to become increasingly likely.

The ageing processes can be characterized as occurring in two phases, namely, Short Term Ageing and Long Term Ageing. Short Term Ageing represents the ageing that an asphalt mix undergoes during manufacture, storage, transport and placement. Long Term Ageing represents the ageing an asphalt mix undergoes after placement, and over the lifetime of the pavement.

This paper reviews the different reaction mechanisms of ageing of bituminous binder as well as the effects of oxidation accelerators such as heat and ultraviolet light. There is also an overview of the physical and chemical properties of bituminous binders that can be used to monitor the rate of ageing.

1. INTRODUCTION

Flexible pavements are structures consisting of well-defined granular and asphalt layers, and designed to receive traffic loads and transfer them to the subgrade at acceptable levels (Domingos & Faxina, 2015). The stiffness of an asphalt layer (whether functioning as a surface or base layer) is a critical characteristic influencing the performance of the layer. This stiffness is affected by temperature and time, as the bituminous component of the asphalt layer ages. As the stiffness increases, the traffic loads on the surface will be distributed differently throughout the pavement in accordance to multi-layered linear elastic theory.

The increasingly aged condition of the asphalt layer will allow the following modes of failure to become increasingly likely:

- Thermal or Shrinkage cracking, which develops as a result of the stresses and strains emanating from the daily expansion and contraction associated with the diurnal temperature differentials. Shrinkage cracking, which results from this repetitive expansion and contraction is a top-down form of cracking;

- Fatigue cracking, which develops from the repeated loading associated with vehicular traffic, and

- Low temperature cracking, which occurs when the temperature of the pavement falls below the critical point where the binder is too stiff to overcome the tensile stress which builds up in the asphalt layer. Low temperature cracking is usually a single event occurrence, not expected to be of major importance in South Africa with its relatively mild winter pavement temperatures.

Even the skid resistance provided by a road is affected as the exposed binder that comes into contact with the tyre surface ages (Kane *et al*, 2010).

A better understanding of the ageing of asphalt mixes can aid the development of technologies, processes and/or specifications that can lead to a reduction of cracking, which has significant economic implications in a third world countries, where limited budgets have competing social requirements.

2. MECHANISMS OF AGEING

A bituminous binder may consist of bitumen only or bitumen modified with an additive, which may enhance the performance of the bitumen. During the ageing of a bituminous binder, ageing mechanisms may apply to the bitumen only or they may apply to the bitumen as well as to the additive/modifier. This overview on ageing focusses on the ageing of the bitumen component, but recognises that ageing of a modifier plays an important role as well.

The mechanism of ageing of bitumen is well discussed in the literature (Peterson, 2009). The following processes have been established to occur during ageing:

- Volatilization: As the bitumen ages, the components of lower molecular mass may dissipate through evaporation (volatilization). This process is especially significant at high temperatures and it relates to a decrease in binder mass. The significance of volatilization is subject to the method of manufacture of the bituminous binder. Traditionally, South African bituminous binders have been manufactured using high temperature processes, including blowing, thereby removing lower molecular mass components during the manufacturing process. Volatilization is, therefore, less applicable for current South African bitumen sources. However, the trend of increased bitumen imports in recent years has resulted in an increased awareness of this process.

- Oxidation involving the incorporation of oxygen into the molecular structure of the bituminous binder. This relates to an increase in binder mass. The incorporation of oxygen takes the form of a carbonyl functional group, which manifests itself as a ketone, carboxylic acid or aldehyde. These functional groups may be eliminated later during oxidative coupling.

- External oxidative coupling, i.e., the joining of two different molecules to form a larger heavier structure. The increase in oxidation number involves the elimination of two hydrogen atoms in the form of water – oxygen is not incorporated. Oxygen may be eliminated as well or may only be involved in the activated complex of the oxidation mechanism. This is the process by which bitumen is “blown” and converted to harder grades in refineries. This relates to a decrease in binder mass.

- Internal oxidative coupling through intramolecular bonding, increasing the rigidity of the molecules. As in external oxidative coupling, this involves the elimination of other atoms, usually hydrogen, but may involve oxygen as well. This also relates to a decrease in mass.

- Exudation: Over time, certain component oils in the maltene phase in the bitumen of the bituminous binder may become absorbed by the voids/pores in the aggregate, which results in a stiffer binder.

- Steric hardening – This is a process by which the molecules rearrange themselves into a more closely packed state of least energy associated with greater thermodynamic stability. This is illustrated by doing a delayed penetration (i.e. after 24 hours).

Ultraviolet (UV) radiation from the sun plays an important role during the oxidation process as the UV energy assists in bond scission leading to the formation of free radicals. Such free radicals are highly reactive and facilitate all forms of oxidation.

