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M.Sc. Thesis

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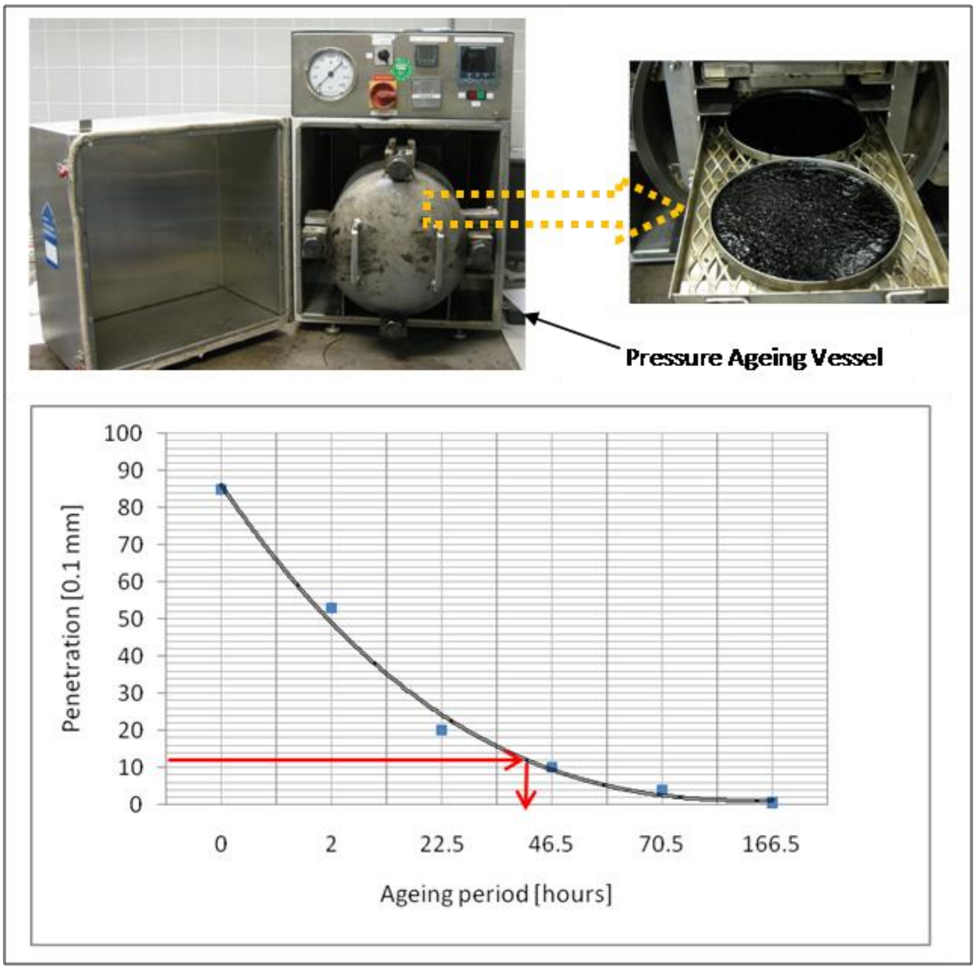

Faculty of Civil Engineering and Geosciences
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DEVELOPMENT OF A LABORATORY AGEING METHOD FOR BITUMEN IN POROUS ASPHALT

By:

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A Thesis

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Executive Summary

Generally porous asphalt has lower durability than commonly used dense asphalt mixtures. Loss of aggregates from the pavement surface, called raveling, is the most common form of distress in porous asphalt. There are several factors that contribute to the accelerated failure or raveling of porous asphalt and among them ageing is believed to be the main reason for raveling failure of porous asphalt. It increases the chance of damage development because of applied traffic loading and thermal stresses at low temperature. During design phase of pavement, it is imperative to know beforehand what the properties of the pavement will be after field ageing. This will help to minimize maintenance cost due to premature failure and to increase the confidence level of the design of the pavement. It is evident; therefore, that there is a need for accelerated laboratory ageing method that can simulate binder properties similar to that of field aged binder. As a result this study was initiated and the objective was to develop a laboratory ageing procedure which is able to mimic binder properties of 7 years field aged porous asphalt pavement.

To achieve the objective, three different ageing protocols were proposed and investigated in the first phase of the research. Then, based on the results, two of the ageing protocols were further refined and examined.

- The first protocol was ageing of mortar by using a pressure ageing vessel
- Ageing of compacted porous asphalt mixture in pressure ageing vessel was the second protocol
- The third ageing method examined was ageing of loose asphalt mixture in an air ventilated oven

In choosing the ageing protocols; the effect of aggregate, sand and filler or at least sand and filler was aimed to be included. That is why mortar and mixture but not bitumen was aged.

In order to compare field and laboratory aging; rheological, chemical and adhesion tests were conducted on binders recovered from field cores and on binders recovered from specimens that were subjected to laboratory aging. Accordingly, various rheological tests including conventional empirical tests such as penetration

and ring and ball tests were performed. The fundamental tests carried out are complex shear modulus and phase angle determination of the binders at different temperatures using the Dynamic Shear Rheometer. The chemical characterization of binders was conducted using Fourier Transform Infrared spectroscopy (FTIR). The surface energy determined by means of Wilhelmy plate test has been used as an indicator for the adhesion property of bitumen.

The possibility that the use of a standard bitumen recovery process may have influence on the recovered bitumen was also investigated. Rheological and chemical tests were carried out on bitumen sample which passed through the standard recovery process and on bitumen sample which is not exposed to the recovery process. Comparison of the two test results revealed that no significant differences have been noticed on the rheological and chemical properties from the two bitumen samples. Following this, the standard bitumen recovery process has been used in this study.

A simple laboratory test procedure which is able to simulate field ageing of porous asphalt pavement has been developed. It involves heating of mortar specimen in oven for 2 hours at a temperature of 165 °C (STA) and then placing the short term aged mortar specimen in pressure ageing vessel at a temperature of 90°C for 7 days under air pressure of 2.1 MPa. Comparison of the rheological (penetration, softening point, complex modulus and phase angle) and chemical test results of the recovered bitumen from laboratory aged specimen with that from 10 years field aged PA shows comparable results.

In addition to the above ageing protocol, it was shown that laboratory ageing of loose porous asphalt mixture in oven is potentially promising laboratory ageing protocol to simulate field aging of PA. An amendment to the aging protocol has been suggested so that it can reasonably mimic field ageing of porous asphalt.

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LIST OF ABBREVIATIONS

AI	Aging Index
ASTM	American Society for Testing and Materials
ATB	Advanced Testing of Bituminous materials
FTIR	Fourier Transform Infrared
BRRC	Belgian Road Research Centre
CROW	The national information and technology platform for infrastructure, traffic, transport, and public space in the Netherlands
DAC	Dense Asphalt Concrete
DI	Ductility Index
DSR	Dynamic Shear Rheometer
EL	Emergency Lane
EN	European Norm
FieldL	Field aged specimen Lower part
FieldU	Field aged specimen Upper part
GPC	Gel-Permeation Chromatography
HMA	Hot Mix Asphalt
IC	Gaestel Index
Ico	Carbonyl Index
IR	Infrared
ISO	International Organization for Standardization
Iso	Sulfoxides Index
ITT	Indirect Tensile Test
LTA	Long Term Aging
MRTFOT	Modified Rolling Thin Film Oven Test
NEN	Dutch Standardization Institute (het nationale normalisatieinstituut)
NL	Netherlands
NRTFOT	Nitrogen Rolling Thin Film Oven Test
P	Protocol (e.g. P1 = aging protocol 1)
PA	Porous Asphalt
PAV	Pressure Aging Vessel

Pen	Penetration test/value
PI	penetration Index
PMB	Polymer Modified Bitumen
RAW	Dutch standard specification for the civil engineering sector
RCAT	Rotating Cylinder Aging Test
RFT	Rotating Flask Test
RWS	Ministry of Transport, Public Works and Water Management in the Netherlands (Rijkswaterstaat)
RILEM	International union of laboratories and experts in construction materials, systems and structures
RLITT	Repeated Load Indirect Tensile Test
RTFOT	Rolling Thin Film Oven Test
SARA	Saturates, Asphaltenes, Resins, Aromatics
SHRP	Strategic Highway Research Program
SL	Slow Lane
SLPA	Single Layer Porous Asphalt
STA	Short term Aging
STD	Standard Deviation
TC	Technical Committee
TFOT	Thin Film Oven Test
TLPA	Two Layer Porous Asphalt
TTS	Time-Temperature Superposition
TU Delft	Delft University of Technology
UTM	Universal Testing Machine
UV light	Ultraviolent light/radiation
WLF	William-Landel-Ferry model

Chapter 1 Introduction

1.1 General

Porous asphalt consists primarily of gap-graded aggregates held together by a bituminous binder to form a matrix with interconnected voids to allow free flow of air and water through the material. Porous asphalt is designed to contain a high air void content, usually in excess of 20%. In effect this high void content means that porous asphalt greatly improves the rate of surface water drainage, thereby reducing spray and splash and headlight glare in wet weather. The other main advantage of porous asphalt is its noise reducing properties. The noise reduction of porous asphalt is based on acoustical absorption (both rolling as well as engine noises are absorbed).

In the Netherlands, more than 20% of the inhabitants are hindered by traffic noise. For that reason the Dutch government has decided to apply noise reducing surface on most of the highways. As a result of this decision, at the end of 2009 more than 80% of the main road network has been surfaced with a porous asphalt concrete wearing course.

Although porous asphalt has its own benefits, it suffers from problems which can affect both its performance and its service life. This is also largely due to its high void content. The open structure exposes a large binder surface area to the oxidative effect of air, the damaging effect of water and other contaminants, leading to rapid aging of the binder, moisture damage of the bitumen aggregate bond and structural distress of the compounds (L.D. Poulikakos 2009). Generally porous asphalt has a lower durability than dense asphalt mixtures. Loss of aggregates from the pavement surface, called raveling, is the most common distress in porous asphalt.

1.1.1 Raveling in porous asphalt

Raveling might be caused by cohesive failure of the bituminous mortar or by failure in the adhesive zone. Poor performance of porous asphalt can be a result of choice of wrong materials, poor mix design or low quality during the construction phase (production, transportation and laying) (Voskuilen, van de Ven and Nijssen 2008). The Influence of temperature during mixing and laying, lack of compaction and mixture composition (such as insufficient or excessive bitumen or/and fines content) contribute to the subsequent deprived performance of the pavement (Hagos 2008).

Porous asphalt concrete is an open, bitumen bonded material. The binding is generated at the stone-stone contact regions where a limited amount of mortar acts as binding agent. Raveling is the result of failure of the weakest link within the stone contact region. This binding failure may be introduced by repeated traffic loads or fatigue mechanism. In recent study by Miradi (2009), it was found that traffic is of most important for damage development in PA after 5 years of construction while climate is the main factor for damage after 8 years of construction. The non-loading associated effects like: aging, moisture, temperature effects such as shrinkage and chemical attack may accelerate the development of raveling (MO 2009). The above factors will be discussed briefly in the paragraphs below.

Moisture is a factor that contributes to the accelerated failure or raveling of porous asphalt. Presence of moisture in the pavement can manifest itself in the loss of cohesion within the bituminous binder itself or the loss of adhesion between binder and the aggregates (stripping). Stripping is a phenomenon which causes the de-bonding of bitumen films from aggregate surfaces due to greater affinity of the aggregate for water than for bitumen. Furthermore, stripping can be caused by hydraulic scouring resulting from repeated generation of pore water pressure. Hence, stripping leads to a weakened pavement that is susceptible to pore water pressure damage and premature cracking (L.D. Poulikakos 2009). However, some researchers argue that the effect of water in raveling of porous asphalt is insignificant. They bring forward the argument that raveling is a surface failure phenomenon in porous asphalt and the presence of water in the upper part of the porous asphalt concrete layer for a longer time is not likely because of the porous nature of the mixture (Herrington et al, 2005 and Hagos, 2008). Hence, the effect of water/moisture is thought to be of secondary importance to the damage development, while traffic load is of prime importance.

Due to the open surface, porous asphalts are more susceptive to damage by chemical attack such as hydrocarbons that penetrate into the top layer. Hydrocarbons like petrol and oil are a potential hazard to bituminous mixes. Especially in urban areas, these liquids trickle into the top layer and penetrate in the bitumen-aggregate interface. This can lead to de-bonding of the bitumen and aggregate (Scholten 2003).

Ageing is believed to be the main reason for raveling of porous asphalt. It increases the chance of damage development because of applied traffic loading and thermal stresses at low temperature and in this way contributes to a lower fatigue life. This factor will be discussed in detail in chapter 2.

1.2 Problem statement

In the Netherlands new construction contracts (performance based contract) have been introduces recently. In this contract the contractors are obliged to guarantee good performance of the pavement for a certain period (usually 7 years) after construction. The lower service life of a porous asphalt layer due to raveling, as stated before, is a major concern for these companies. Aging of the binder is believed to be a main contributor to poor performance of porous asphalt. To minimize maintenance cost due to premature failure and to increase the confidence level of the design of the pavement, it is important to know the change in properties of the pavement due to ageing. It is evident, therefore, that there is a need for accelerated laboratory ageing methods that can mimic binder properties similar to that of in service (field) aged binder.

Currently there are standard laboratory ageing methods to simulate field ageing properties of binders. Nevertheless, the ageing phenomenon in the field is still poorly understood and these laboratory accelerated ageing methods have not always been a success in simulating long term field ageing properties of porous asphalt. Therefore, it is important to develop a laboratory ageing procedure which is able to simulate field aged binder properties of porous asphalt.

1.3 Research objective

The main objective of this research program is to develop and define an accelerated laboratory ageing procedure (ageing protocol) for porous asphalt which is able to mimic an ageing period of 10 years in the field by using only standard road laboratory equipment and a maximum ageing period of 7 days (1 week) in the laboratory.

1.4 Scope of the research

The scope of this project is to define a laboratory ageing protocol which is able to mimic 10 years of field ageing of bitumen in porous asphalt in a period shorter than one week. In order to verify that the defined protocol can simulate field ageing, binders from field and laboratory aged samples were compared based on the change in the physical and chemical properties of the binder due to ageing. Ageing indicators commonly used in practice are either empirical parameters describing a change in binder viscosity while fundamental properties are designating a change in the viscoelastic behavior of the binder or are a measure of the change of binder chemical composition indicated by a change in colloidal structure after ageing. To investigate the above properties, the following tests were conducted on the recovered binder:

- Empirical tests on binder (Penetration and Softening point test)
- Rheological test (DSR-Complex modulus and phase angle test)
- Chemical test (Fourier Transform infrared Spectroscopy-FTIR test)
- Wilhelmy plate test (surface energy or adhesion test)

Moreover, repeated load indirect tensile test to determine stiffness and indirect tensile test to determine strength have been conducted on porous asphalt specimens from the field.

1.5 Organization of the report

This report is divided into six distinct chapters including this introductory chapter (Chapter 1) which serves as an introduction, stating the nature of the problem to be addressed, objectives and scope of the research.

Chapter 2 provides a literature review on age hardening of bituminous pavement materials, ageing mechanisms and its assessment techniques. A review of existing laboratory accelerated ageing test methods both for the binder and the asphalt mixture is also given in this chapter.

Chapter 3 describes the materials, material properties and testing program of the study. It also describes various test methods used to evaluate the ageing properties of the binder.

In chapter 4 an analysis is made of the results from the preliminary ageing protocols which have been conducted to simulate the properties of field aged binder.

Chapter 5 presents the test results and an analysis of the revised/improved ageing protocols which have been deployed to simulate the properties of field aged binder

Finally, in chapter 6 the conclusions and recommendations section for the research work conducted under this study are given.

Chapter 2 Literature Review

In this chapter the findings of a general literature survey on bitumen and asphalt mixture (especially porous asphalt mixture) age hardening will be presented. Age hardening of bituminous pavement materials, ageing mechanisms and its assessment techniques or ageing indicators are also dealt with briefly. Finally, a review of existing laboratory accelerated ageing test methods both for the binder and the asphalt mixture has been given ample attention.

2.1 Age hardening and ageing mechanisms

Hot mixed bituminous materials start to age as soon as the binder is heated and mixed with the hot aggregates in the asphalt plant. The expression ‘age hardening’ has been used by scientists to imply an undesirable change in the properties of the mixture which occurs with time, mainly associated with the volatilization of the binder and oxidation of the placed material on site. Age hardening results in increase of the binder stiffness and a stiffening of the mixture. This causes a reduction in pavement flexibility which may lead to a brittle mode of distress and subjects the asphalt mixture to wear due to its sensitivity to traffic loading and other influences such as water damage(Hagos 2008) and(Khalid 2002).

Generally asphalt mixture ageing is classified into two categories, short term and long term ageing. Short term ageing is associated with the loss of volatile components and oxidation of the bitumen during asphalt mixture production. A considerable amount of ageing happens during hot mix asphalt production in the asphalt plant and continues with a slower rate during storage, transportation, laying and compaction stages because in these stages the mix is still at relatively high temperature which facilitates age hardening. Long term ageing is a progressive oxidation of the in-place material in the field during service life of the pavement. After pavement construction, age hardening continues at a slower rate for the first few years (2 to 3 years). Later, the rate of hardening even further decreases and longer periods are required to notice the changes in rheological properties of the binder during its service period.

2.1.1 Ageing mechanisms

Like many other organic substances, bitumen is affected by the presence of oxygen, ultraviolet radiation and changes in temperature. These external influences cause the bitumen to harden, resulting in substantial rheological changes like a decrease in penetration, an increase in softening point, and an increase in viscosity. This tendency for bitumen to harden under the above mentioned factors has been known and studied for many years. Several factors that influence bitumen ageing have been identified in the past decades. Many researchers have reported factors that have a significant effect on age hardening of bitumen. Six factors seem to represent the general categories referred to by most investigators (Khalid 2002). These factors are:

(a) **Oxidation**: Oxidation is the reaction of oxygen with bitumen, the rate depending on the binder characteristics and the temperature. The degree of oxidation is highly dependent on temperature, time and film thickness of the bitumen.

(b) **Volatilization**: Volatilization is the evaporation of the light constituents from bitumen and is primarily a function of temperature.

(c) **Polymerization**: Polymerization is a combination of similar molecules to form larger ones, causing progressive hardening.

(d) **Thixotropy**: Thixotropy is progressive hardening due to the formation of a structure within the bitumen over a period of time, which can be reversed to a degree by reheating and working the material.

(e) **Syneresis**: Syneresis is an exudation reaction in which the thin oily liquids are exuded to the surface of the bitumen film. With the loss of these oily constituents, the bitumen becomes harder.

(f) **Separation**: Separation is the removal of the oily constituents, resins or asphaltenes from the bitumen caused by selective absorption of some porous aggregates.