3. RATE OF AGEING

There are many factors which influence the rate of ageing via the mechanisms discussed in Section 2. They include:

- The chemical composition of the bitumen of the bituminous binder, which is, in turn, determined by the crude sources and method of bitumen manufacture;

- The chemical composition of any additives or modifiers present within the bituminous binder, as well as the mechanism of interaction between such modifiers and the bitumen;

- The voids present within the asphalt layer, which regulates accessibility to oxygen;

- The film thickness of the bituminous binder which regulates the diffusion rate of oxygen through the binder;

- The thickness of the asphalt layer which regulates the diffusion rate of oxidized material throughout the layer;

- The construction method of the asphalt layer, i.e. whether it was constructed using one lift or two lifts (Bernier *et al*, 2014);

- The viscosity of the bituminous binder which regulates the diffusion rate of oxygen through the binder;

- The presence of antioxidants such as lime within the mix (Edler *et al*, 1985). The use of polymers, phosphorus-based compounds and zinc-based compounds have all been reported to reduce ageing or counteract the effects of ageing (Domingos *et al*, 2015; Sá Araujo *et al*, 2013);

- The latitude, which affects the intensity of the UV radiation;

- The climate, which determines the effects of moisture, temperature and cloud cover;

- The aggregate which may promote exudation or not, and which may or may not contain oxidation catalysts, and

- The partial pressure of oxygen, which is affected by the altitude. Sá Araujo *et al* (2013) claim that the action of the tyres on the asphalt layer affect the partial pressure of the oxygen, and hence the rate of oxidation.

4. MONITORING THE RATE AND EXTENT OF AGEING

The ageing of bituminous binders may be monitored using the physical or chemical properties of the bituminous binders.

4.1. Physical Properties

The physical properties of bituminous binders are described by tests such as:

- Penetration. The determination of the consistency of a sample of bituminous binder by determining the distance in tenths of a millimetre that a standard needle vertically penetrates the bitumen specimen under known conditions of loading, time and temperature. (EN 1426, 2007);

- Softening Point. Two horizontal disks of bituminous binder, cast in shouldered brass rings, are heated at a controlled rate in a liquid bath while each supports a steel ball. The softening point is reported as the mean of the temperatures at which the two disks soften enough to allow each ball, enveloped in sample, to fall a distance of 25 mm. (ASTM D36, 2014);

- Absolute viscosity. The basic absolute viscosity test measures the time it takes for a fixed volume of sample to be drawn up through a capillary tube by means of vacuum, under closely controlled conditions of vacuum and temperature (ASTM D2171, 2010);

- Kinematic Viscosity. The kinematic viscosity of a liquid is the absolute (or dynamic) viscosity divided by the density of the liquid at the temperature of measurement. The basic kinematic viscosity test measures the time it takes for a fixed volume of sample to flow through a capillary viscometer under closely controlled conditions of head and temperature (ASTM D2170, 2010);

- Apparent Viscosity by rotational viscometer. The apparent viscosity of bituminous binder is evaluated by a rotational viscometer which measures the torque generated by a calibrated spindle rotating at a selected speed into a sample heated at a precise temperature (ASTM D4402, 2015);

- Fraass Breaking Point. The Fraass breaking point is the temperature at which bituminous binder first becomes brittle (as indicated by the appearance of cracks) when a thin film of sample on a metal plaque is cooled and flexed under specific conditions. (EN 12593, 2007);

- Ductility. The ductility test gives a measure of adhesive property of bituminous binder and its ability to stretch. It is measured by the distance in centimetres to which it will elongate before breaking when two ends of standard briquette specimen of material are pulled apart at a specified speed and specified temperature. (ASTM D113, 2007; DIN 52013, 2007), and

- Complex Modulus (G*) and Phase Angle (δ). The physical characterization of bitumen, in terms of rheology, is characterized by means of the Dynamic Shear Rheometer (DSR) (Figure 1). Current concepts derived from G* and δ include:
    - G*/Sin δ, also referred to as the “rutting parameter” (ASTM D7175, 2015);
    - G*.Sin δ; the so-called “fatigue parameter” (ASTM D7175, 2015);
    - Multiple Stress Creep Recovery, Jnr, (ASTM D7405, 2015);
    - Master curves of G* and phase angle, δ, (ASTM D7175, 2015); and

❖ Black Diagrams (G* vs δ), which can be used to determine the most appropriate temperatures at which ageing studies can be carried out (Mturi and O'Connell, 2012)

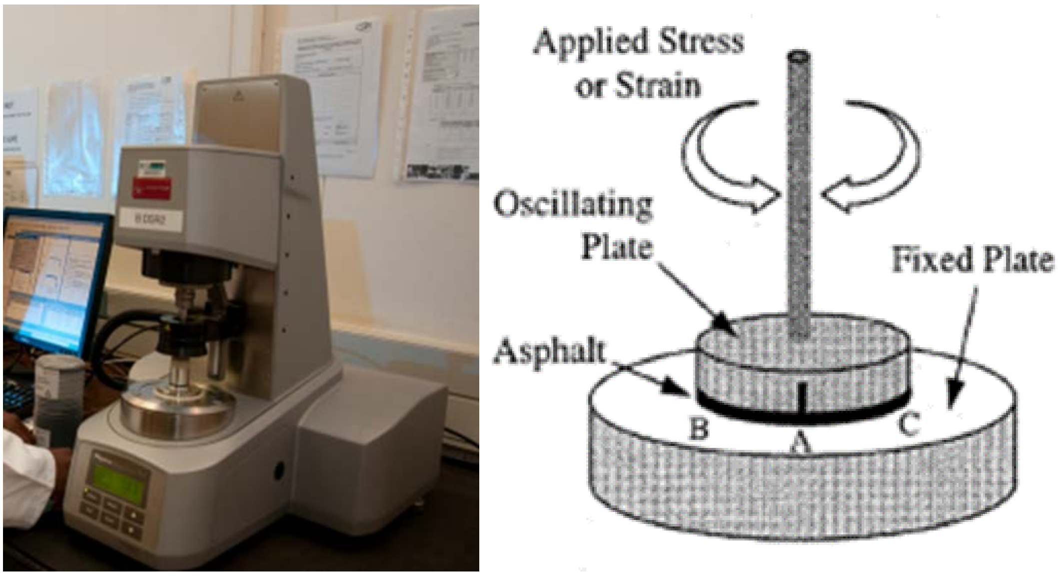

Figure 1: The Dynamic Shear Rheometer at the CSIR.

Sometimes the binder is not tested, but the asphalt is tested directly during ageing studies. Asphalt tests may include such physical tests such as Indirect Tensile Strength (ITS), Dynamic Modulus or even Cantabro (Miro *et al*, 2001).

Ageing trends determined by empirical tests can provide different results than that found using rheological parameters generated by the DSR. (Domingos & Faxina, 2015). This is most relevant for polymer-modified binders. This indicates that empirical properties such as penetration, softening point and ductility are limited in scope with regards to their determination of the intrinsic rheological properties of bituminous binders. During the execution of these empirical tests, strain rates and stress are variable and unmeasurable, making the interpretation of the results problematic.

4.2. Chemical Properties

Secondary to the international research and development into new physical test methods to determine the fundamental engineering properties, has been a limited drive regarding the chemical composition of bitumen, and to relate the chemical composition to performance characteristics such as durability, rheology and co/adhesion (i.e. correlation between chemical composition and fundamental engineering properties).

Such a correlation would enable bitumen consumers to identify poorly or well performing bitumens in advance, as well as help identify those crude resources that would contribute to a potentially good- or poor performing binder. A consequence of this work has been the adoption of existing chemical techniques to follow the oxidation and ageing of bitumen as a component of bituminous binder.

The rate and extent of ageing can be monitored using the following physicochemical and chemically based methods:

- Infra-Red analysis (IR) (Bernier *et al*, 2014). Fourier transform infrared (FT-IR) spectroscopy has confirmed that an increase in viscosity of aged binders is related to an increase in their carbonyl content as indicated by the IR absorbance spectrum. It has also been demonstrated that an increase in recycled asphalt pavement (RAP) content correlates with the increase in carbonyl content in the RAP-modified mixes. Diffused Reflection Infrared Fourier Transform Spectroscopy (DRIFTS) is the most successful sampling method for analysis of powdered asphalt samples recovered from the surface of asphalt layers.

- Atomic Force Microscopy (AFM). AFM or Scanning Force Microscopy (SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution on the order of fractions of a nanometre (Wikipedia, 2015). The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. Another major application of AFM (besides imaging) is force spectroscopy, the direct measurement of tip-sample interaction forces as a function of the gap between the tip and sample (the result of this measurement is called a force-distance curve). These measurements have been used to measure nanoscale contacts, atomic bonding, Van der Waals forces and Casimir forces. Steyn (2008) has demonstrated the qualitative evaluation of the ageing of bitumen using AFM (Figure 2).

- Elemental analysis. Elemental analysis is a process where a sample of bitumen is analysed for its elemental composition or CHNX analysis - the determination of the mass fractions of carbon, hydrogen, nitrogen, and heteroatoms (X) (halogens, sulphur). Elemental analysis can be qualitative, and it can be quantitative. The quantitative analysis for bitumen is not highly reproducible. Oxygen is usually determined by difference of total mass. The total mass of oxygen can give an indication of the rate of ageing.

- Gel Permeation Chromatography (GPC) or Size-Exclusion Chromatography (SEC) is a chromatography tool whereby a sample is separated according to molecular size. Ruan *et al* (2003) have shown through SEC studies that the oxidative ageing of SBS-modified binders results in the degradation of the SBS polymer to smaller sized molecules.

- Thermal Analysis. Thermal analysis can be used for studying physicochemical properties using methods such as Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Thermogravimetry (TG), Derivative Thermogravimetry (DTG), Dilatometry (DT) and Penetrometry (TMA).

- SARA (Saturates, Aromatics, Resins and Asphaltenes) separation of bitumen into four fractions using open column chromatography, thin layer chromatography (TLC,

Figure 3) or high performance chromatography (HPLC). Petersen *et al* (1993) established a direct relationship between the increase in asphaltene content during ageing and the rate of increase in bitumen stiffness (Leiva-Villacorta *et al*, 2014) reported a decrease in asphaltene content with increased ageing, which is in contradiction to most research findings).