Beside the above points, the effect of the chemical reaction with hydrated lime has been reported to have an influence on age hardening (Learning from the road, TU Aachen 2006). The filler for porous asphalt in the Netherlands has to contain at least 25% hydrated lime.

As can be seen from the above points, it is not only the binder, but also the binder-aggregate interaction that should be taken into consideration in the ageing process. Depending on the aggregate type (mineralogical nature of the aggregate and surface characteristics), the ageing performance of the same binder mixed with different aggregates can differ due to the mineral contents of the aggregate surface, adsorption properties of the aggregate, and orientation of the polar molecules in the binder in the vicinity of the binder-mineral surface interface (Hagos 2008; Jiantao Wu and Gordon Airey 2009). According to Wu and Airey, aggregates can affect binder ageing in two main ways. First, the adsorption of binder fractions by the aggregate surface will break the fractional proportional balance within the bitumen, which may lead to a less well dispersed binder and this may promote the rate of bitumen ageing. Further, some mineral components on the surface of aggregates may catalyze bitumen oxidation.

Another main factor that influences bitumen hardening on the road is the void content of the mixture. A higher rate of ageing is expected in a porous asphalt mixture compared to dense asphalt. The effect of ageing over the entire thickness of a porous asphalt pavement layer was reported by researchers. In recent research by Hagos (2008), it was found that binders recovered from the upper and lower zones of the field aged porous asphalt specimen show nearly similar rheological characteristics. This indicates the severity of ageing in porous mixtures. The reason is attributed to the high amount of voids in porous asphalt that allows access to oxygen and water. Thus, the binder film is constantly exposed to oxygen, which enhances hardening and oxidation resulting in changes in the binder property over the whole thickness within a relatively short period of time. As a result, substantial rheological changes take place such as a decrease in penetration, an increase in softening point, and an increase in viscosity of the binder due to age hardening.

Figure 2.1 shows the in situ bitumen properties of five year old asphaltic concrete with void contents ranging from 3 to 12%. At void contents less than 5%, very little hardening occurred in service. However, at void contents greater than 9%, the in situ penetration (in 0.1mm or dmm) drop from 70 to less than 25. This shows how important the void content is for age hardening.

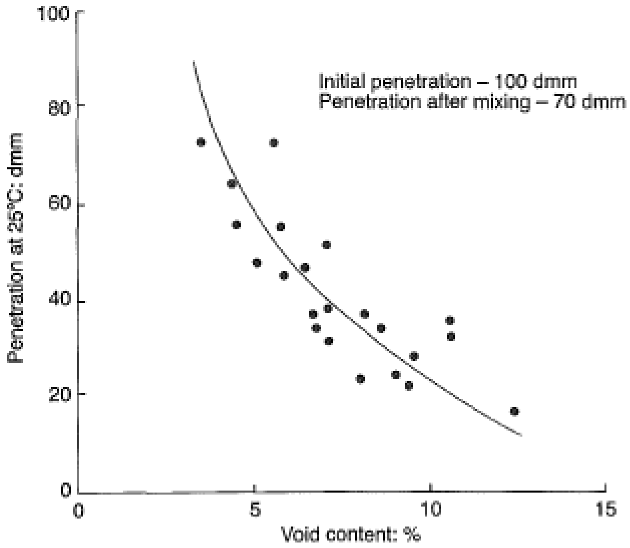


Figure 2.1: The effect of void content on the hardening of bitumen on the road after 5 years of hardening (Source: the shell bitumen hand book)

2.2 Assessment techniques or Ageing indicators for bitumen and asphalt mixtures

Ageing changes the rheological, mechanical, and chemical properties of the binder and the bituminous mix. The changes in property of the binder and asphalt mixture can be quantified by means of ageing indicators. There is a wide variety of tests that can be used to assess the effect of ageing on asphalt mixtures and on the binder recovered from the mixture by measuring properties before and after ageing. Ageing indicators commonly used in practice are either empirical parameters describing change in binder properties, fundamental properties designating change in the viscoelastic behavior of the binder and the mix or a measure of the change of binder chemical composition indicating the change in colloidal structure after ageing. The requirements for assessment procedures are similar to those for ageing techniques in that they enable comparison with field data, are cost-effective and simple, and experience and expertise exist in their use (Hagos 2008) and (Khalid 2002).

2.2.1 Binder ageing indicators

Binder age hardening assessment techniques often include well-known standardized procedures to evaluate properties like viscosity, penetration, Ring and Ball temperature (softening point) and mass loss. In bitumen specifications original bitumen values and measured values after ageing are used to determine some kind of indices which show the extent of ageing. Some of these indices are shown below (Freddy L. Roberts 1996).

$$\%\ retained\ penetration = \frac{penetration\ of\ aged\ binder}{penetration\ of\ original\ binder} * 100\% \qquad (2.1)$$

$$Aging\ index = \frac{viscosity\ of\ aged\ binder}{viscosity\ of\ original\ binder} \qquad (2.2)$$

$$change\ in\ Ring\ and\ Ball\ temperature, \Delta T_{R\&B} = T_{R\&B\ aged} - T_{R\&B\ original} \qquad (2.3)$$

$$mass\ loss/gain = mass\ of\ aged\ bitumen - mass\ of\ original\ bitumen \qquad (2.4)$$

Mass loss is related to the short term ageing of binders during mix production. For conventional binders, higher values of the ageing index indicate that the bitumen is more sensitive to ageing (hardening). Viscosity measured at 60ºC and penetration measured at 25°C are often used in specifications for age hardening characteristics to indicate the relative performance at high and intermediate pavement temperatures.

In recent years, more searching approaches have been used. A significant number of researchers have used more fundamental properties to evaluate the aged properties of binders. This includes establishing master curves of the complex modulus and phase angle as a function of frequency over a wide spectrum of temperatures (Khalid 2002). For plain (unmodified) bitumen, ageing increases the complex modulus and decreases the phase angle over a range of frequencies, indicating that the aged bitumen shifts viscous characteristics and shows increase in stiffness as shown in Figure 2.2 below. For certain modified binders, the phase angle master curve shows unique behavior towards the low frequency region.

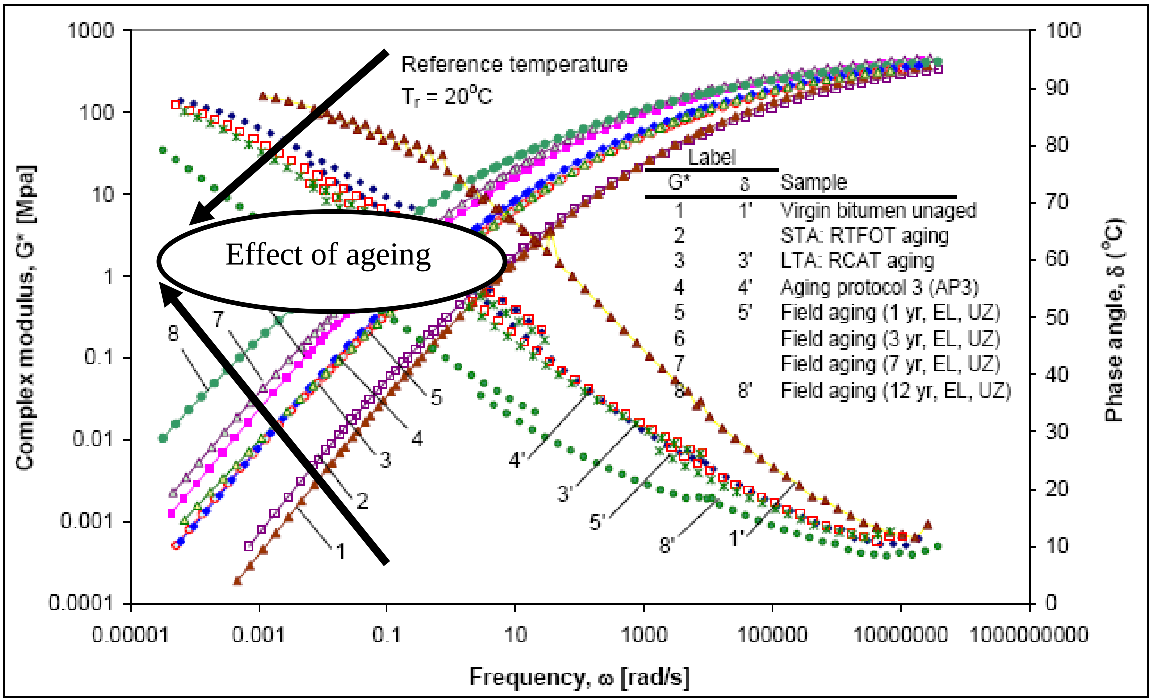


Figure 2.2: Effect of ageing on complex modulus and phase angle (source: Hagos, 2008)

The ageing process can also be explained by the changes in binder chemical composition. Binders exposed to age hardening show an increase in the so called Gaestel Index (IC), an interpretation of the chemical composition of the binder that explains its internal colloidal structure. The Gaestel Index (IC) is expressed as the ratio of the asphaltenes and saturates to aromatics and resins (Ishani 1996). The Gaestel index is given in Equation 2.5 below.

$$Gaestel\ index\ (IC) = \frac{Asphaltenes + Saturates}{Aromatics + Resins} \qquad (2.5)$$

Fourier transform infrared spectroscopy as well as gel permeation chromatography have been used effectively by researchers both quantitatively and qualitatively to evaluate the changes in bitumen properties due to ageing. In Fourier transform infrared spectroscopy, as the functional groups responsible for bitumen ageing are sulfoxides (S=O) and ketones/carbonyl (C=O) groups, generally the peak areas and peak heights of the infrared spectrum at wavenumbers 1030 cm^{-1} (sulfoxides) and 1700 cm^{-1} (ketones) are used to characterize chemical changes due to ageing.

Ageing results both in an increase of the peak height and peak area of the infrared spectrum. Gel permeation chromatography can be used to show the effect of ageing on the Molecular Weight Distribution of the binder. The effect of ageing can be related to an increase in the large molecular size portion of the molecular weight distribution.

2.2.2 Asphalt mixture ageing indicators

Mixture assessment techniques mainly deploy the ratio or comparison of resilient modulus of the aged and unaged specimens. Different test methods are used by different researchers to determine the resilient modulus of the mix. To gauge the extent of ageing, Bell et al. (C. A. Bell 1994) utilized the ratio of the aged resilient modulus to the unaged resilient modulus as an ageing indicator for asphalt mixtures (Equation 2.6 below).

$$Resilient\ modulus\ ratio = \frac{Resilient\ modulus\ after\ aging}{Resilient\ modulus\ before\ aging} * 100\% \qquad (2.6)$$

Herrington et al. used the Cantabro tests to measure the effect of mix oxidation (Herrington 2005). The percentage weight loss after the Cantabro test gives an indication of the cohesion and abrasion resistance of an open graded porous asphalt mix, which indirectly is a result of age hardening. Kim et al[1] on the other hand adopted fatigue testing to assess ageing effects on mixture fatigue life.

According to a literature survey by Hagos (2008), the ratio of the slopes (or intercept) of the creep curve (log strain versus log time) which is referred to as the “Ductility Index”, before and after oxidation was used by Kumar & Goetz (Kumar 1997) as an indicator for the ageing of asphalt mixtures (Equation 2.7).

$$Ductility\ Index\ (DI) = \frac{m_1}{m_0} \qquad (2.7)$$

Where:

m_0 = the slope of a creep curve for unaged mixture,

m_1 = the slope of a creep curve for aged mixture.

[1] Source: Khalid, 2002

2.3 Laboratory accelerated ageing test methods for bituminous pavement materials

Oxidative ageing is the major factor for age hardening of bituminous materials which includes physical and chemical processes. In a simplified description, oxygen from the environment has to diffuse physically into the binder before it reacts with the bitumen components to result in hardening. Temperature serves two purposes here: softening the binder and in this way increasing the diffusion rate of oxygen, and accelerating the chemical reaction. Based on this hypothesis of the ageing phenomenon, two alternatives were used to accelerate laboratory ageing of bituminous materials: decreasing the film thickness and increasing the amount of asphalt surface exposed to oxygen, and using pure oxygen and accelerating its diffusion by pressure (David A. Anderson 1994).

Over the last decades several attempts have been made by researchers to simulate field ageing of bituminous materials in the laboratory by accelerated ageing of the materials. The most important techniques for accelerating oxidation reaction are: increasing temperature, decreasing binder film thickness, increasing binder surface exposed to oxygen, increasing air flow, and increasing pressure. Existing ageing tests combine the above techniques to accelerate oxidation.

Accelerated laboratory tests related to ageing of bituminous materials can be performed on bitumen, mastic, mortar or on bituminous (asphalt) mixtures. In all cases, tests are aimed to simulate age hardening of the bituminous materials during mix production and construction phase (short term ageing) and age hardening during service life of the pavement (long term ageing). The following sections review and discuss the existing test methods for age hardening of bituminous pavement materials.

2.3.1 Ageing tests for bituminous binders

Many attempts have been made recently to correlate accelerated laboratory ageing of bitumen with field performance. Most of this research was based mainly on two major test groups: the use of oven tests and pressure oxidation. Extended heating procedures tend to be used to simulate short-term ageing (hardening) of bitumen associated with asphalt mixture preparation activities while the pressure oxidization technique is mainly used to simulate long term age hardening of the bitumen binder related to the service life of the pavement.

2.3.1.1 Short term binder ageing

The short term ageing of binder occurs primarily due to air oxidation and the loss of more volatile components during mix production (when heated aggregate is mixed with hot bitumen binder). So the laboratory-accelerated technique for short term ageing should reproduce these effects.

According to a literature survey by Hagos (2008), the overall mass change in short term ageing of bitumen depends on two competing phenomena. A portion of the sample volatilizes (i.e. volatilization of oily components), causing the sample to lose mass, and oxygen reacts with the sample (oxidation), causing the sample to gain mass. The net sum of these two effects determines whether the sample has an overall mass gain or an overall mass loss.

The most commonly used standardized tests, to simulate the short-term ageing of conventional, unmodified bitumen, are thin film oven test (TFOT), rolling thin film oven test (RTFOT) and the rotating flask test (RFT) (Airey 2003).

2.3.1.1.1 Thin Film Oven Test (TFOT)

The Thin Film Oven Test is a standard binder test (EN 12607-2, ASTM D 1754) used for measuring the combined effects of heat and air on a film of bitumen or bituminous binder. This test method has a main purpose to reproduce the extent of ageing of bituminous binder during mixing in an asphalt mixing plant. In the test, a thin film of bitumen is placed in a pan (50 ml of sample in a cylindrical pan of 140 mm inside diameter and 9.5 mm deep with a flat bottom will give a film thickness of approximately 3.2 mm), which is held in a convection oven at 163ºC for 5 hours. The effect of hardening is determined on the basis of the change in mass (expressed as a percentage) and/or as a change in the bituminous binder’s characteristics of penetration, softening point or dynamic viscosity before and after oven ageing.

According to Airey (2003), a major criticism of the Thin Film Oven Test (TFOT) is that the thick binder film which results in a large volume to exposed surface area for the aged binder. As the bitumen is not agitated or rotated during the test, there is a concern that ageing may be limited to the “skin” of the bitumen sample. This concern has led some researchers to the use of a Modified Thin Film Oven Test (Airey 2003), which tests bitumen in microfilm thickness and extended exposure time (a film thickness of 100 µm, at a temperature of 163 ºC and exposure period of 24 hours).

2.3.1.1.2 Rolling Thin Film Oven Test (RTFOT)

The rolling thin film oven test (RTFOT) is one of the most commonly used standardized tests (EN 12607-1, ASTM D 2872) and is probably the most significant modification of the thin film oven test (TFOT) to simulate the short-term ageing of binders. This test is used to measure the combined effects of heat and air on a thin film of bitumen or bituminous binder in permanent renewal. It simulates the hardening which a bituminous binder undergoes during the mixing, transporting and compacting processes, which is the short-term ageing. The RTFOT in accordance with EN 12607-1 involves rotating eight glass bottles, each containing 35 g of bitumen, in a vertically rotating shelf, while blowing hot air into each sample bottle. During the test, the bitumen flows continuously around the inner surface of each container in relatively thin films at a temperature of 163 °C for 75 min. The vertical circular carriage rotates at a rate of 15 revolution/min and the air flow is set at a rate of 4 L/min.

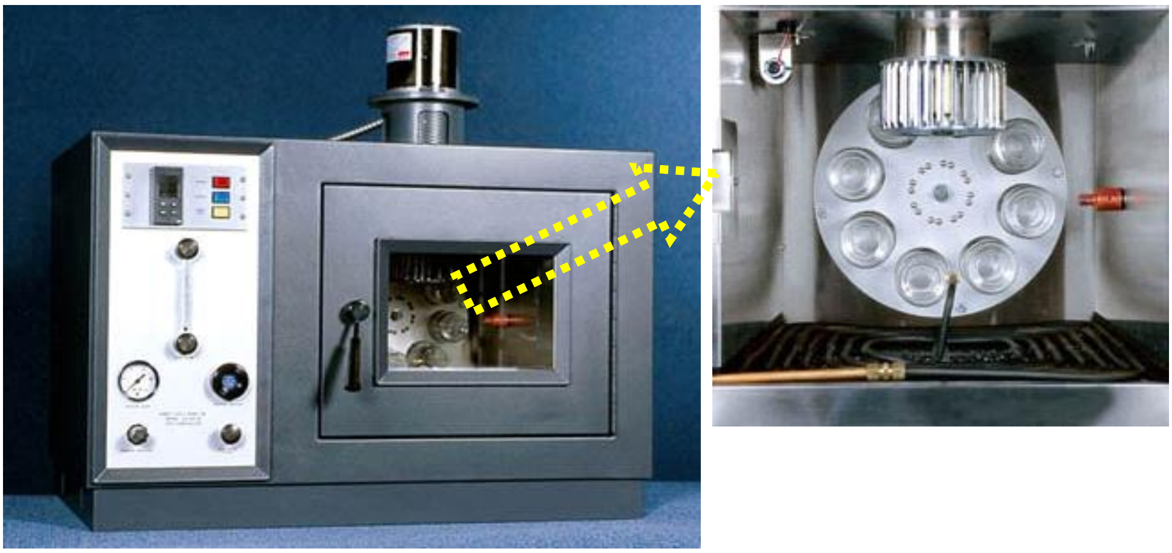


Figure 2.3: Rolling Thin Film Oven (left) and interior view (right)

The method ensures that all the bitumen is exposed to heat and air and the continuous movement ensures that no skin develops to protect the bitumen. The method described is not applicable to some modified binders or to those where the viscosity is too high to provide a moving film (EN 12607-1:2007). The effects of this treatment are determined from measurements of the properties of the binder before and after the test and from determining the change in mass

2.3.1.1.3 Modified Rolling Thin Film Oven Test (MRTOT)

The major problems related to the use of the RTFOT for binders with high viscosity (example: polymer modified bitumen) is that these binders will flow much more slowly inside the glass bottles during the test under the influence of gravity. On the other hand, a material with low consistency will flow much faster. As a result, in the case of high viscous binders less fresh surface is exposed to air resulting in a lower oxidation and the opposite is true with low consistency binders (Oliver 1997). In addition, during the test in RTFOT some binders have a tendency to roll out of the bottles.

To overcome these problems, the modified rolling thin film oven test (MRTFOT) was developed. The test is identical to the standard RTFOT except that a set of 127 mm long by 6.4 mm diameter steel rods are positioned inside the glass bottles during oven ageing. The principle is that the steel rods create shearing forces to spread the binder into thin films, thereby overcoming the problem of ageing high viscosity binders. Initial trials of the MRTFOT indicate that the rods do not have any significant effect on the ageing of conventional penetration grade bitumen. Moreover, recent research work has indicated that using the metal rods in the MRTFOT does not solve the problem of roll-out of modified binder and this is the reason that the method is used hardly ever.

2.3.1.1.4 The Nitrogen Rolling Thin Film Oven Test (NRTFOT)

The Nitrogen Rolling Thin Film Oven Test (NRTFOT) is one of the modifications of the RTFOT test. The test procedure is identical to the standard RTFOT test except that nitrogen, instead of air, is blown over the exposed surface of the bitumen samples. The mass change before and after the test is used to evaluate the ageing characteristics of the binder. This test method is developed to enable the determination of the extent of evaporation and oxidation process taking place in the short-term ageing. According to Parmeggiani (2000), the NRTFOT test reflects the extent of the loss of volatiles and hence the strength of the bonding forces holding the hydrocarbon molecules together at high temperatures occuring during asphalt production. On the other hand, the test can be used to distinguish the sensitivity of different binders to ageing as the loss of oily components is a crucial element in the subsequent performance of the binder (Parmeggiani 2000).

2.3.1.1.5 Rotating Flask Test (RFT)

The Rotating Flask Test is one of the standardized (EN 12607-3) short term ageing tests. The RFT test method consists of ageing a 100 g sample of bitumen in a rotating spherical flask of the rotary evaporator for a period of 150 minutes at a temperature of 165 °C (an oil bath is used to maintain the temperature) and a constant air flow of 0.5 l/min. The material forming the surface of the specimen is constantly replaced because the flask is rotated at 20 rpm, preventing the formation of a skin on the surface of the bitumen. The dynamic nature of the test also has an additional advantage that it avoids the separation or segregation of polymers which makes it suitable to test polymer modified binders. The test is conducted in an oil bath, which allows rapid sample heating and eliminates the radiant heating problems associated with some ovens.

The effect of short term age hardening is determined based on the change in mass (expressed as a percentage) or as a change in the bituminous binders' characteristics such as penetration, softening point (ring and ball) or dynamic viscosity, before and after hardening. Comparison with the RTFOT and TFOT suggest that the RFT is roughly one-third as severe as the other tests in producing volatiles, which means less ageing (Airey 2003).

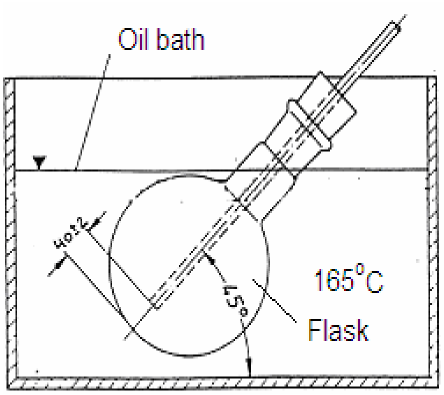


Figure 2.4: Flask assembly during rotation

2.3.1.2 Long term binder ageing

In hot-mixed materials, the bitumen or any other bituminous binder during its life is subjected to two successive types of ageing. The first one is the rapid ageing in construction phase termed as short term ageing. The second one is the slow ageing in service (ageing during service life of the pavement called long term ageing) comprises all the changes occurring on site in the binder, in the prevailing climatic environment of the road surfacing. Standard tests such as RTFOT or RFT discussed in the previous section can simulate ageing during the production and compaction phase in an adequate way. However, their high temperatures make them unsuitable for simulating field ageing (A. F. Verhasselt 1997).

A number of test methods have been developed to simulate field ageing of binders. In the subsequent section attention will be given to the most important existing laboratory test methods.

2.3.1.2.1 Pressure Ageing Vessel (PAV)

The Pressure Ageing Vessel (PAV) was developed in the SHRP project to simulate long term, in-service oxidative ageing of bitumen in the field (long term ageing). The method involves hardening of bitumen in the RTFOT or TFOT (short term ageing) followed by oxidation of trays of binder at elevated temperatures under pressurized conditions in a pressure ageing vessel (Airey 2003). According to the European standard for the PAV test (EN 14769), the PAV procedure entails ageing 50 g of bitumen in a 140 mm diameter container (giving a binder film that is approximately 3.2 mm thick) within the heated vessel, pressurized with air to 2.1 MPa at typical conditioning temperatures of 85 °C (for 65 hours), 90 °C (for 20 hours), 100 °C (for 20 hours) or 110 °C (for 20 hours). The higher temperatures may make this ageing procedure unsuitable for evaluation of binders containing some polymers as they could exhibit separation and/or degradation in a way that does not occur during natural ageing. Verhasselt and Vanelstraete (2000) have found that the higher temperature of the PAV resulted in some segregation of the polymer in some of the polymer modified binders. Figure 2.5 below shows the pressure ageing vessel(A. F. Verhasselt 2000).

Figure 2.5: Pressure ageing vessel

2.3.1.2.2 Rotating Cylinder Ageing Test

The Rotating Cylinder Ageing Test (RCAT) is a standardized accelerated ageing test (EN 15323), first developed at the Belgian Road Research Center (BRRC) to simulate both the short and the long-term ageing of binders. This European standard test specifies an accelerated ageing/conditioning procedure for bitumen, bituminous binders (including modified binders) and bituminous mastics. The procedure involves binder ageing at moderate temperatures in a large cylinder rotating in an oven under oxygen flow conditions.

Before commencing the long term ageing test by RCAT, the binder is first preconditioned as necessary to simulate the condition in which it would be applied to the road. This can be done by one of the standard short term ageing test methods RTFOT (EN 12607-1) or TFOT (EN 12607-2). Short-term ageing/conditioning can also be performed directly in the RCAT, which reduces intermediary sample handling operations (A. F. Verhasselt 2002). This is one of the major advantages of RCAT compared to other long term ageing test methods.

Figure 2.6: Rotating cylinder ageing test apparatus

In the long term ageing test procedure the cylinder is filled with 550 g of bitumen. The cylinder is then placed in a frame which rotates the cylinder at 1 revolution/min and oxygen flows through the aperture at a rate of 4.5 l/h. Rotation of the roller within the cylinder distributes the bitumen into an even 2mm thick film on the inner wall of the cylinder. Tests are conducted at temperatures not more than 100°C, typically at 90°C (RCAT90) for 140 hours. At discrete intervals, approximately 25–30 g of bitumen is removed from the cylinder with a view to monitoring the ageing process. Due to the large initial quantity of bitumen, the procedure allows numerous evaluations to be made and progressive changes in the bitumen chemistry and physical properties to be investigated.

2.3.2 Ageing tests for bituminous mixtures

In addition to artificially ageing binders, a number of attempts are also made to develop methods for accelerated ageing the bituminous (asphalt) mixture. According to Airey (2003), the methods can broadly be divided into four categories:

- Extended heating procedures;

- Oxidation tests;
- Ultraviolet/Infrared treatment; and
- Steric hardening.

The effects of ageing on parameters like stiffness, viscosity, strength…etc are assessed after accelerated ageing of the asphalt mixture. Extended heating procedures naturally expose the mixture to high temperatures for a specified period of time while oxidation tests in general make use of a combination of high temperature and pressure. On the other hand Ultraviolet/infrared treatment involves exposing specimens to either ultraviolet or infrared radiation (Airey 2003).

In the subsequent sections some of the major test methods for asphalt mixture ageing are presented.

2.3.2.1 Ageing procedures developed under the SHRP-A-003A project

Both short term and long term ageing procedures are developed under the SHRP project. The short-term methods involved conditioning loose mixtures, while the long-term methods involved conditioning compacted samples.

The SHRP procedure for short term oven ageing requires that loose mixtures to be heated (aged) in a forced draft oven for 4 hours at 135ºC prior to compaction with the condition that they be stirred and turned every hour. This was found to represent the condition during mixing and placing and also represents less than 2 years in service for dense mixtures.

The recommended procedure for long-term ageing is to age compacted mixture, previously subjected to short term oven ageing, specimens in a forced-draft oven for 5 days at 85°C. Measurements on the aged specimens included resilient modulus, indirect tensile strength and dynamic mechanical analyses. Correlation with field sites (typically 5% air voids) showed that the long term oven ageing method is roughly equivalent to 5-15 years in the field depending on climate.

2.3.2.2 Weatherometer ageing (A protocol adopted by Hagos, 2008)

Hagos (2008) used in his research a weatherometer for long term ageing of porous asphalt mixture. The simulation of ageing in the laboratory was conducted under the influences of temperature, UV light, and humidity to replicate the prevailing environmental factors which have an influence on age hardening of the pavement in the field. He followed three ageing procedures in his research, which are:

- Protocol 1: Temperature ageing
- Protocol 2: Temperature + UV light ageing (the effect of UV on the ageing susceptibility or degradation),
- Protocol 3: Temperature + UV light + moisture/humidity ageing (combined influences of weathering actions)

The first two protocols were conducted using cylindrical specimens. The third protocol was performed with asphalt beams cut from a PA slabs. Table 2.1 below shows the test conditions in detail.

Table 2.1: Ageing protocols and conditions used by Hagos

Ageing Protocols	Exposure conditions			
	UV light (300-400nm) (W/m^2)	Humidity (%)	Temperature (^{0}C)*	Duration (hours)
Protocol 1	–	–	60	1000
Protocol 2	60	–	60	1000
Protocol 3	60	70	60	1000
*temperature at the surface of the specimen				

Hagos (2008) compared results of laboratory ageing procedure (both the weatherometer and the standard ageing procedures) with results from field ageing of porous asphalt. It was found that the laboratory ageing methods are not as severe as the long term field ageing of porous asphalt. The long term laboratory ageing of bitumen using the standard ageing procedure and the new mixture ageing protocol 3 seem to predict only the ageing characteristics of the field binder after construction and 3 years service, respectively. The binders recovered from the mixture ageing under ageing protocol 1 and 2 in the laboratory have resulted in even less severe ageing compared to the standard binder ageing method and ageing protocol 3.

2.3.2.3 The RILEM TC-ATB-TG5 mixture ageing method

Recently under the framework of the RILEM technical committee of advanced testing of bituminous materials (ATB), a new experimental laboratory ageing procedure for asphalt mixtures has been developed aiming at reproducing the ageing of bituminous materials until the end of the service life(C. de la Roche 2009). The protocol is divided in short and long term ageing protocols to simulate the two phases of ageing. For both cases it is proposed to age the loose asphalt mixture. The procedures are:

- For short term ageing process, the loose mix is placed in an air-draft ventilated oven for 4 hours at 135°C. Each hour the material is stirred for 1 minute and placed back into the oven. The stirring action is only for homogenization.
- The long term ageing procedure includes the ageing of the short term aged loose mixture by placing it in air ventilated oven at 85°C for 9 days. The procedure recommends taking samples and stirring the mixture after 2, 5, 7 and 9 days.

As this test protocol is in its experimental stage, comparisons with field ageing data were not available and not found at the time of writing this literature review.

2.3.2.4 The New Zealand test method for compacted open graded porous asphalt

A new laboratory test method has been developed in New Zealand to assess the durability of open graded asphalt mixes in the field. The test involves conditioning loose mix at 125°C (or the appropriate plant mixing temperature) for two hours to simulate oxidation during manufacture and handling. The conditioned mix is compacted into standard Marshall test sized specimens (100 mm diameter and 65mm height), which are heated at 80°C and kept at this temperature for three days (72 hours) under 2070 kPa air pressure by using a pressure vessel (Herrington 2005).

According to Herrington et al, comparison of the viscosity of the recovered binder from field samples of aged open graded porous asphalt shows that the procedure results in oxidation approximately equivalent to 4.5 years in the field. The effect of binder oxidation on the abrasion resistance of the mix is measured with the cantabro test (300 revolutions at 30 rpm and a temperature of 25°C).

One of the main concerns from previous researchers was the possibility that the use of high air pressure in the test may mechanically damage the compacted specimens. Herrington et al mentioned in their report that although no visible damage occurred, specimen dimensions increased slightly. To find out if this was significant they have tested specimens by using an inert nitrogen atmosphere at 2070 kPa to preclude oxidation, leaving other variables unchanged. They compared the mass loss after the cantabro test on Nitrogen treated specimen with un-oxidized specimens and the results showed no significant difference. They concluded that the damage caused by the use of high pressure is negligible.

2.4 Conclusion from the literature review

Major conclusions or lessons learnt from the literature review are:

- Raveling is the main form of distress of porous asphalt. Age hardening of the binder is the main reason for raveling failure of porous asphalt. Raveling might be caused by cohesive failure of the bituminous mortar or by adhesive failure in the binder aggregate interface or a combination of both.
- Asphalt ageing is generally classified into two phases short term and long term ageing. Short term ageing occurred during the production and construction phase and long term ageing is predominantly a continuation of the oxidation process during the service life of the pavement. A considerable amount of ageing happens during hot mix asphalt production. For laboratory accelerated ageing test, this entails the need to apply short term ageing before conducting long term ageing test.
- The ageing characteristics of binders are affected by the type of mineral aggregate with which they come into contact and thus age hardening is influenced by both the bitumen and the mineral aggregate. Therefore, in laboratory accelerated ageing test it is wise to age the asphalt mixture or the mortar so that effects of aggregate and/or fillers can be included.
- Ageing changes the rheological, mechanical, and chemical properties of the binder and the mechanical properties of the mix. The changes in property of

the binder and asphalt mixture can be quantified by means of ageing indicators. Ageing indicators commonly used in practice are either empirical parameters describing change in binder property, fundamental properties designating change in the viscoelastic behavior of the binder or a measure of the change of binder chemical composition indicating the change in colloidal structure after ageing. Consequently, the ageing indicator tests selected to be used in this research include the rheological, mechanical and chemical tests.

- The standard laboratory accelerated ageing test methods are not as severe as the long term field ageing of porous asphalt. The long term laboratory ageing of bitumen using the standard ageing procedure seems to predict only the ageing characteristics of the field binder after construction of porous asphalt. This necessitates the need to develop an ageing protocol which is severe than the standard ageing test methods.

2.5 Preliminary Ageing Protocols proposed to be used in this research

Based on the literature review and experience from laboratory ageing test by others, three ageing protocols have been proposed to be used in this research as a starting point. The first protocol focuses on ageing of mortar (a mixture of bitumen, filler and sand fraction passing sieve size less than 0.5 mm). The sand fraction less than 0.5 mm has been adopted because in previous research carried out at TU Delft aggregates smaller than 0.5 mm were observed to segregate during mixing and were defined as a mortar and asphalt mixture greater than 0.5 mm has been considered as aggregate skeleton (Muraya 2007). The two other protocols deal with aging of asphalt mixtures. In the following paragraphs the three proposed preliminary accelerated laboratory ageing protocols to be deployed in this research are explained.

2.5.1 Ageing Protocol 1 (ageing of mortar)

Protocol one is about ageing of mortar by using the pressure ageing vessel. The mortar has been prepared according to NEN-EN-12697-35+A1 (the percentage composition of materials and detailed explanation on preparation of test samples are explained in chapter 3). First, materials (bitumen, filler and sand) are mixed at a temperature of 155 ºC for 3 minutes (the temperature has been adopted after consultation with BAM). This is just to make the mortar ready for short term ageing.

- After preparation of the mortar, 50 g has been poured in to a circular plate of diameter 140 mm. The sample was subjected to a short term ageing (STA) at a temperature of 165 ºC in an oven for a duration of two hours.
- Subsequent to a short term ageing, a pressure ageing vessel (PAV) with a temperature of 80 ºC and a pressure of 2.1 MPa (300 psi) has been used for 7 days for long term ageing (LTA) of the specimens.
- After LTA the specimens have been heated by oven at a temperature of 150 ºC for 30 minutes to ease the removal of the aged samples from the circular plates.

2.5.2 Ageing Protocol 2 (ageing of compacted asphalt mixture)

This ageing protocol concerns with ageing of a compacted mixture by using a pressure aging vessel. A standard method depicted in NEN-EN-12697-35+A1 has been used to prepare a loose asphalt mixture. Then the loose asphalt mixture has been placed in an oven with a temperature of 135 ºC for 4 hours (short term ageing). Every hour the mix has been turned and stirred. Then the short term aged mix has been heated up to a temperature of 155 ºC and compacted with gyratory compaction to produce a cylindrical specimen of 100 mm diameter and a thickness of 50 mm. These compacted specimens are placed in a pressure ageing vessel with a pressure of 2.1 MPa for duration of 7 days. During this period, the temperature is increased step by step (70 ºC for the first 3 days and 80 ºC for the last 4 days).

2.5.3 Ageing protocol 3 (ageing of a loose asphalt mixture)

In this protocol, the aging procedure from RILEM TC-ATB-TG5 has been adopted. The only deviation from this technical group procedure is the mixture used for ageing was 5 kg instead of 15 kg in a steel box with a dimension of 50 cm *30 cm * 8 cm. The weight is reduced to minimize the thickness of the loose mixture so that it gives higher ageing. The protocol is described below:

- For short term ageing, the loose mix is placed in an air-draft ventilated oven for 4 hours at 135 ºC. Each hour the material is stirred for 1 minute and placed back into the oven. The stirring action is only for homogenization.
- Then the short term aged loose mixture has been placed in an air ventilated oven at a temperature of 85 ºC for duration of 7 days (long term ageing).

2.6 Research plan

The research plan includes, for the first trial, laboratory ageing of mortar and porous asphalt mixture using the accelerated laboratory ageing test protocols mentioned in the preceding sections.

In the mortar ageing test (protocol 1), binder recovery follows directly after long term ageing for further tests (rheological and chemical tests). Rheological tests on the binder proposed in this research are; penetration, ring and ball and DSR (complex modulus and phase angle) tests. Fourier transform infrared spectroscopy (FTIR) is selected for chemical test on the binder. Moreover, Wilhelmy plate test is chosen to determine the adhesion characteristics of the aged binder.