During ageing, the saturates remain largely unchanged, but there is a general conversion from aromatics to resins and from resins to asphaltenes. By monitoring these changes, the rate and extent of ageing can be monitored. Petersen *et al* (1993) established a direct relationship between the increase in asphaltene content during ageing and the rate of increase in bitumen stiffness. (Leiva-Villacorta *et al* (2014) reported a decrease in asphaltene content with increased ageing).

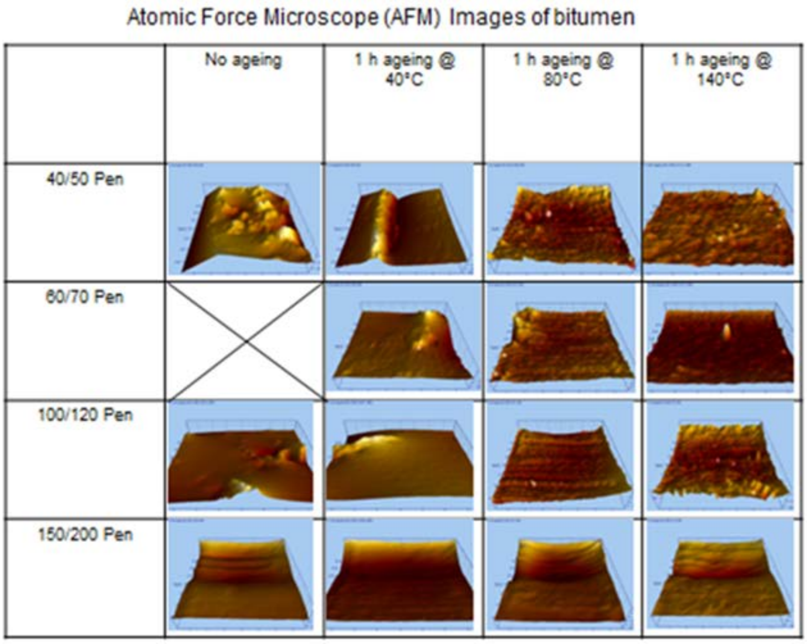

Figure 2: Ageing study of bitumen using AFM (Steyn, 2008).

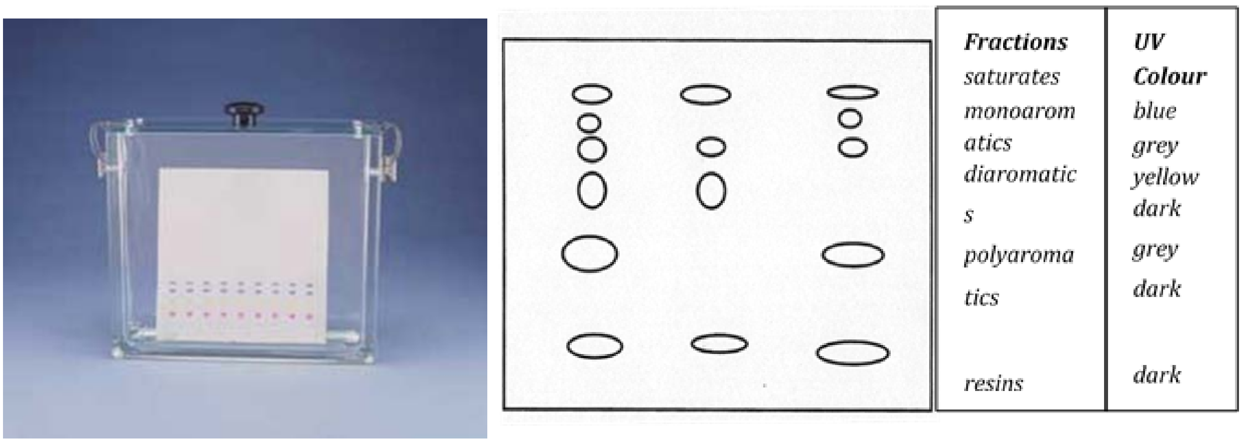

Figure 3: The Developing Tank and interpretation of TLC spots.

5. STAGES OF AGEING

During the lifetime of an asphalt layer, the ageing of the binder in an asphalt layer can be divided into two distinct phases, namely short term ageing (STA) and long term ageing (LTA).

5.1. STA

STA represents the ageing that the binder in an asphalt mix undergoes during the manufacture, storage, transport and placement of the asphalt mix. STA is a high temperature process which would favour high energy oxidation mechanisms and volatilization. The high rate of ageing that occurs during high temperatures requires that upper limits be placed on the mixing temperatures and the time that asphalt mixes spend at these temperatures (O'Connell *et al*, 2011)

For binder specification purposes, a test is required to simulate the ageing a binder undergoes during STA. In South Africa, the Rolling Thin Film Oven Test (RTFOT) (ASTM D 2872, 2012) is prescribed, and it is the most prevalent test prescribed internationally. During the RTFOT, bitumen rotates in a moving thin film in a glass bottle in a forced draft oven at 163°C for 85 minutes. Developed by the State of California Department of Public Works in 1963, it gave a relatively good indication of ageing for a 50/70 penetration type binder used in dense continuously graded mixes for that place and time.

Other well established STA methods include the Thin Film Oven method (ASTM D1754, 2014) and the Rotating Cylinder Ageing Test – RCAT (EN 15323, 2007). A major disadvantage all of these tests, including RTFOT, have in common is that they are not pressurized. The rate of oxidation is dependent on the partial pressure of oxygen, and is therefore altitude dependent, resulting in variations in results from laboratory to laboratory. A pressurized test would eliminate such variation.

The question remains as to how valid the RTFOT simulation is today for South African conditions, considering the wide range of mixes ranging from warm mix to SBS-modified binders and the large variations in mixing temperatures and hauling distances. Poor rutting results have been reported for warm asphalt mixes due to lower stiffness of the binder as a result of insufficient ageing occurring during the STA phase (Bernier *et al*, 2014). Kim *et al* (2014) goes so far as advocating an increase in warm mix temperatures to improve mix properties. Needless to say this militates against the purpose of the warm mix technology. Some researchers have reported improved rutting results for warm mix asphalts (Yang *et al*, 2014), especially where the warm mix asphalt additive has a dual function as a rut resistant additive as well. However, the results are highly dependent on the levels of the warm mix additive and the warm mix temperatures.

STA can also be carried out on an asphalt mix in the laboratory. One protocol is the SUPERPAVE short term aging procedure. The method, as described by Von Quintus *et al* (1991), consists of placing the prepared mix back into the oven and leaving it there for four hours at 135°C before compaction. A slight adjustment to this method has been made as part of the CSIR test protocol development, whereby the mix is aged at the compaction temperature for that mix (Anochie-Boateng *et al*, 2010).

5.2. LTA

LTA represents the ageing that the binder of an asphalt mix undergoes after placement, and over the lifetime of the pavement. However, for the purposes of defining LTA with regards to correlation with laboratory ageing, and especially for specification purposes in mind, LTA can be defined as the ageing a pavement layer undergoes during a period of 5 to 10 years after placement. LTA is a medium temperature process ranging between - 5°C and 70°C in South Africa. It would favour lower energy oxidation mechanisms and volatilization would not be a major factor, unless the bituminous binder has been cut back with solvents or oils.

For bituminous binder specification purposes, a test is required to simulate the ageing a binder undergoes during this LTA process, representing a period of five to ten years, depending on the climate where the mix is placed, the latitude and the mix properties. The most popular test is the Pressure Ageing Vessel (PAV) test (ASTM D 6521). During the PAV test, a thin film (3.2 mm) of bitumen taken from the RTFOT is placed in a pressurized oven (2.1 kPa, 90-110°C) for 20 hours (Figure 4).

Figure 4: The PAV Ageing Oven at the CSIR.

There is much debate as to what the results of the PAV ageing represents and little work has been done for South African mixes to date. The PAV test ageing conditions are considered by some to be more severe than field ageing after 5 to 10 years of binder in relatively thick asphalt layers (Von Holt *et al*, 2008), whereas others have an opposing point of view (Glover *et al*, 2005; Wu *et al*, 2008). Li *et al* (2006) recovered three different binders from three different asphalt layers after 5 years. One of the binders had approximate the same stiffness as the PAV aged original binder, while two of the three binders had not yet reached the PAV-aged stiffness. Farrar *et al* (2006) recovered four binders after four years and the average binder ageing for the entire asphalt thickness had not attained PAV ageing condition yet. An important point to note is that the laydown viscosity exceeded RTFOT viscosity in all case by a substantial margin. It gives field ageing an unfair disadvantage in that it started at an “advanced stage” of ageing. It may well be that PAV ageing could simulate 5 to 10 years of field ageing if the starting point, i.e., RTFOT ageing and lay-down ageing were at approximately the same state of ageing.

It is interesting to note that when the comparisons were made using the Bending Beam Rheometer (BBR) stiffness as opposed to viscosity or G*/sin δ used in the previous paragraph none of the binders are close to approaching the PAV stiffness (Li *et al*, 2006). This confirms that the oxidative ageing mechanism in the PAV chamber differs with that taking place in nature.

There are other long term ageing methods but none are well established. All accelerated ageing methods should be based on simulations which strive to yield residues which would have properties similar to binders after defined periods of *in situ* field ageing (Von Holt *et al*, 2008). Verhasselt *et al* (1993) have proposed that laboratory tests to simulate in-service ageing should be conducted at temperatures below 100°C (70 to 95°C is advised) since, at higher temperatures, the reaction mechanism differs from that occurring in the field.

Work done on the RCAT to simulate the PAV has been done (Shen et al, 2006). The weatherometer (Airy GD, 2003; Sá Araujo, 2013), which involves cyclical exposure to UV light, moisture and heating conditions, is also increasingly been researched as a method to simulate long term ageing.