For a mixture ageing test (protocol 2 and 3), two mechanical tests have been selected to be conducted after long term ageing. These are: a stiffness test using the repeated load indirect tensile test (RLITT) and a strength test using the indirect tensile test (ITT). After the mechanical tests, the binder will be recovered from the specimens for the same purpose as in protocol 1 (similar binder tests mentioned for protocol 1 will be conducted).

Finally, test results (from binder and a mixture) will be compared to similar test results of reference materials. The reference materials are; 70/100 pen virgin bitumen, and 10 years field aged porous asphalt mixture. After comparison of test results of laboratory aged material with 10 years field aged reference materials, a test protocol which gives the most promising results is proposed. The flow chart in Figure 2.7 shows the above explained research plan.

A standard binder recovery procedure will be used in this research. However, there is a concern that solvents used for binder recovery may have some influence on the recovered binder. To determine the effect of the binder recovery, a test scheme has been proposed to be deployed in this research. This test is schematically shown in Figure 2.7.

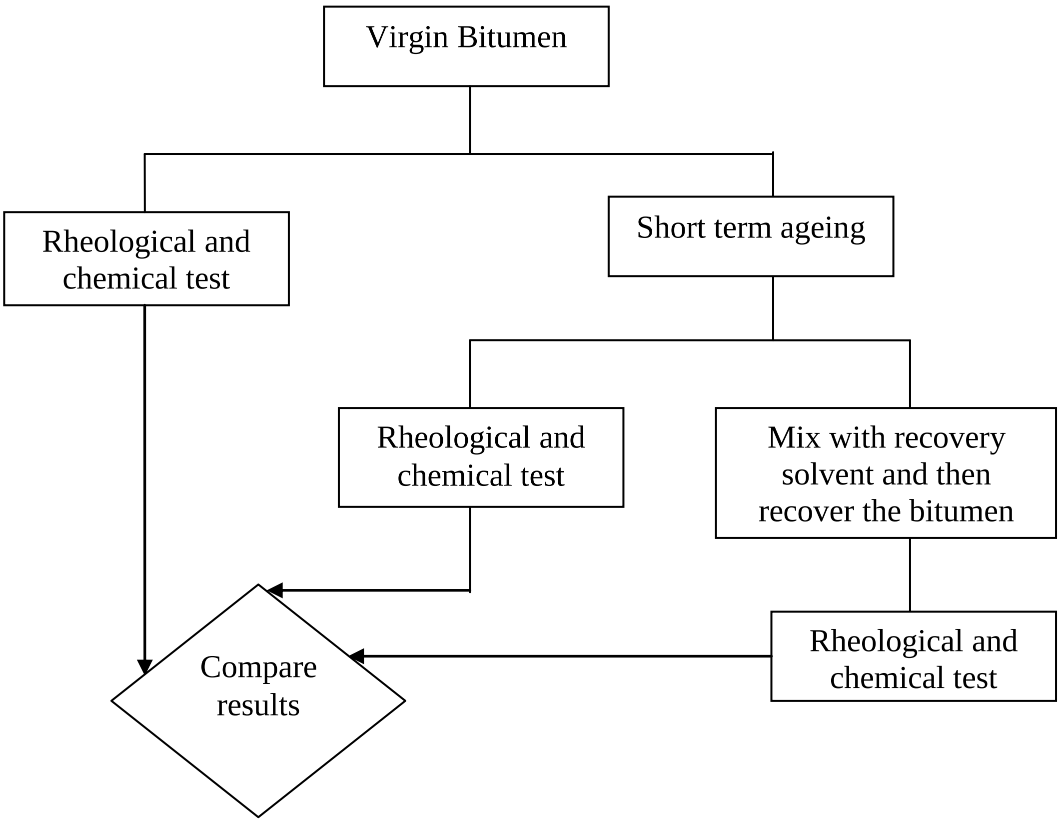


Figure 2.7: Test scheme to determine the effect of binder recovery on the recovered bitumen

The effect of the binder recovery solvent can be easily detected by comparing the three rheological and chemical composition results, i.e. results from virgin bitumen, short term aged bitumen and short term aged then mixed with the recovery solvent and finally recovered bitumen. For short term ageing (STA), the rotating thin film oven test (RTFOT) has been used and the FTIR test was used to determine the chemical composition. Penetration, softening point, and DSR tests are the selected rheological tests to be conducted.

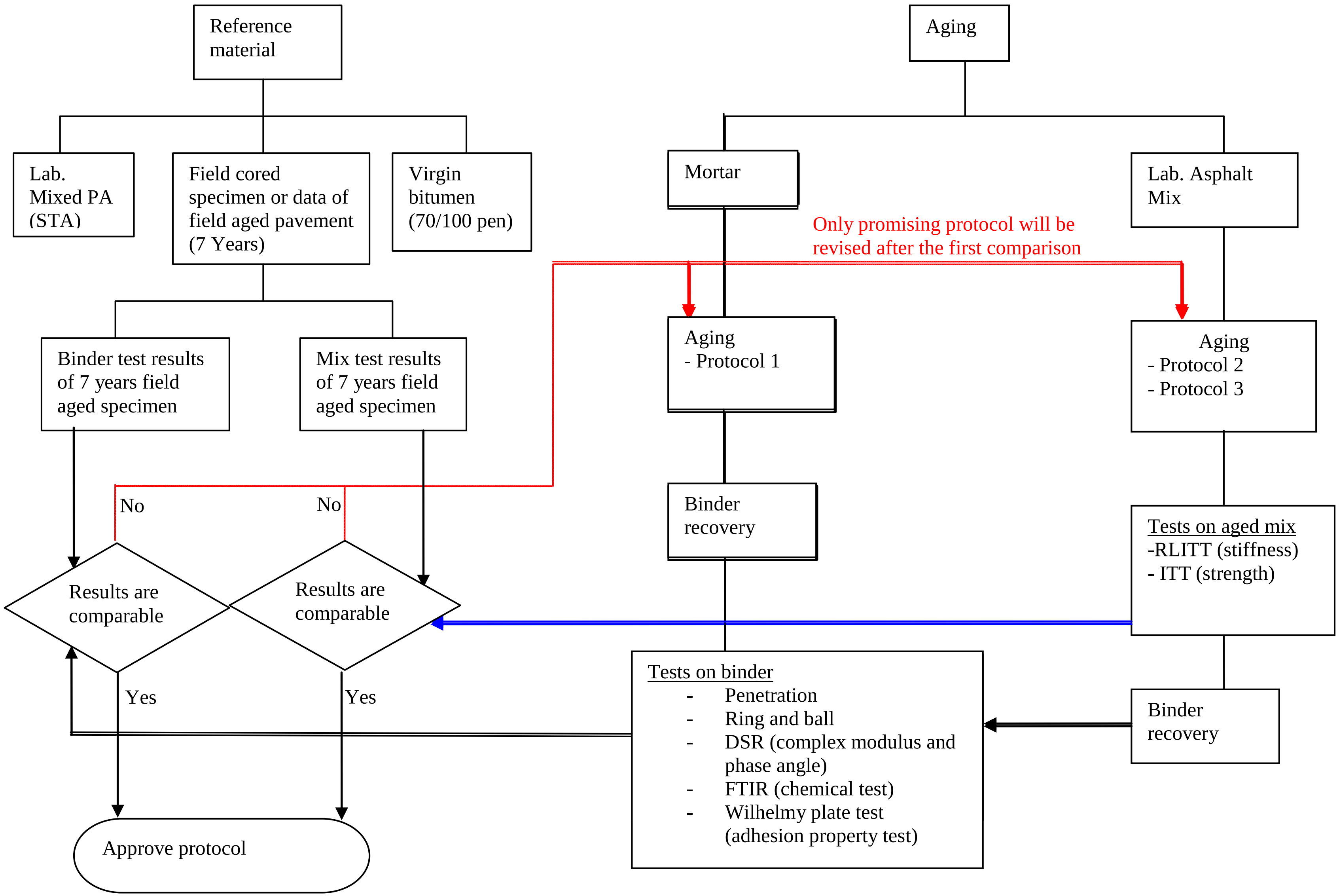


Figure 2.8: Flow chart for the research plan

Chapter 3 Materials and Test Methods

In this chapter a summary and detailed description is given of the materials used in this research. Also attention is paid to the preparation of specimens, the aging methods, testing conditions and test methods.

3.1 Materials

The materials used in this research are the same as the materials used to construct porous asphalt pavement layers. All the materials used in this research are obtained from BAM Wegen, Utrecht. BAM provided field cores, the virgin bitumen, aggregate, sand and filler. as well as the mix design of laboratory prepared specimens and the properties of field cored materials used in this study will all be described in the following section.

3.1.1 Bitumen

A penetration grade virgin binder 70/100 was used in this study. The binder was a product of TOTAL Nederland N.V. The properties of the virgin bitumen are given in Table 3.1 below:

Table 3.1: Virgin asphalt binder properties

Binder Grade	Penetration [0.1 mm]	Softening Point in ºC	Penetration Index	Density [kg/m^3]
70/100	70	44.6	-1.9	1.035

3.1.2 Aggregates, Sand and Filler

BAM delivered crushed moraine aggregate, crushed granite sand, and Wigro 60K fillers.

The virgin aggregate used in this study consisted entirely of a crushed moraine aggregate. The sampled aggregates were transported to the laboratory of Road and Railway Engineering section, TU Delft. The samples were oven dried to a constant mass and sieved. Aggregate size fractions separated during the sieving operation were then stored in individual containers until recombined by mass batching in order to satisfy a specified gradation for asphalt mixture sample fabrication. Table 3.2 shows the density of each aggregate fraction.

Table 3.2: Density of crushed aggregate fractions

Material Fraction [mm]	**Density [kg/m^3]**
Stone 11/16	2650
Stone 8/11	2659
Stone 4/8	2665

The type of sand used in this study was a crushed granite sand fraction in the range from 0.063 - 2 mm (The sand gradation is shown in Table 3.3). The sampled sand was transported to the laboratory of Road and Railway Engineering section, TU Delft, where it was oven dried to a constant mass for further use. The density of the sand and the filler are shown in Table 3.4.

Table 3.3: Crushed granite sand gradation

Sieve size (mm)	**% retained**	**Cumm. % retained**
2	6.4	6.4
0.5	59.5	65.9
0.18	23.1	89
0.063	9.2	98.2
<0.063	1.8	100

Table 3.4: Density of sand and filler

Material	**Density [kg/m^3]**
Crushed granite sand	2650
Filler (Wigro 60K)	2570

3.1.3 Field cored porous asphalt specimens

In order to compare field ageing with accelerated laboratory ageing, cores were taken from a porous asphalt (PA) pavement taking into account age or service period of the pavement. Specimens from 10 years of field aged porous asphalt pavement were cored and used as reference material.

The cores were taken from one motorway in order to ensure that they were all exposed to similar conditions in the field. The A4 motorway near Burgerveen was chosen for the sampling of the specimens. All the cores were taken from the emergency lane (shoulder) of the pavement in order to avoid the effect of traffic load and noxious waste.

To get enough amount of recovered bitumen from the field cored samples, a total of 30 cores were taken i.e. 20 cores with a diameter of 100 mm and 10 cores with a diameter of 150 mm. The total height of the cores was about 35 cm, and the PA layer has been separated from the rest of the pavement layers by sawing. From the total height of field cores the PA layer is roughly 50 mm.

Mechanical tests were performed on the field specimens before recovering the bitumen. The results of these tests and their interpretation are presented in the next chapter. The binder of the field core specimens has been recovered for physical and chemical characterization. The field PA specimens were cut into two segments the upper and lower parts (Figure 3.1) and the binder recovery process was conducted separately for these two parts of the specimens. In this research the upper part of the porous asphalt layer is given special attention since raveling takes place at the surface of the pavement.

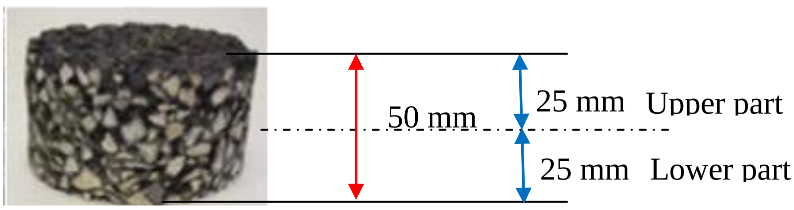


Figure 3.1: The upper and lower part of field specimens

3.2 Material preparation for laboratory accelerated ageing tests

The material preparation can be broadly categorized into two main groups based on the type of specimens to be aged. The first group dealt with ageing of the mortar (protocol 1, protocol 1A and protocol 1B) and the second one was dealing with ageing of the porous asphalt mixture (protocol 2 and protocol 3). These protocols were discussed in detail in Section 2.6. In the subsequent sections, material preparations for different ageing protocols are explained:

3.2.1 Specimen for ageing protocols 1, 1A and 1B

The mortar used in this study consisted of bitumen, filler and fine sand (sand less than 0.5 mm) mixed at a mass ratio shown in Table 3.5. The fine sand used to prepare the mortar is smaller than 0.5mm. The reason for this is that according to previous research in TU Delft, it was found that the aggregate skeleton of porous asphalt only consists of aggregates larger than 0.5mm (Muraya 2007).It means that the mortar in porous asphalt can be defined as a mixture of bitumen and any of aggregates smaller than 0.5mm. The sand percentage (m/m) in the mortar has been determined by using the total sand percentage in the asphalt mixture recipe delivered by BAM Wegen (Figure 3.2) and by multiplying this value with the percentage of sand fraction less than 0.5 mm from the sand gradation (Table 3.3). The final mix composition for the mortar is shown in Table 3.5 below:

Table 3.5: Percentage composition of materials in the mortar (m/m)

Material	***% composition (m/m)***
Sand (< 0.5 mm and $\geq$ 0.063mm)	28.4
Filler (Wigro 60 K)	34.1
Bitumen (70/100)	37.5
Total	100

The mortar has been prepared according to NEN-EN-12697-35+A1 standard “Bituminous mixtures - test methods for hot mix asphalt - part 35: Laboratory mixing”. The dry filler and fine sand have been heated in the oven at a temperature of 160°C for a minimum of 8 hours. The bitumen was heated to a temperature of 155°C and mixed with the sand and filler. The chosen temperatures were used after consulting BAM Wegen.

Immediately after mixing, 50 g of mortar is poured into a circular plate with a diameter of 140 mm (Figure 3.1). During making of the samples the bulk mix has been placed on a hot plate to keep the mortar flowing and in order to avoid segregation, it has been stirred well before pouring on a plate.

Figure 3.2: Mortar sample on a circular plate of diameter 140 mm

3.2.2 Specimen for ageing protocols 2 and 3

The mix recipe used to produce porous asphalt mixtures for both protocol 2 and 3 is obtained from BAM Wegen. The same mix recipe has been used to produce mixtures of the porous asphalt pavement constructed 10 years back in the road section where the reference specimens were cored. In this way it was possible to compare the ageing properties of field aged and laboratory aged specimens. The material composition (mass percentage of constituent materials) is shown in Figure 3.2.

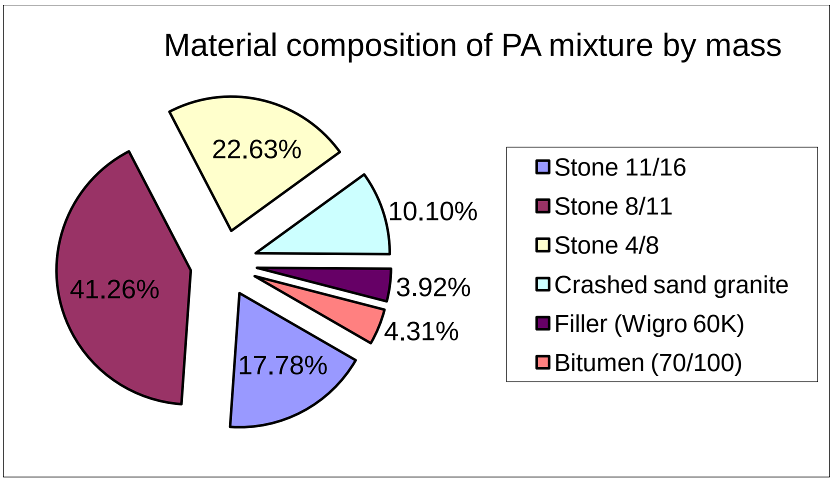


Figure 3.3: Material composition of PA mixture by mass as used in the field

The PA mixture was prepared according to NEN-EN-12697-35+A1 standard “Bituminous mixtures - test methods for hot mix asphalt - part 35: Laboratory mixing”. All the dry mineral aggregate including the filler has been heated at a temperature of 160 ºC. The mixing bowl and the bitumen are heated to a temperature of 155 ºC. Finally all the materials are brought together with the right amount and mixed for 3 minutes. The above temperatures are chosen after consultation with BAM Wegen.

For protocol 3, loose asphalt mixture of 5 kg produced in the above procedure is placed in a steel box with a dimension of 50 cm*30 cm*8 cm for ageing test. For protocol 2, the mixture is compacted by using gyratory compaction with a target void content of 21%. By considering the percentage amount and specific gravities of the constituent material, the theoretical maximum density is calculated by using Equation 3.1.

$$\rho_{\max} = \frac{100}{\sum_{i=1}^{n} \frac{P_i}{\rho_i}} \tag{3.1}$$

Where:

$\rho_{\max}$ = theoretical maximum density of the mixture [kg/m^3]

P_i = proportion (mass percentage) of constituent material i [%]

ρ_i = the apparent density of the constituent material i [kg/m^3]

n = number of constituent materials in the mixture [-]

A maximum density of 2486 kg/m^3 has been calculated for the porous asphalt mixture. The bulk density of the mixture can be easily determined from the results of the maximum density and the void content from the following relation:

$$\rho_{bulk} = \rho_{\max} - \frac{V_m * \rho_{\max}}{100} \tag{3.2}$$

Where:

$\rho_{\max}$ = theoretical maximum density of the mixture [kg/m^3]

ρ_{bulk} = the bulk density of the mixture [kg/m^3]

V_m = the air void content of the mixture (v/v) [%]

For 21% air void content, a bulk density of 1960 kg/m^3 has been computed. This value was used as a target compaction value for the gyratory compaction. First cylindrical specimens with a diameter 100 mm and a thickness of 70 mm were produced and then all the specimens were sawed and polished on both sides to a final thickness of 50 mm.

3.3 Test Methods

In this research different laboratory tests have been carried out on bitumen, mortar and porous asphalt mixture. Mechanical tests on field cored specimens, tests to see the effect of binder recovery solvent on bitumen, laboratory accelerated ageing tests and furthermore tests on recovered binder from laboratory aged mix to compare with properties of field aged binder have been conducted. In the following paragraphs a detailed description of the various test methods and the test programs is given.