Protocols have been developed for the LTA of asphalt mix in the laboratory. To simulate the ageing of the mix over a period of five to ten years, the LTA procedure recommended by Bell *et al* (1994) is commonly used. After compaction, specimens made from the STA mix are put back into the oven and aged for five days at a temperature of 85°C. Asphalt briquettes can also be stored in a forced draught oven for 6 days at a temperature of 80 °C (Superpave LTA procedure), which supposedly simulates 5 to 8 years in service ageing.

5.3. Schematic presentation of ageing

STA and LTA are schematically represented in Figure 5.

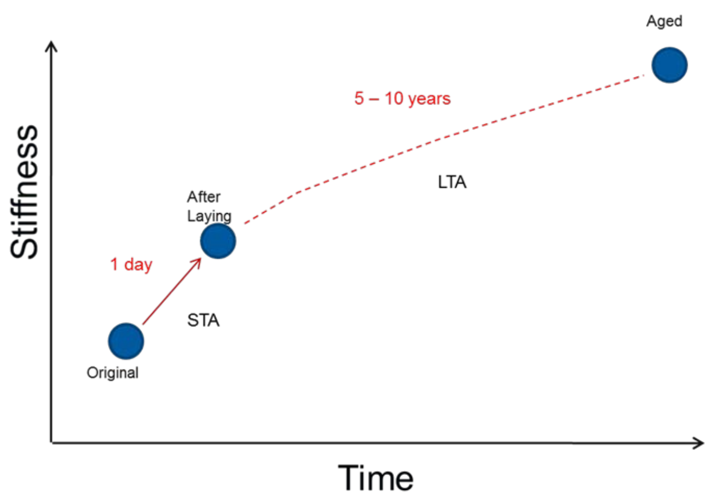

Figure 5: Graphical Representation of STA and LTA.

6. INTERPRETATION OF RESULTS

Historically, many ageing studies have been carried out with limited expert chemical analysis. This has frequently resulted in the misinterpretation of data and ageing trends. A few examples include:

- Shen *et al* (2006) followed the extent of Rolling Thin Film Oven (RTFO) ageing with increasing temperature using Infra-Red analysis. They used the transmittance (wave height) at wave number 1680 cm^{-1}, representing the carbonyl (C=O) oxidation product, to follow the difference in rate of ageing when changing the oven temperature from 163°C to 185°C. They found a slight decrease in the peak height at the higher temperature and wrongly concluded that there was no increase in oxidation rate at the higher temperature. The significantly higher temperature activated additional oxidation mechanisms which allowed for not only the formation of carbonyl products, but also increased elimination of carbonyl products during secondary oxidative coupling processes occurring at the higher temperature. This would be evidenced by higher molecular weights (shown with GPC) or an increase in asphaltene content.

- Ruan *et al* (2003) have interpreted SEC studies to show that the oxidative ageing of SBS-modified binders results in the degradation of the SBS polymer to smaller sized molecules. However, it may be that the oxidation of the SBS polymer resulted in poorer association and packing of the SBS molecules, leading to a disassociation in the SEC column, resulting in a misinterpretation regarding molecular mass distribution.

- Conclusions could be misleading when the repeatability or standard deviation for the test is not taken into account. In other words, significant conclusions are drawn from what appears to be insignificant differences in results, the variability of which falls within the repeatability of the test.

- Radziszewski *et al* (2003) did ageing studies on bitumen-rubber (as have many other researchers) using viscosity as an ageing indicator, but without taking into account the stage of digestion of the product with relation to the viscosity digestion curve (Mturi *et al*, 2011). Bitumen rubber has a digestion curve with regards to viscosity against time as the bitumen rubber at first absorbs the rubber and then the rubber particles are “digested” (scissions of the sulphur-sulphur linkage bonds). This results in erroneous conclusions. Bitumen rubber ageing studies can only be done in the terminally digested phase or alternatively, be done at low temperatures, where the digestion remains unaffected.

7. DISCUSSION AND CONCLUSION

The fatigue properties of bituminous binders play an important role in the rate of ageing that an asphalt layer will undergo, resulting in pavement deterioration (cracking, pothole formation). It is therefore important to improve our understanding of the mechanisms and rates of ageing and the influence they have on the economic sustainability of our pavement network.

It has long been the goal of researchers to find rapid methods to simulate the ageing of asphalt pavements, but at the same time, maintain the identical ageing mechanisms experienced in the field. In this way all the properties of the binder can be simulated over the entire temperature range experienced by the binder in the asphalt layer. This is an unattainable goal, as the very act of simulation implies a shorter time, which necessitates or drives a change in ageing mechanisms.

At best we can aim for ageing methods which roughly simulate ageing to give comparable properties for the simulated binder and field binder at high and low temperatures, which can be used for specification purposes. It is important to understand the limitations of ageing methods, and how they affect the correlation between laboratory and field binders. In this way we can appreciate the importance of having realistic fatigue specifications for binders, while realising at the same time, that it is but one of many factors controlling the ageing rate of an asphalt layer.