3.3.1 Indirect tensile test (ITT)

Indirect tensile test has been carried out on field cored specimens according to EN 12697-23 “Test methods for hot mix asphalt – Part 23: Determination of the indirect tensile strength of bituminous specimens”. This test is sometimes called a splitting test where a cylindrical specimen is loaded diametrically by a vertical compressive load at a specified test temperature and speed of displacement. This generates horizontal tensile stresses in the vertical plane that will make the specimen crack. The tensile strength is the tensile stress calculated from the peak load applied at break and the dimensions of the specimen. For each test specimen the indirect tensile strength, ITS, was calculated according to Equation 3.3:

$$ITS = \frac{2P}{\pi DH} \qquad (3.3)$$

Where:

ITS = Indirect tensile strength, expressed in (MPa)

P = Peak load, expressed in (kN)

D = the diameter of the specimen, expressed in (mm);

H = Height (thickness) of the specimen, expressed in (mm).

The test was done on cylindrical specimens with roughly 100 mm diameter and 50 mm thickness. The recommended standard test temperature is 5 ºC, to obtain an indirect tensile break line. However, as the lower temperature properties of the aged PA pavement are critical, the thesis committee has agreed to do the test in a lower temperature. Consequently a test temperature of 1ºC has been chosen. The test specimen was brought to the specified test temperature and placed in the compression testing machine between the loading strips, and loaded diametrically along the direction of the cylinder axis with a constant speed of displacement 50 mm/minute until it breaks. Four cylindrical specimens were tested and the indirect tensile strength has been calculated for each individual specimen according to Equation 3.3 and the average value is taken as indirect tensile strength of the field cored material.

3.3.2 Repeated Load Indirect Tensile Test (RLITT)

Asphalt cores from road sections with an age of 10 years were tested using the Repeated Load Indirect Tensile Test (RLITT) according to NEN EN 12697-26, “bituminous mixtures - test methods for hot mix asphalt – Part 26: Stiffness”. The RLITT was performed to determine the resilient modulus of the asphalt specimens. The test was conducted at low stress levels not exceeding 10% of the failure stress to ensure linear response of the materials. Haversine loading 5 pulses with 3000 ms pulse repetition period were applied. The total recoverable diametrical strain was measured from an axis perpendicular to the applied load.

The tests were conducted at five temperatures and six different frequencies. The frequency of the haversine loading pulse is defined as the reciprocal value of the pulse width (f = 1/T).The test conditions are:

Temperature (ºC)	5	10	15	23	35	
Frequency (Hz)	0.5	1	2	4	8	12

Six specimens were tested at all the temperatures and frequencies. The resilient modulus test results are the average of five independent measurements performed at each combination of the test conditions for every specimen. The RLITT was performed with a Universal Testing Machine (UTM). The equipment has a temperature controlled chamber for maintaining constant temperature during the test. The specimens were conditioned at the testing temperature for a minimum of 3 – 4 hours before conducting the test. Cylinder shaped specimens with 100 mm diameter and 50 mm thickness were tested. During testing, the loading was applied along the vertical diameter of the specimen and the resulting deformations along the horizontal diameters were measured. The resilient modulus computation was performed using Equation 3.4.

$$S_{mix} = \frac{F*(\nu + 0.27)}{z*h} \tag{3.4}$$

Where:

S_{mix} = the measured stiffness modulus [MPa]

F = the peak value of the applied vertical load [N]

z = total recoverable horizontal deformation [mm]

h = the mean thickness of the specimen [mm]

ν = Poisson’s ratio

3.3.2.1 Master curve construction for the resilient modulus

A sigmoidal model was adopted to quantify the time–temperature dependency of the field materials. When asphaltic mixtures are tested in their linear visco-elastic range, the time-temperature superposition principle holds. A master curve of the stiffness of a bituminous mix at any reference temperature (T_{ref}) can be defined as the relationship between the mix stiffness and the reduced frequency. The master curves are constructed by shifting the data points obtained at test temperatures above the reference horizontally to the left (lower frequencies) and the data points obtained at test temperatures below the reference temperature to the right (higher frequencies). The data at the reference temperature remain unchanged. The resulting master curve of the stiffness composed in this way describes the time dependency of the material. The shift value required at each temperature to form the master curve describes the temperature dependency of the material.

In this study, the master curve at a reference temperature of 15 ºC was constructed from the resilient modulus results obtained at different test temperatures and loading frequencies. The shift factors were determined using the Arrhenius equation and curve fittings were done using the sigmoidal model given by Medani et al. (T.O. Medani 2004). The shift factor α_T is calculated by means of an Arrhenius type of equation:

$$\alpha_T = e^{\frac{\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)} \qquad (3.5)$$

Where:

ΔH = activation energy [J/mol]

R = ideal gas constant [8.314 J/mol.K]

T = considered temperature in Kelvin [K]

T_{ref} = reference temperature in Kelvin [K]

α_T = shift factor [-]

f_{red} = reduced frequency [Hz]

f = loading frequency [Hz]

The sigmoidal model used to fit the master curve is given as:

$$S_{mix} = a_0\left\{1 - e^{-\left(\frac{f_{red}}{a_1}\right)^{a_2}}\right\} \qquad (3.6)$$

In this formula S_{mix} is the mixture stiffness and a_0, a_1 and a_2 are regression constants. The ΔH and the values of the coefficients are obtained using the non-linear Excel Solver analysis, using solver to minimize the mean squared error of the measured and modelled mixture stiffness.

3.3.3 Bitumen recovery

To characterize and compare laboratory aged and field aged specimens, rheological and chemical tests have been conducted on bitumen samples. To do this, the binder was recovered from both laboratory aged specimens (porous asphalt mixtures and mortars) and field cored specimens. This process is called bitumen extraction. For field cored specimens, characterization of the recovered bitumen was conducted independently for the top and bottom part of the mixture and hence the binder is recovered from the top and bottom part separately. Therefore, before the extraction process the porous asphalt samples were sawed in to two parts.

The bituminous mixture was soaked in a solvent. The bitumen was separated from the sample by dissolving it in dichloromethane (Methylene Chloride) solvent. After removal of undissolved solids from the bitumen solution, the bitumen was recovered from it by vacuum distillation using a rotary evaporator.

The extraction apparatus was fitted with different sieve sizes so that during the washing process the aggregate and sand fractions retained on the different sieve sizes. The solution of the binder with solvent, insoluble filler and dust were separated in the centrifuge apparatus. The insoluble materials retained in the filter ring in the bowl. The washing process was continued approximately for 30 minutes until the solvent that comes from the sieves becomes colorless. After that the solution of the binder and the solvent were collected for further recovering process.

The recovery of the binder from the bituminous mixture was performed according to the European standard NEN-EN 12697-3 “bituminous mixtures - test methods for hot mix asphalt – Part 3: bitumen recovery: rotary evaporator”. The purpose of the binder recovery process was to separate the binder from the dichloromethane solvent for further binder testing. The bitumen was recovered with a rotary evaporator distillation apparatus (Figure 3.3). The apparatus incorporates a rotating evaporating flask, which can be operated under vacuum. It has an oil bath capable of maintaining temperatures of up to 170 ºC. During the distillation process cold water passes through the condenser so that the evaporated solvent is collected in the receiving flask. The distillation process continues until the evaporation of solvent is completed.

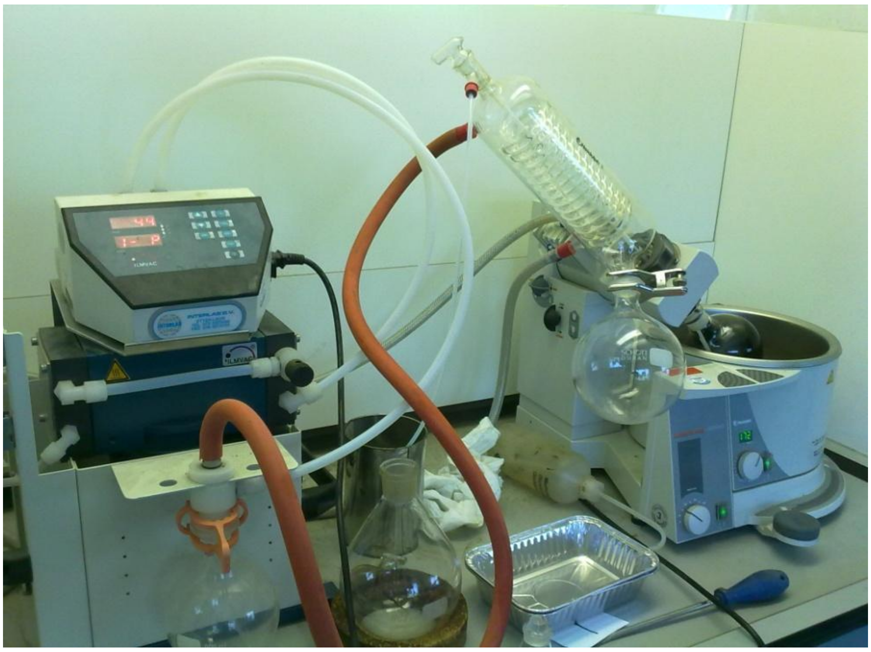


Figure 3.4: Rotary evaporator distillation apparatus

3.3.4 Penetration and Softening point

Penetration and softening point (ring and ball temperature) are empirical test methods used to describe the viscosity characteristics of bitumen. In this research these bitumen characterization methods, in combination with other properties, have been used as ageing indicators for bitumen recovered both from laboratory aged and field aged specimens.

The penetration test was done according to NEN-EN1426 "bitumen and bituminous binders - determination of needle penetration". Penetration results are expressed as the distance in tenths of a millimeter that a standard needle of 100 g penetrates vertically into a sample of the material at a temperature of 25 ºC for loading duration of 5 seconds.

The standard procedure NEN-EN 1427 "*bitumen and bituminous binders-determination of the softening point - ring and ball method*" was adopted to determine the softening point of binders. Two horizontal discs of bituminous binder, cast in shouldered brass rings have been heated at a rate of 5 ± 0.6 ºC per minute in a deionized water bath (the bath has an initial temperature of 5 ºC) while each specimen supports a steel ball on top of it. The softening point is the mean of the temperatures at which the two discs soften enough to allow each ball, enveloped in bituminous binder, to fall a distance of 25 mm.

From the standard penetration and softening point values the temperature susceptibility of the bitumen, well known as penetration index (PI), can be calculated mathematically as given in Equations 3.7.

$$PI = \frac{1952 - 500\log(pen) - 20T_{R\&B}}{50\log(pen) - T_{R\&B} - 120} \qquad (3.7)$$

Where:

Pen = penetration result [0.1 mm]

$T_{R\&B}$ = ring and ball temperature [ºC]

The PI values for bitumen used in asphalt pavement range from around -2 for highly temperature susceptible bitumen to around +2 for bitumen with low temperature susceptibility (Molenaar 2007).

3.3.5 Dynamic Shear Rheometer (DSR)

Dynamic shear tests were conducted using Dynamic Shear Rheometer (DSR) from AR Series of TA instruments. The DSR test was basically conducted to determine the viscoelastic properties i.e. the response or dependence of the materials on temperature and loading time. In this regard, the complex modulus and phase angle at different temperatures and loading frequencies were determined.

The tests were conducted on bitumen recovered both from laboratory aged and field cored specimens. Oscillating shear stress (sinusoidal loading) with constant strain at different loading frequencies are applied to samples of bitumen sandwiched between two parallel plates at different loading frequencies and temperatures. The test is carried out in a temperature controlled chamber where the temperature is controlled with air or nitrogen gas. Liquid nitrogen usage was kept to a minimum by switching from gas to liquid nitrogen only when cooling was required. The controlling mechanism and data acquisition is performed by a computer connected to the DSR equipment. Figure 3.4 shows the test equipment.

Figure 3.5: Dynamic Shear Rheometer

The test was conducted at seven temperatures (-10, 0, 10, 20, 30, 40 and 50 ºC). Every test was carried out at frequencies ranging between 0.01 – 400 rad/s. Two parallel plate geometries with a diameter of 8 mm and 25 mm were used for the test. For lower temperature (less than and including 20 ºC), the 8 mm diameter plate has been used and for high temperatures (greater than 20 ºC) a plate with a diameter of 25 mm has been used. The thickness of bitumen specimens tested was 1 mm and 2 mm for a plate diameter of 25 mm and 8 mm respectively. Before starting the test and during a change in test temperature the samples were left for a minimum period of 10 minute after reaching a test temperature for conditioning purpose.

The frequency sweep tests were performed in the region where the material response is linear. Therefore, prior to each frequency sweep test at a given temperature, a strain sweep test was performed on the same specimen to determine the linear region of the complex modulus. The frequency sweep tests were then conducted at strains level where the material response remains in the linear region.

3.3.5.1 Modeling of complex modulus and phase angle

The DSR results for complex modulus and phase angle are given for combinations of temperature and frequency. These results can be presented graphically as isotherms. A master curve can be built up from the values obtained at different temperatures and frequencies by shifting the results along the frequency scale by a shift factor. Master curves provide a fundamental rheological understanding of viscoelastic materials and allow an estimation of mechanical properties at wide ranges of temperature and frequency. A mathematical model developed by Bahia et al. (H. U. Bahia 2001) was used for constructing the master curve. The complex modulus master curve was constructed using the model given by Equation 3.8 and for the phase angle master curve Equation 3.9 was used. The determination of the model parameters (S-curve) was performed independently but simultaneously by minimizing the sum of errors of the shifted test data points with the respective models.

$$G^* = G^*_{min} + (G^*_{max} - G^*_{min}) * S \tag{3.8}$$

$$\delta = \delta_{max} - (\delta_{max} - \delta_{min}) * S \tag{3.9}$$

$$S = \left[1 + \left({}^{\omega_c}/_{\omega'}\right)^k\right]^{\frac{-m_e}{k}} \tag{3.10}$$

$$\omega' = \alpha_T * \omega \tag{3.11}$$

Where:

G^*	=	complex modulus [MPa]
G^*_{min}	=	complex modulus as ω → 0 [MPa]
G^*_{max}	=	complex modulus as ω → ∞ [MPa]
δ	=	phase angle [º]
δ_{min}	=	phase angle as ω → ∞ [º]
δ_{max}	=	phase angle as ω → 0 [º]
ω	=	frequency [rad/s]
ω_c	=	location parameter [rad/s]
ω'	=	reduced frequency [rad/s]
k, m_e	=	shape parameters [-]
α_T	=	shift factor [-]

The Williams–Landel–Ferry (WLF) formula (Equation 3.12) was also used in the model to express the temperature shift factor in this study. The time temperature superposition principle was used to generate master curves of the complex modulus and phase angle at a reference temperature of 20 ºC.

$$log\alpha_T = \frac{C_1(T-T_R)}{C_2+T-T_R} \tag{3.12}$$

Where:

$\alpha_T =$ shift factor at temperature T [-]

$T_R =$ reference temperature [º]

$C_1 =$ constant [-]

$C_2 =$ temperature constant [-]

3.3.6 Fourier Transform Infrared spectroscopy (FTIR)

3.3.6.1 Theory

Infrared spectroscopy is a widely used technique to identify functional groups in organic compounds. It is an effective method to investigate the chemical composition of materials. It is a valuable tool to identify the chemical composition of materials at molecular level. FTIR spectroscopy makes use of the Infrared part of the electromagnetic spectrum. Absorption of this lower energy radiation causes vibrational and rotational excitation of groups of atoms within the molecule.

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which infrared (IR) wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs (Wikipedia 2009)

A molecule absorbs a unique set of IR light frequencies. Its IR spectrum is often compared to a person's fingerprints. These frequencies match the natural vibrational modes of the molecule. A molecule absorbs only those frequencies of IR light that match vibrations that cause a change in the dipole moment of the molecule. Bonds in symmetric N_2 and H_2 molecules do not absorb IR because stretching does not change the dipole moment, and bending cannot occur with only 2 atoms in the molecule (Volland 1999).

The regions of an IR spectrum where bond stretching vibrations are seen depends primarily on whether the bonds are single, double, or triple or bonds to hydrogen. Table 3.6 shows where absorption by single, double, and triple bonds are observed in an IR spectrum.

Table 3.6: IR absorption for single, double and triple bond and bonds to hydrogen (University of Colorado)

Bond	Absorption region [cm^{-1}]
C-C, C-O, C-N	800-1300
C=C, C=O, C=N, N=O	1500-1900
C ≡C, C≡N	2000-2300
C-H, N-H, O-H	2700-3800

A plot of an IR spectrum shows the wavenumber ($\bar{\nu}$) on the horizontal axis versus percent absorbance (A) on the vertical axis. Alternatively, the wavelength (λ) can be used instead of wavenumber and transmittance (T) instead of percent absorbance.

A wavenumber is the inverse of the wavelength in cm:

$$\bar{\nu} = {}^{1}/_{\lambda} \qquad (3.13)$$

Where:

$\bar{\nu}$ = wave number [cm^{-1}]

λ= wavelength [cm]

Absorbance is the logarithm, to the base 10, of the reciprocal of the transmittance:

$$A = \log({}^{1}/_{T}) \qquad (3.14)$$

The infrared part of electromagnetic spectrum is divided in to three regions, i.e. near (approx. 4000– 12800 cm^{-1}), middle (approx. 200 – 4000 cm^{-1}) and far (approx. 10 – 200 cm^{-1}) infrared regions which are named with respect to their relation to the visible spectrum. The mid-infrared region is used to study the fundamental vibrations and associated structure of molecules. The “finger-print” region of the middle infrared spectrum (600 - 1800 cm^{-1}) is the most useful region to study the development of oxidation products (ketones and sulfoxides) as a result of aging of bitumen.

3.3.6.2 Test method and qualitative analysis of Infrared spectrum

The apparatus used to conduct the FTIR test was PerkinElmer spectrum 100 series FTIR spectrometer (Figure 3.5). A thin layer of binder sample that is enough to cover the tip of the crystal in the spectrometer is placed for scanning. Every time a background scan was run before scanning of the sample. The purpose of running a background scan was to take into account changes in moisture level or other occurrences that might have an influence on the testing results. The scanning was performed in the middle infrared region (600 – 4000 cm^{-1}). For every sample, a second repetition scan was conducted and the agreement between the two scans was checked. The tip of the crystal was cleaned by means of asphalt remover and acetone after every test to make it ready for the next scan. The IR test was conducted at room temperature. An absorption spectrum diagram through Fourier transformation function is produced with a computer program which is connected to the test apparatus. Alternatively the test data is also available in excel format and in a file format compatible with software called “KnowItAll” for further analysis.