REFERENCES

Airey, GD. 2003. State of the Art Report on Ageing Test Methods for Bituminous Pavement Materials, International Journal of Pavement Engineering. 4:3. 165-176. http://dx.doi.org/10.1080/1029843042000198568.

Anochie-Boateng, J., Denneman, E., O'Connell, J., Mturi, G. & Ventura, D. 2010. Hot-mix asphalt testing for the South African pavement design method. Conference proceedings of the 29th Southern African Transport Conference, South Africa, 16-19 August 2010.

ASTM D36/D36M-14e1. 2014. Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus). American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

ASTM D113-07. 2007. Standard Test Method for Ductility of Bituminous Materials. American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

ASTM D1754/D1754M-09(2014). 2014. Standard Test Method for Ductility of Bituminous Materials. American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

ASTM D2170/D2170M-10. 2010. Standard Test Method for Effects of Heat and Air on Asphaltic Materials (Thin-Film Oven Test). American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

ASTM D2171/D2171M-15. 2015. . Standard Test Method for Viscosity of Asphalts by Vacuum Capillary Viscometer. American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

ASTM D2872-12e1. 2012. . Standard Test Method for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin-Film Oven Test). American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

ASTM D4402/D4402M-10. 2010. . Standard Test Method for Viscosity Determination of Asphalt at Elevated Temperatures Using a Rotational Viscometer. American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

ASTM D7175-15. 2015. . Standard Test Method for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer. American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

ASTM D7405-15. 2015. . Standard Test Method for Multiple Stress Creep and Recovery (MSCR) of Asphalt Binder Using a Dynamic Shear Rheometer. American Society for Testing and Materials International. Vol. 04.03. West Conshohocken, PA.

Bell, CA., Ab Wahab, Y., Cristi, ME. & Sosnovske, D., 1994. Selection of Laboratory Aging procedures for Asphalt-Aggregate Mixtures. SHRP-A-383, Prepared for Strategic Highway Research Program, Oregon State University, Corvallis.

Bernier, A., Yut, I., Parker, F. & Dargie D. 2014. Long-Term Performance Of A Warm-Mix Asphalt Overlay On An Airport Major Taxiway: Case Study. 93rd Annual Meeting of the Transportation Research Board. TRB Paper No. 14-0967. Washington D.C.

DIN 52013:2007-06. 2007. Bitumen and bituminous binders - Determination of ductility. Deutsches Institut für Normung. Berlin.

Domingos, MDI. & Faxina, AL. 2015. Accelerated short-term ageing effects on the rheological properties of modified bitumens with similar high PG grades. Road Materials and Pavement Design. Taylor and Francis. http://dx.doi.org/10.1080/14680629.2014.995209.

Edler, AC., Hattingh, MM., Servas, VP. & Marais, CP. 1985. Use of aging tests to determine the efficacy of hydrated lime additions to asphalt in retarding its oxidative hardening. Report no RR 444. Built Environment, CSIR. Pretoria.

EN 1426. 2007. Bitumen and bituminous binders - Determination of needle penetration. European Committee For Standardization (CEN). Technical Committee CEN/TC 336 “Bituminous binders” . Brussels.

EN 12593. 2007. Bitumen and bituminous binders - Determination of the Fraass breaking point. European Committee For Standardization (CEN). Technical Committee CEN/TC 336 “Bituminous binders” . Brussels.

EN 15323. 2007. Bitumen and bituminous binders - Accelerated long-term ageing/conditioning by the rotating cylinder method (RCAT). European Committee For Standardization (CEN). Technical Committee CEN/TC 336 “Bituminous binders” . Brussels.

Farrar, MJ., Harnsberger, PM., Thomas, PK. & Wiser, W. 2006. Evaluation of Oxidation in Asphalt Pavement Test Sections after four years of Service. International Conference on Perpetual Pavements. Columbus. Ohio.

Glover, CJ., Davison, RR., Domke, CH., Ruan, Y., Juristyarini P., Knorr, DB. & Jung, SH. 2005. Development Of A New Method For Assessing Asphalt Binder Durability With Field Validation. Report No. FHWA/TX-05/1872-2. Texas Transportation Institute. Texas Department of Transportation and the U.S. Department of Transportation, Federal Highway Administration. Texas.

Kane, M., Zhao, D., Do, M., Chailleux E. & De-Lalarrard, F. 2010. Exploring the Ageing Effect of Binder on Skid Resistance Evolution of Asphalt Pavement, Road Materials and Pavement Design, 11:sup1, 543-557, http://dx.doi.org/10.1080/14680629.2010.9690346.

Kim, SU., Lee, S-J., Youn, Y. & Kim, K-W. 2014. Evaluation of Optimum Short-term Aging Temperature for SBS-modified Warm-Mix Asphalt Mixtures. 93rd Annual Meeting of the Transportation Research Board. TRB. Washington D.C.