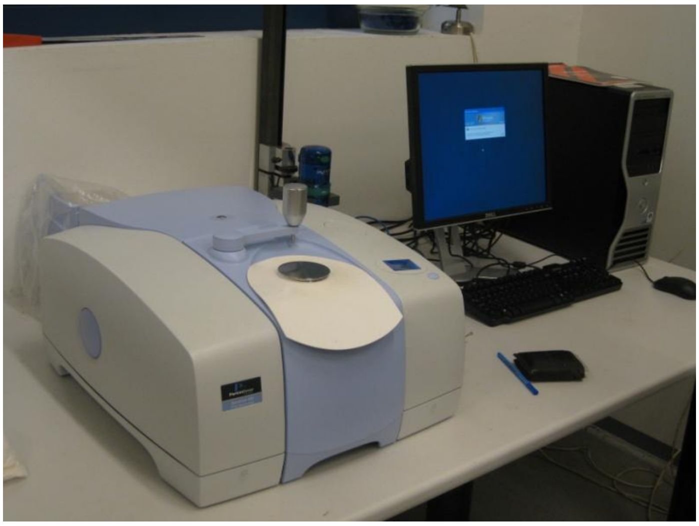


Figure 3.6: FTIR Spectrometer

The quantitative analysis of the IR spectrum of binder samples was carried out based on a relative comparison of the absorption peaks characterizing the formation of aging products, especially ketones and sulfoxides. The aging indicators at 1700 cm^{-1} (ketones C=O) and 1030 cm^{-1} (Sulfoxides S=O) are the two characteristic bands at which the peak height and the area under the peak were used for the assessment of the effect of aging of the binder samples.

According to a method used at RILEM TC-ATB-TG5 (RILEM-Technical Committee-Advanced Testing of Bituminous Materials-Task Group5) for analyzing FTIR results, the evolution of carbonyl and sulfoxides indices are assumed to well represent the evolution of oxidation inside the bitumen. Carbonyl and sulfoxides indices are defined in Equations 3.15 and 3.16 (C. de la Roche 2009).

$$Ico = \frac{Area\ around\ \ 1700\ cm^{-1}}{Area\ around\ \ 1460\ cm^{-1} + Area\ around\ \ 1375\ cm^{-1}} \qquad (3.15)$$

$$Iso = \frac{Area\ around\ \ 1030\ cm^{-1}}{Area\ around\ \ 1460\ cm^{-1} + Area\ around\ \ 1375\ cm^{-1}} \qquad (3.16)$$

Figure 3.6 below shows an example of a spectrum and the determination of the peak areas used to analyze the development of the functional groups, C=O (carbonyls/ketones) and S=O (sulfoxides), after aging.

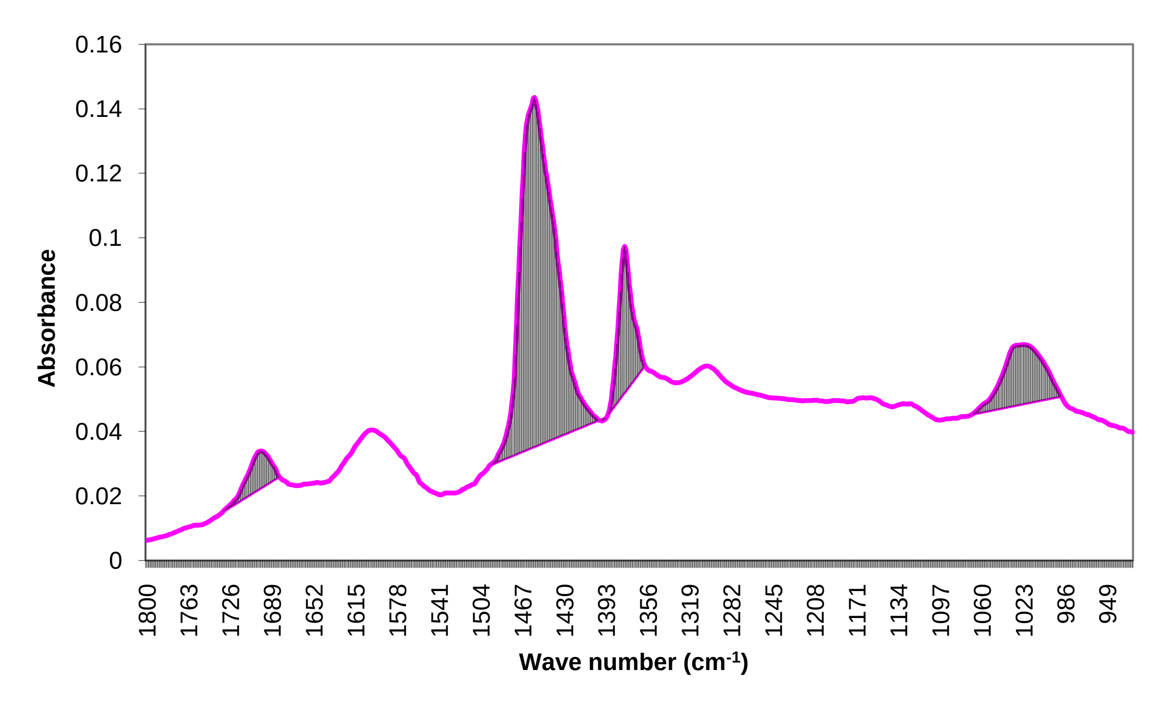


Figure 3.7: Example of spectrum resulting from FTIR analysis

The area under the peaks (shaded area in Figure 3.6 above) is bound by a baseline that connects the lowest points of the curve. The peak height determination was carried out from the tip of the curve to the base line.

3.3.7 Wilhelmy plate test

The Wilhelmy plate test has been used to assess and compare the adhesive property of bitumen regained from laboratory aged and field cored specimens. The test method uses thermodynamic theory to determine surface free energy of the material. The thermodynamic theory is based on the concept that an adhesive (for example bitumen) will adhere to a substrate (for example aggregate) due to established intermolecular forces at the interface provided that intimate contact is achieved. The magnitude of these fundamental forces can generally be related to thermodynamic quantities, such as surface free energies of the materials involved in the adhesive bond.

3.3.7.1 *Surface energy theory*

Molecules in the bulk of a material are surrounded at all sides by other molecules, and as a result these molecules have a higher level of bond energy compared to the molecules on the surface. Therefore, work must be done in order to extract the molecules from the bulk and create a new area of surface molecules. This work is equal to the surface free energy of the material. A formal definition of surface free energy is the magnitude of work required to create a unit area of a new surface of the material in a vacuum and is commonly denoted by the Greek letter Gamma (γ). The term “free energy” is used in this context since the definition is based on work done, which is different from the total excess energy. The most commonly used unit of surface free energy is mJ/m^2. The terms surface tension, surface energy, and surface free energy are often used interchangeably, although surface free energy is technically the correct term when used in the context of the principles of thermodynamics(Bhasin 2006).

Several different theories concerning the composition of the surface energy components and the derivation of the work of adhesion have been proposed. The two most popular theories are the two-component theory (Fowkes theory) and the acid-base theory.

Fowkes introduced the idea that the total surface free energy of a material is actually made up of two components. He attributed these components to dispersion forces (non-polar intermolecular interactions such as Lifshitz-van der Waals (LW) forces) and forces related to specific interactions such as hydrogen bonding. He also proposed that the total surface free energy or surface tension is a linear combination of these interactions expressed in Equation 3.17 below:

$$\gamma_{Total} = \gamma^{Dispersive} + \gamma^{Specific} \qquad (3.17)$$

This model which separates the surface free energy of materials into its components is also referred to as the two -component theory.

The other theory that is widely applied to explain the surface energy component of various materials is the Good - van Oss - Chaudhury or acid-base theory. According to this theory, the total surface free energy of any material is divided into three components based on the type of molecular forces on the surface. These components are: 1) the non-polar component also referred to as the LW or the dispersive component, 2) the Lewis acid component, and 3) the Lewis base component. The total surface free energy is obtained by combining these components as follows:

$$\gamma_l^{Total}(1 + cos\theta_{sl}) = 2\left(\sqrt{\gamma_l^{LW} * \gamma_s^{LW}} + \sqrt{\gamma_l^- * \gamma_s^+} + \sqrt{\gamma_l^+ * \gamma_s^-}\right) \qquad (3.18)$$

Where:

γ_l^{Total} = total surface free energy of liquid (test liquid used)

θ_{sl} = contact angle between solid and liquid

γ_l^{LW} = free energy of Lifshitz-Van der Waals forces of liquid

γ_s^{LW} = free energy of Lifshitz-Van der Waals forces of solid

γ_l^- = contribution of Lewis base of liquid

γ_s^+ = contribution of Lewis acid of solid

γ_l^+ = contribution of Lewis acid of liquid

γ_s^- = contribution of Lewis base of solid

For this reseach, in the above relation the solid represents the bitumen sample and the liquid represents the different liquids used for the Wilhelmy plate test. In Equation 3.18, there are three unknown surface energy components for the solid (in this research bitumen). In order to solve these unknown components, at least three liquids with different and known polarities are needed to measure the contact angles on bitumen surface. Distilled water, diiodomethane, and glycerol have been used to carry out Wilhelmy plate test in this research. The surface energy components for these liquids according to Good-van Oss-Chaudhury scale are given in Table 3.7 below.

Table 3.7: Surface energy component of reference liquids in mJ/m2 (Little, 2005)

Reference liquid	γ_l^{Total}	γ_l^{LW}	γ_l^+	γ_l^-
Distilled water	72.8	21.8	25.5	25.5
Diiodomethane	50.8	50.8	0.00	0.00
Glycerol	64.0	34.0	3.92	57.4

The surface energy components of a bitumen sample can be determined by arranging Equation 3.18 three times, one for each reference liquid, into a system of equations. In Equation 3.19 a system of equations is given for a liquid set consisting of water, diiodomethane and glycerol.

$$\left.\begin{aligned} 72.8 * (1 + cos\theta_{sw}) &= 2\left(\sqrt{21.8 * \gamma_s^{LW}} + \sqrt{25.5 * \gamma_s^{+}} + \sqrt{25.5 * \gamma_s^{-}}\right) \\ 50.8 * (1 + cos\theta_{sd}) &= 2\left(\sqrt{50.8 * \gamma_s^{LW}} + \sqrt{0.00 * \gamma_s^{+}} + \sqrt{0.00 * \gamma_s^{-}}\right) \\ 64.0 * (1 + cos\theta_{sg}) &= 2\left(\sqrt{34.0 * \gamma_s^{LW}} + \sqrt{57.4 * \gamma_s^{+}} + \sqrt{3.92 * \gamma_s^{-}}\right) \end{aligned}\right\} \qquad (3.19)$$

θ_{sw}, θ_{sd}, and θ_{sg} are contact angles measured between a bitumen sample and the reference liquids, i.e. distilled water, diiodomethane and glycerol respectively. After determining the three surface energy components of bitumen, the total surface energy can be calculated by using Equation (3.20).

$$\gamma_s^{Total} = \gamma_s^{LW} + 2 * \sqrt{\gamma_s^{+} * \gamma_s^{-}} \qquad (3.20)$$

3.3.7.2 Test method and material preparation for Wilhelmy plate test

The Wilhelmy plate test method is based on kinetic force equilibrium when a thin plate, suspended from a highly accurate balance, is immersed or withdrawn from a liquid at a very slow and constant speed. The dynamic contact angles that develop between the bitumen coated glass plates and liquids are obtained. The basic principle is schematically illustrated in Figure 3.7. The dynamic contact angle measured during the immersion process is called the advancing contact angle (a wetting process), while the dynamic contact angle measured during the withdrawal process is called the receding contact angle (Arno and Dallas, 2005).

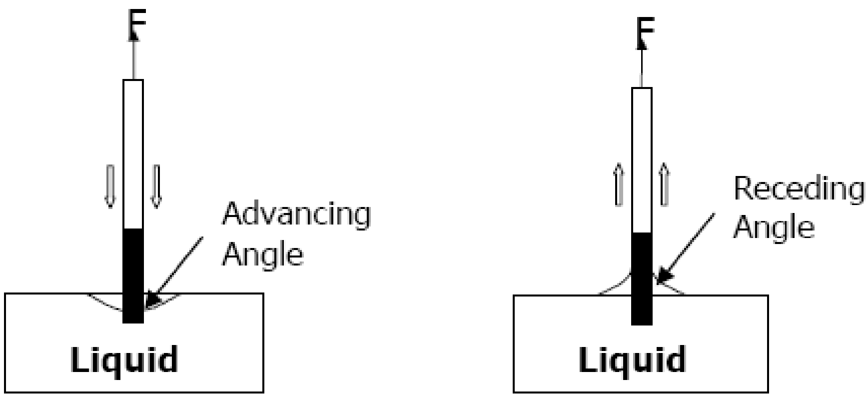
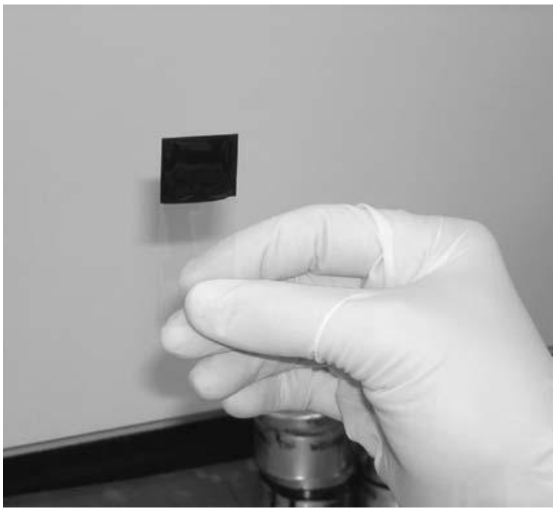


Figure 3.8: Schematic illustration of Wilhelmy plate test technique (Arno and Dallas, 2005)

To prepare the test sample, the container with bitumen and the glass slide have been heated in an oven to a temperature (app. 150 ºC) for about 1 hour. The glass slide was dipped into the molten bitumen to a depth of approximately 20 mm. The excess binder has been allowed to drain from the slide until a fairly thin layer remains on the glass slide. The slide has been turned with the uncoated end downward which gives a very thin and uniform thickness of bitumen on both sides of the slide (Figure 3.8). It is important to have a uniform thickness over its width and for at least 10 mm from the edge that will be immersed in the probe liquid to reduce variability of the test results.



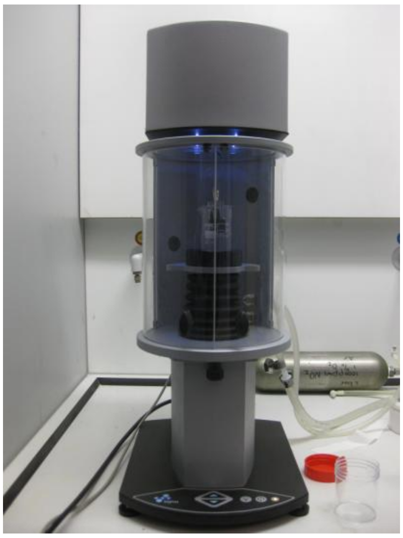


Figure 3.9: Bitumen sample (left) and tensiometer (right)

The Wilhelmy Plate test was conducted with a KSV Sigma 701 Tensiometer at the Geo Science department (Figure 3.8). A microbalance in the tensiometer measures the change in force when the bitumen is immersing into the reference liquid. Data acquisition software connected to the test setup calculates automatically the contact angle of the reference liquids and the bitumen. The relation between the change in force and the contact angle is:

$$\cos\theta_{sl} = \frac{\Delta F + V_{im}(\rho_L - \rho_{air})g}{P_t * \gamma_L^{Total}} \quad (3.21)$$

Where:

- θ_{sl} = determined contact angle of the reference liquid
- ΔF = change in force measured by the micro balance
- V_{im} = volume of bitumen coated plate immersed in the reference liquid
- ρ_L = density of the reference liquid
- ρ_{air} = density of air
- g = local constant of gravitational acceleration
- P_t = perimeter of the bitumen coated plate
- γ_L^{Total} = total surface energy of the reference liquid

Chapter 4 Results and Analysis-Preliminary ageing protocols

This chapter discusses the results and analysis of test data obtained from the first three preliminary ageing protocols examined in this study. The data analysis will compare recovered bitumen test results for the three laboratory ageing methods with field aged bitumen properties. The first ageing protocol deals with ageing of mortar by using a pressure ageing vessel at a pressure of 2.1 MPa and temperature of 80 ºC for duration of 7 days. The second ageing protocol is ageing of compacted porous asphalt mixture in pressure ageing vessel at a pressure of 2.1 MPa and temperature of 80 ºC for 7 days. The third ageing method examined was ageing of loose asphalt mixture in an air ventilated oven at a temperature of 85 ºC for 7days.

The following test results will be discussed:

- Penetration and softening point test
- Complex modulus and phase angle test (DSR test)
- Fourier Transform Infrared Spectroscopy (FTIR) test result
- Wilhelmy plate test (surface energy test)

Mechanical test (indirect tensile strength test and repeated load indirect tensile test) results obtained on field cored porous asphalt specimens are also presented in this chapter. Furthermore, test results and analysis of the effect of a standard binder extraction and recovery process on the properties of recovered bitumen are discussed in the first part of this section.

4.1 The effect of binder extraction and recovery on the properties of the recovered Bitumen

There was a concern that a standard binder recovery procedure can have a significant influence on the properties of the recovered bitumen. For that reason, a test scheme has been deployed to verify the effects of binder extraction and recovery on the recovered binder before using the standard binder recovery procedure in this research.

The virgin 70/100 bitumen used in this study has been short term aged by using RTFOT in accordance with EN 12607-1. The short term aged bitumen was divided into two halves. The first half has been sent to BAM Wegen, in Utrecht, to pass through the standard extraction and recovery process (mixing it with dichloromethane and recover the bitumen using a rotary evaporator distillation apparatus) and the other half was kept untouched. The effect of binder recovery can easily be seen (if any) from the comparison of the test results of the two samples i.e. the short term aged sample (STA) and the short term aged and then recovered sample (STA + recovered). Empirical and fundamental rheological tests as well as chemical tests have been conducted on these two samples and the results are shown below.

4.1.1 Penetration and Softening Point

The penetration and softening point results for the two bitumen samples are shown in the Table 4.1and Figure 4.1.

Table 4.1: Test results of penetration and softening point

Name	Penetration (0.1 mm)	Ring and Ball (°C)	Penetration Index (-)
Virgin	70	44.6	-1.9
STA	50	48.6	-1.6
STA + recovered	48	49	-1.6

The above values are presented graphically in the Figure 4.1 below. From the above results it can be seen that the recovered bitumen shows 2dmm decrease in penetration and with only 0.4 ºC increase in softening point temperature (which is within a measurement error). Hence, it can be said that the penetration and softening point of the short term aged and the short term aged then recovered bitumen are comparable to one each other. This shows that the effect of standard binder recovery procedure has very little effect on penetration and ring and ball results of the recovered bitumen.

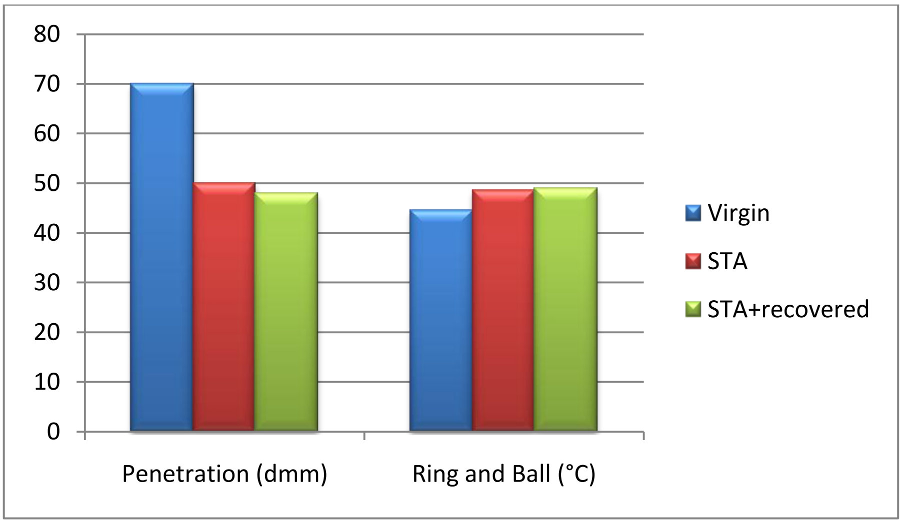


Figure 4.1: Penetration and softening point of Virgin, STA and STA+ recovered bitumen

4.1.2 Dynamic Shear Rheometer (DSR)

DSR frequency sweep tests at different temperatures (-10, 0, 10, 20, 30, 40 and 50 ºC) has been conducted for a short term aged (STA) and short term aged and recovered bitumen. A master curve with the WLF shifting (Equation 3.10) of the curves has been constructed at a reference temperature of 20 ºC for both bitumen samples. In Figure 4.2, the master curves for the two bitumen specimens are shown. Table 4.2 presents model parameters and coefficient of determination for the calculation of the master curves.

The DSR test results shown in the master curve confirm the outcome from the empirical rheological test results (penetration and softening point test result). The complex modulus for the recovered binder is slightly higher and the phase angle is somewhat lower compared to the unrecovered bitumen. Both the complex modulus and phase angle for the two bitumen samples (the STA and STA+recovered) are fairly close to each other. This shows that the standard binder recovery procedure has only a marginal effect on the rheological properties of the recovered bitumen.

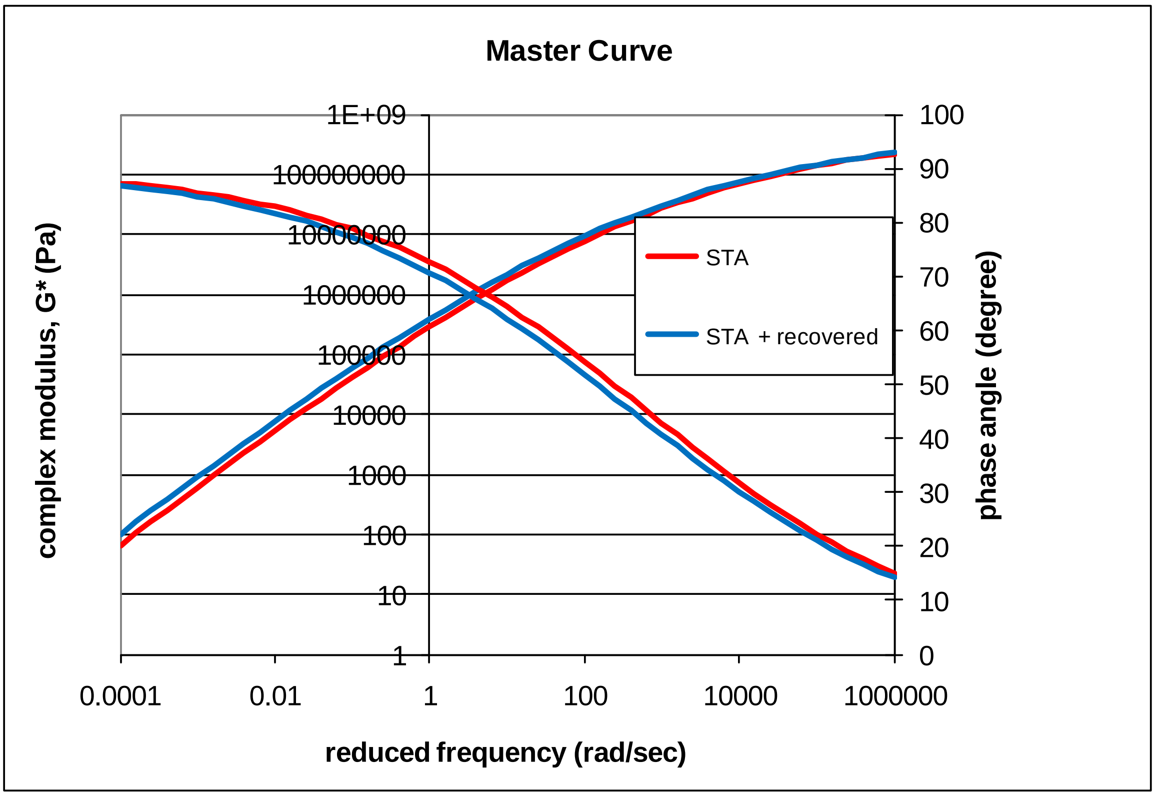


Figure 4.2: Master curves for STA and STA + recovered bitumen specimens at reference temperature of 20 °C

Table 4.2: WLF model parameters and coefficient of determination (R^2)

	STA	STA + recovered
C1	12.318	13.550
C2	104.655	108.046
R^2 G*	0.999	0.997
R^2 Phase angle	0.995	0.992

4.1.3 Infrared Spectroscopy

Fourier Infrared Spectroscopy (FTIR) test has been carried out on the short term aged bitumen sample and on bitumen recovered after short term ageing. The effect of recovery process on the chemical composition at molecular level can be seen from FTIR result. The spectrum in Figure 4.3 shows the FTIR results for the two bitumen samples.

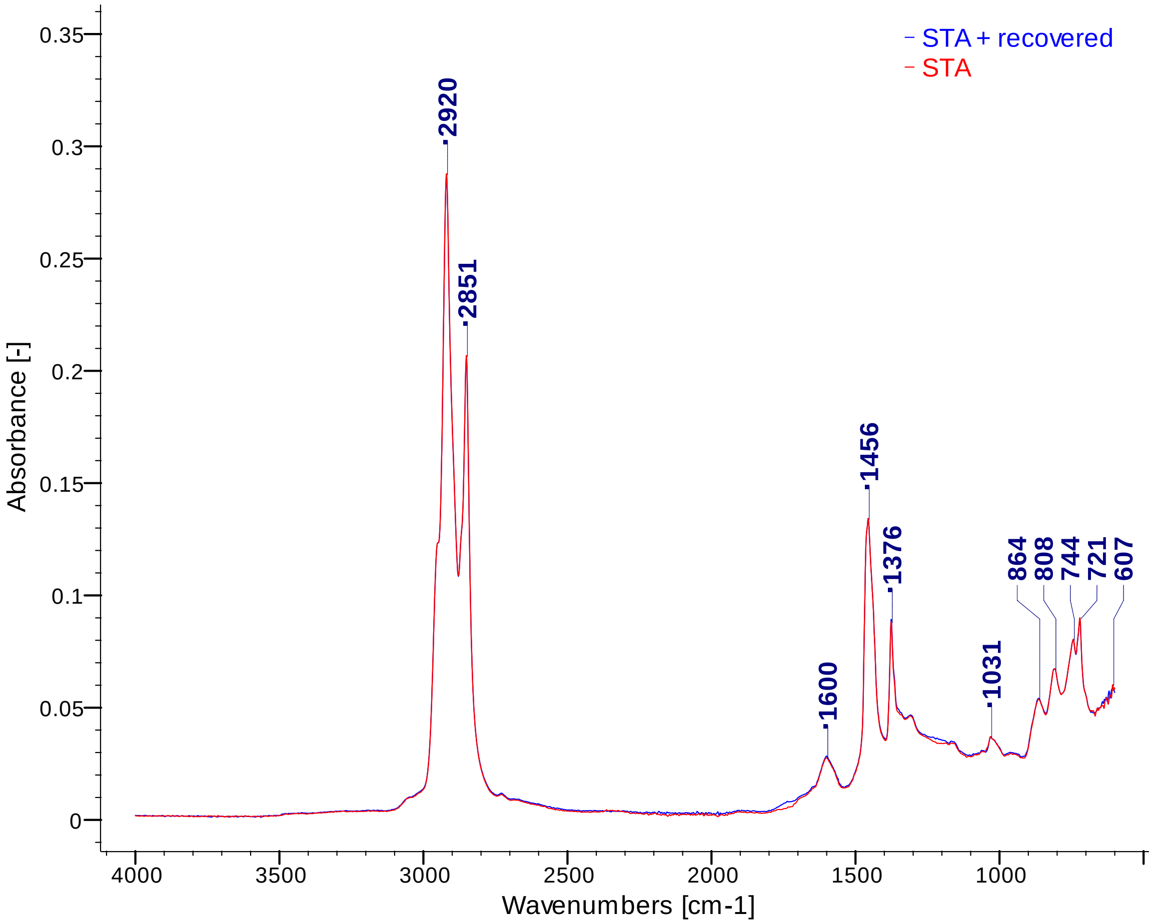


Figure 4.3: Infrared spectra of STA and STA + recovered bitumen

To see clearly the formation of oxidation products, the above spectra can be presented only in the finger-print region (Figure 4.4). The carbonyl and sulfoxides indices (Ico and Iso) in Table 4.3 are determined by using Equation (3.13) and (3.14). The carbonyl index and the result of the 1700 and 1030 cm^{-1} peak height values for the two bitumen samples are identical but the sulfoxides index value differ with only a very small margin.

Table 4.3: Ketones and sulfoxides indices and peak height at 1700 and 1030 wavenumbers

	Sample name	
	STA	STA + recovered
Ico	0.0000	0.0000
Iso	0.0321	0.0335
1700 peak height	0.0000	0.0000
1030 peak height	0.0058	0.0058

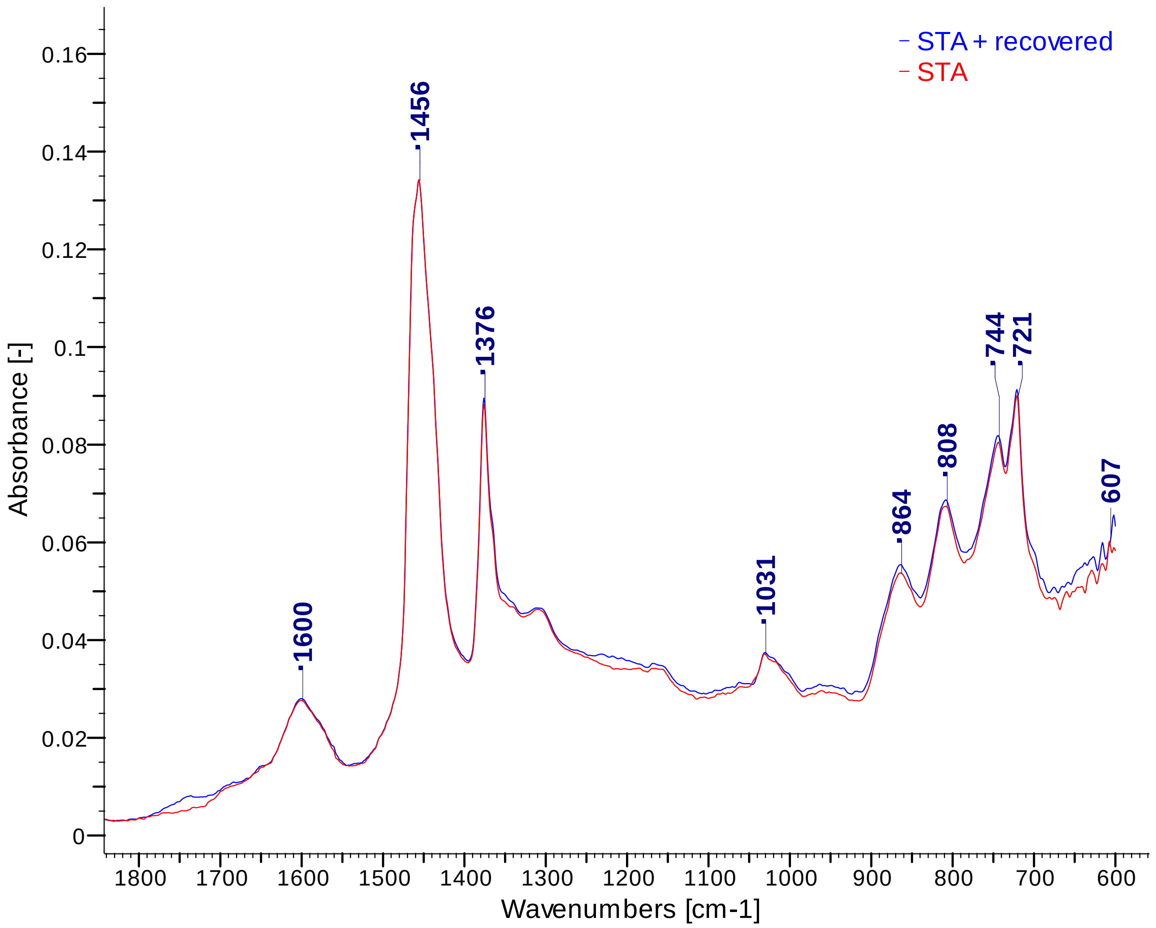


Figure 4.4: IR spectra of STA and STA + recovered bitumen in 'finger-print' region

It is clear from the above figures that the two bitumen samples i.e. the one which passes through the standard bitumen recovery process (STA + recovered) and the one which is not exposed to the recovery process (STA), have very similar FTIR results. Chemical analysis on both bitumen samples using the infrared spectrometer to determine whether there was a change in the carbonyl (C=O) and sulfoxides (S=O) peak height and peak area did not show a notable change. However, with only a slight margin the spectrum for the recovered bitumen stays on the top of the unrecovered bitumen. This test result is in agreement with the empirical and fundamental rheological test (penetration, ring and ball, and DSR test) results discussed in the previous sections.

4.1.4 Conclusion

All the above test results demonstrate that the effect of binder recovery on the properties of the bitumen is insignificant. Therefore, the standard binder recovery method can be deployed in this research.

4.2 Tests on field cored porous asphalt as a reference material

In order to compare field ageing with accelerated laboratory ageing, cores were taken from a porous asphalt (PA) pavement taking into account the age or service period of the pavement. Specimens from 10 years field aged porous asphalt pavement were cored from one major road in order to ensure that they were all exposed to similar conditions in the field. The A4 motorway near Burgerveen was chosen for the sampling of the specimens. All the cores were taken from the emergency lane (shoulder) of the pavement in order to avoid the effect of traffic load and noxious waste.

Mechanical tests (strength and stiffness tests) were performed on the field specimens before recovering the bitumen. The results of these tests and their interpretation are presented in the subsequent paragraphs.

4.2.1 Indirect Tensile Strength test (ITT) results

The test was done in cylindrical specimens of 100 mm diameter and thickness of 50 mm. The Indirect Tensile Strength was measured by applying a vertical load at a constant rate of deformation of 50 mm/min. The strength test was terminated when the applied load went to zero (i.e. total failure of the specimen occurred). Indirect tensile strength test results consists the measurements of compressive vertical load and vertical displacements. The tensile strength is the maximum tensile stress calculated from the peak load applied at break and the dimensions of the specimen. For each test specimen the indirect tensile strength, ITS, was calculated according to Equation (3.3).

Indirect tensile tests on field cored porous asphalt have been conducted at a temperature of 1 ºC on four specimens and the average value was taken as indirect tensile strength. Typical force displacement curve is shown below for one of the specimens.

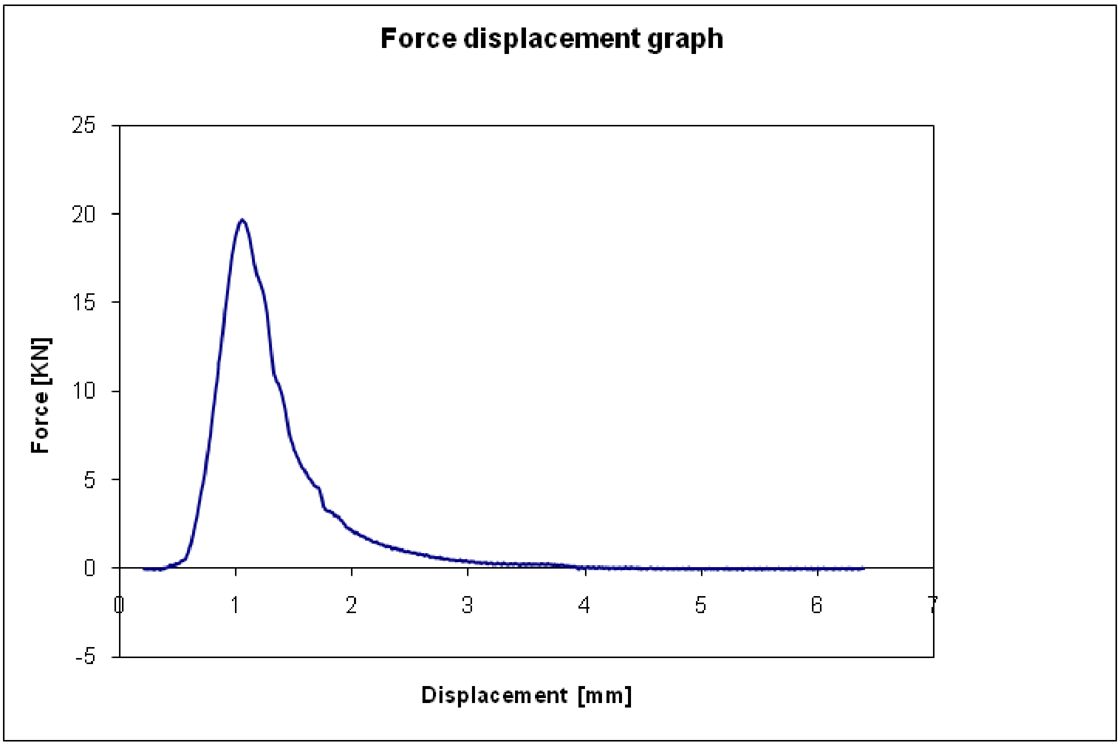


Figure 4.5: Typical force displacement graph for ITT test at 1 ºC

In Tables 4.4 and 4.5, the dimensions of the specimens and the computed indirect tensile strength are presented.