Leiva-Villacorta, F., Villegas-Villegas, FE., Aguiar-Moya, JP. Salazar-Delgado, J. & Loría-Salazar, LG. 2013. Effect Of Aging On Rheological, Chemical And Thermodynamic Properties Of Asphalt Components. 93rd Annual Meeting of the Transportation Research Board. Washington.

Li, X., Zofka, A., Marasteanu, M. & Clyne, TR. 2006. Evaluation of field aging effects on asphalt binder properties, Road Materials and Pavement Design, 7:sup1, 57-73, http://dx.doi.org/10.1080/14680629.2006.9690058.

Mturi, GAJ. & O’Connell, J. 2011. Rheological analysis of crumb rubber modified binder, Conference proceedings of the 30th Southern African Transport Conference, South Africa, 11-14 July 2011.

Mturi, GAJ. & O'Connell, J. 2012. Monitoring ageing of bituminous binders, Conference proceedings of the 31st Southern African Transport Conference, South Africa, 9-12 July 2012.

Miró, R. & Pérez-Jiménez F. 2001. Procedure for the Evaluation of Asphalt Binders Ageing in contact with Aggregates and Application of this Procedure to Analyze the Influence of the Aggregate Type on Binder Ageing. Road Materials and Pavement Design. 2:1. 97-110. http://dx.doi.org/10.1080/14680629.2001.9689895.

O'Connell, JS., Mturi, GA. & Maina, JW. 2011. Adjusting the standard rolling thin film oven procedure to improve the prediction of short term ageing, Proceeding from Conference on Asphalt Pavements for Southern Africa [CAPSA11], 10th, 2011, KwaZulu-Natal, South Africa.

Peterson, JC., Branthaver, JF., Robertson, RE., harnsberger PM., Duvall, JJ. & Ensley, EK. 1993. Effects of physico-chemical factors on asphalt oxidation kinetics. Asphalt cement and asphalt/polymer blends. Transportation Research Record 1391.

Peterson, JC. 2009. A Review of the Fundamental of Asphalt Oxidation – Chemical, Physicochemical, Physical Property, and Durability Relationships. Transportation Research Circular No. E-C140. Transportation Research Board.

Radziszewski, P., Ziolkowski R. & Čygas D. 2003. Technological Ageing Influence On Viscosity Of Selected Bitumens, Journal of Civil Engineering and Management, 9:1, 20-24, http://dx.doi.org/10.1080/13923730.2003.10531297.

Ruan, Y., Davison, RR. & Glover, CJ. 2003. The effect of long-term oxidation on the rheological properties of polymer modified asphalts. Fuel. v. 82. p. 1763-73. http://dx.doi.org/10.1016/S0016-2361(03)00144-3.

Sá Araujo, MFA., Leite, LFM., Pasa, VMD. & Lins, VFC. 2013. Rheological And Thermal Behavior Of Weathering-Aged Polymer Modified Bitumen. Brazilian Journal of Petroleum and Gas. Vol 7. No. 4. P 155-167. ISSN 1982-0593. www.portalabpg.org.br/bjpg.

Shen, J., AmirkhaniaN, S. & Tang, B. 2006. Influence of accelerated aging test temperature on the properties of binders, International Journal of Pavement Engineering, 7:3, 191-198, http://dx.doi.org/10.1080/10298430500533186.

Steyn, W. 2008. Focus on nanotechnology for use in transportation infrastructure. CSIR eNews. October 2008 edition. http://www.csir.co.za/enews/2008_oct/be_04.html.

Verhasselt, AF. & Choquet, FS. 1993. Comparing field and laboratory ageing of bitumens on a kinetic basis. Asphalt cement and asphalt/polymer blends. Transportation Research Record 1391.

Von Holt, J., Van Assen, E., Von Wissel, M. & Mokone, L. 2008. Phase 2: Laboratory study of various accelerated binder ageing test methods to predict binder durability on a comparative scale. Technical Report No: CSIR/BE/IE/IR/2008/0104/B. CSIR. South Africa.

Von Quintus, HL., Scherocman, JA., Hughes, CS. & Kennedy, TW. 1991. Asphalt aggregate mixture analysis system. NCHRP report 338. Prepared for Transportation Research Board, Brent Rauhut Engineering Inc, Austin, Texas.

Wikipedia, Atomic force microscopy,
http://en.wikipedia.org/wiki/Atomic_force_microscopy, 03 March 2015.

Wu, S., Pang, L., Mo, L., Qiu, J., Zhu, G., & Xiao, Y. (2008). UV and thermal aging of pure bitumen – comparison between laboratory simulation and natural exposure aging. Road Materials and Pavement Design, 9(suppl. 1), 103–113.
http://dx.doi.org/10.1080/14680629.2008.9690161.

Yang S-H., Keita, A. & Wang, H. Comparison of Field Aging Characteristics of Warm Mix Asphalt. 93rd Annual Meeting of the Transportation Research Board. TRB Paper No. 14-3293. Washington D.C.

Yen TF. & Chilingarian G.V. (editors), Asphaltene and Asphalts II, Amsterdam-Lausanne-New York-Oxford-Shannon-Tokyo, 2000.