Table 4.4: Dimensions of the specimens tested

Specimen name	**Diameter (mm)**					**Height (mm)**				
	1	2	3	4	average	1	2	3	4	average
F1	101.5	101.5	101	102	101.3	49	50	50.5	49.5	49.8
F2	101.5	101.5	102	102	101.7	50	51	50.5	50	50.4
F3	101.5	101.5	101	101.5	101.3	50	49.5	49.5	51	50.0
F4	101.5	102	101	101.5	101.5	50.5	52	52	51	51.4

Table 4.5: Indirect tensile strength

Specimen name	**Peak load (kN)**	**ITS (MPa)**
F1	19.67	2.482
F2	14.66	1.821
F3	15.46	1.943
F4	21.53	2.627
Average		**2.218**

4.2.2 Repeated Load Indirect Tensile Test (RLITT) results

The RLITT was performed to determine the resilient modulus of the asphalt specimens. Cylindrical specimens from road sections with an age of 10 years were tested according to NEN EN 12697-26. The total recoverable diametrical strain was measured from the axis perpendicular to the applied load.

The resilient modulus computation was performed using Equation (3.4). The test has been conducted at a range of temperatures and frequencies. These temperatures and frequencies were selected so that it is possible to construct a master curve for resilient modulus of the samples. The test results are presented in Table 4.6 below.

Table 4.6: RLITT test results for field cored specimens

Temperature (°C)	Frequency (Hz)	Stiffness (MPa)						
		Sample name						
		F1	**F2**	**F3**	**F4**	**F5**	**F6**	**Average**
5	0.5	7210	7701	8100	8542	7789	7026	7728
5	1	7744	8193	8711	9183	8378	7413	8270
5	2	8567	8770	9519	10006	9141	8040	9007
5	4	9262	9507	10235	10790	9919	8492	9700
5	8	10589	11150	11772	12680	11386	9882	11243
5	12	11243	11517	12560	13064	12291	10077	11792
10	0.5	5782	4541	4970	5063	4418	5372	5024
10	1	6361	5062	5440	5579	4895	5861	5533
10	2	7479	5784	6128	6424	5532	6583	6321
10	4	8438	6498	6914	7268	6436	7179	7122
10	8	10110	7789	8052	8418	7616	8216	8366
10	12	11035	8730	8943	9599	8655	8752	9285
15	0.5	2940	3025	3600	3376	3187	3218	3224
15	1	3359	3385	4070	3795	3628	3608	3640
15	2	4032	3986	4742	4524	4352	4210	4307
15	4	4974	4852	5735	5530	5162	4971	5204
15	8	5969	5847	6829	6635	6210	5856	6224
15	12	6899	6486	7766	7422	7041	6459	7012
23	0.5	1224	1234	1246	1116	1210	1081	1185
23	1	1466	1477	1472	1269	1443	1300	1404
23	2	1908	1938	1960	1671	1875	1686	1839
23	4	2466	2534	2612	2262	2415	2223	2418
23	8	3209	3259	3374	2919	3191	2890	3140
23	12	3699	3851	3975	3617	3710	3390	3707
35	0.5		356	409	385	543	498	438
35	1	315	438	532	478	684	588	505
35	2	348	688	780	674	913	839	707
35	4	474	965	1019	938	1184	1104	947
35	8	717	1309	1359	1441	1541	1580	1324
35	12	652	1493	1821	1673	1802	1797	1539

The average values of the six test specimens have been used to construct the stiffness master curve at a reference temperature of 15 ºC by using the sigmoidal model (section 3.3.2.1) and the Arrhenius equation for the determination of the shift factor. The model parameters describe the curve of the shifted rheological data and are determined by minimizing the sum of deviations between the data and the model.

Material	ΔH (kJ/mol)	Model parameters [-]		
		a_0	a_1	a_2
Field cored specimen	236.72	14067.74	52.13	0.302

The fitted data (the master curve) at a reference temperature of 15 ºC is shown in Figure 4.6 for a porous asphalt specimen from road section with a service life of 10 years. The plot of the logarithm of the shift factor vs. temperature is presented in Figure 4.7.

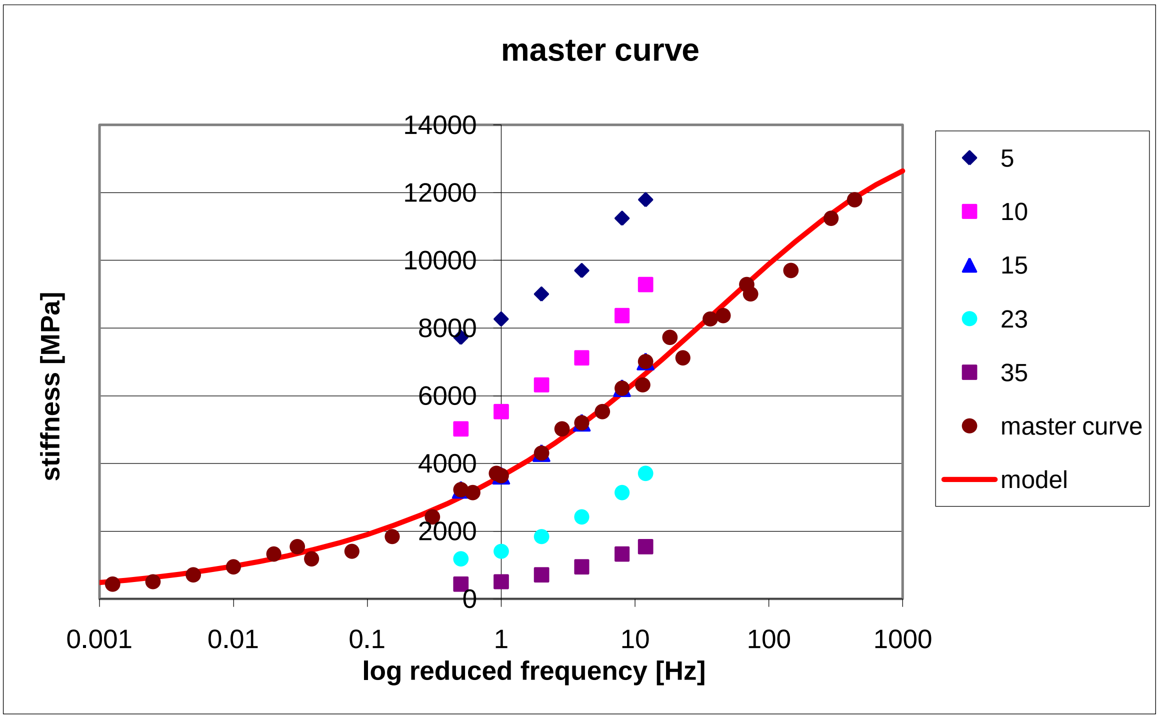


Figure 4.6: Stiffness master curve at reference temperature of 15 °C for field cored specimen

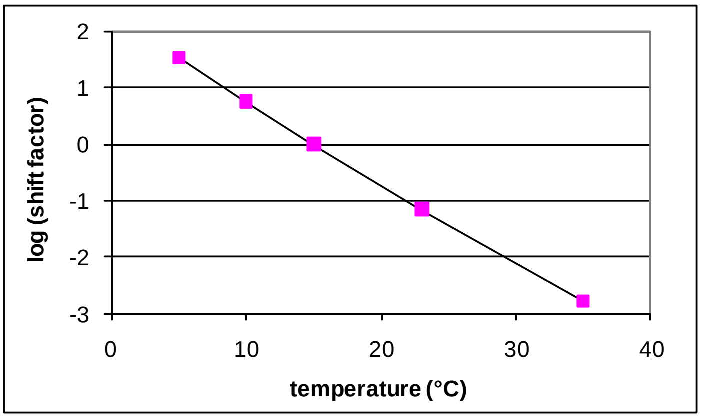


Figure 4.7: The logarithm of shift factor vs. temperature for Tref = 15 °C

4.3 Comparison of preliminary ageing protocols with field result

After the mechanical tests on field cored specimens were performed, the binder has been recovered for physical and chemical characterization. The field specimens were cut into two segments the upper and lower parts and the binder recovery process was conducted separately for these two parts of the specimens. In this research the upper part of the porous asphalt layer was given special attention since raveling takes place at the surface of the pavement.

The recovery of the bitumen from specimens aged under laboratory ageing protocols was conducted in the same manner as the recovery of bitumen from field materials. So, the correlation of the binder properties will be based on the same approach which avoid any bias with respect to the effects of recovery procedure on the binder property.

Three preliminary accelerated laboratory ageing protocols (Protocol 1, Protocol 2 and Protocol 3) are examined in this section. The ageing protocols are explained in detail in section 2.5. The results of rheological, mechanical, chemical and adhesion tests performed on laboratory aged bituminous materials are presented and compared to field aged materials. Based on the analysis of the results, the most promising laboratory accelerated aging protocol will be selected.

From the three preliminary proposed ageing protocols, protocol 2 failed the competition at the early stage of the race. In this ageing protocol the loose asphalt mixture has been placed in an oven with a temperature of 135 ºC for 4 hours (short term ageing). Every hour the mix has been turned and stirred. Then the short term aged mix has been compacted by means of gyratory and placed in a pressure ageing vessel with a pressure of 2.1 MPa for 7 days. During this period, temperature was increased step by step (70 ºC for the first 3 days and 80 ºC for the last 4 days).

After 7 days it was found that the specimens were highly deformed/damaged and bitumen was drained to the bottom of the plate. Figure 4.8 below shows the damaged specimens after the test.

Figure 4.8: Damaged specimens from ageing protocol 2

Recovery of bitumen was not carried out on specimens from protocol 2 and therefore it was not possible to make a comparison with field data. In this study protocol 2 is no more a candidate as ageing protocol to simulate field ageing. Consequently, only the results from protocol 1 and protocol 3 are discussed in the subsequent paragraphs. In the next paragraphs the brief descriptions of these two ageing protocols are given:

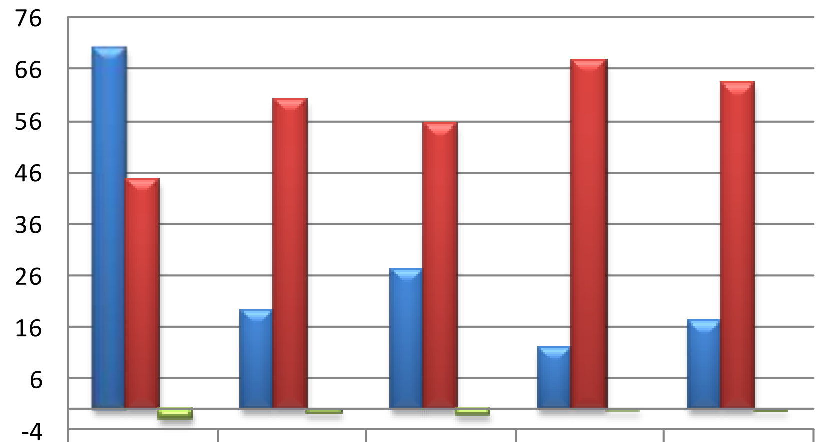
Protocol 1(ageing of mortar) i.e. 50 g of mortar has been poured into a circular plate with a diameter of 140 mm. The sample was subjected to a short term ageing (STA) in an oven at a temperature of 165 ºC for two hours. After that the short term ageing, a sample has been placed in a pressure ageing vessel (PAV) at a temperature of 80 ºC and a pressure of 2.1 MPa (300 PSI) for 7 days.

Protocol 3 (ageing of loose asphalt mixture) i.e. 5 kg of loose mixture has been placed in oven for 4 hours at a temperature of 135 ºC for short term ageing. Every hour it has been stirred and turned for uniformity. Following the STA, the loose mixture is subjected to a long term ageing protocol by placing it in an oven at a temperature of 85 ºC with good air ventilation for 7 days.

4.3.1 Penetration and Softening Point

The materials presented in this section include virgin bitumen, bitumen recovered from specimens aged in the laboratory and bitumen recovered from field specimens. The penetration and softening point results for all the materials including penetration index (PI) values are given in Figure 4.9.

From the test results it can be seen that the penetration and softening point result for binder recovered from the upper and the lower part of the field porous asphalt specimens show differences in the viscosity characteristics. It is apparent that the upper part has a lower penetration and higher ring and ball temperature compared to the lower part of the field porous asphalt pavement. This means that the upper part shows a higher degree of ageing compared to the lower part of porous asphalt. The upper part has a penetration which is 29.4% lower and a softening point which is 7.3% higher relative to the lower part.



	Virgin	Protocol 1	Protocol 3	Field aged upper part	Field aged lower part
Penetration [dmm]	70	19	27	12	17
Ring and Ball [°C]	44.6	60	55.2	67.6	63
Penetration Index [-]	-1.9	-0.97	-1.3	-0.45	-0.63

Figure 4.9: Penetration and softening point test results

The penetration and softening point (ring and ball temperature) test results of laboratory and field materials reveal that the laboratory ageing protocol 1 and 3 were not severe enough to simulate the aging of the top part of porous asphalt layers in the field. However, results from ageing protocol 1 are close to the results from the lower part of porous asphalt from the field. The results from protocol 3 are far away from both the lower and upper part of porous asphalt from field.

4.3.2 Dynamic Shear Rheometer (DSR)

DSR frequency sweep test was conducted on bitumen recovered both from laboratory aged and field cored specimens. This test was basically conducted to determine the viscoelastic properties i.e. the response or dependence of the materials on temperature and loading time. In this regard, the complex modulus and phase angle at different temperatures and loading frequencies were determined. The test conditions are mentioned in section 3.3.5.

A better understanding and analysis of rheological properties of viscoelastic materials can be made with the use of master curves. Master curves allow the estimation of properties at a wider range of temperatures and frequencies. A master curve with the WLF shifting of the curves (explained in section 3.3.6) has been constructed at a reference temperature of 20 ºC. The same procedure has been adopted for all the bituminous materials in constructing the master curves. In Figure 4.10, the master curves of recovered bitumen from laboratory aged and field cored specimens are shown. The effect of aging on the rheological behavior of the materials is clear from the figure. The increase in complex modulus due to aging is accompanied by a decrease in the phase angle

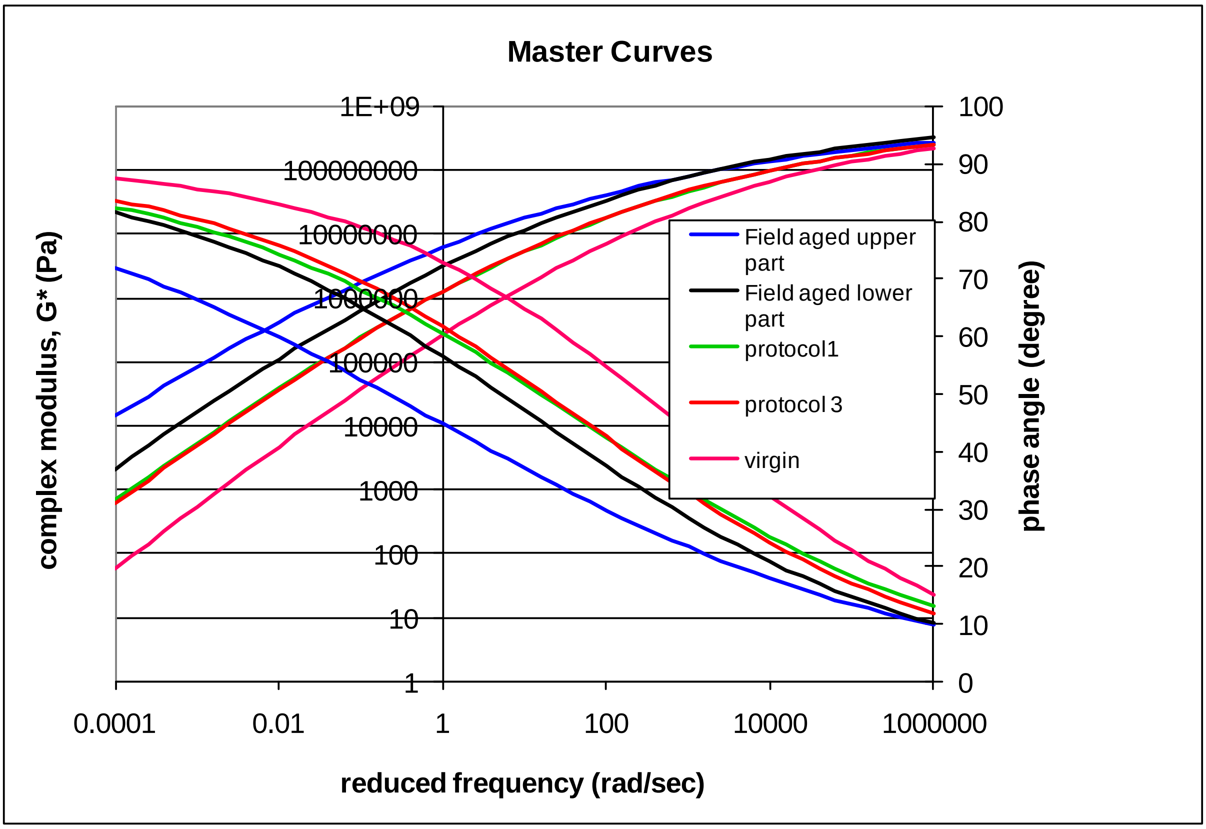


Figure 4.10: Master curves at a reference temperature of 20ºC

The model parameters and coefficient of determination of the master curves for both laboratory aged bitumen and field aged bitumen are shown in Table 4.7.

Table 4.7: WLF model parameters and coefficient of determination (R^2)

	Parameters	Sample name				
		Virgin	Protocol 1	Protocol 3	Field aged upper part	Field aged lower part
Shift factor	C1	15.119	11.577	17.829	28.692	20.401
	C2	118.725	96.937	136.979	206.066	169.204
Coefficient of determination	R^2 (G*)	0.988	0.985	0.990	0.994	0.998
	R^2 (Phase angle)	0.994	0.977	0.993	0.984	0.954

The DSR result shown in Figure 4.10 above are compatible with the penetration and softening point test results discussed earlier. Bitumen recovered from the top and bottom part of field aged specimens exhibits a higher complex modulus values and lower phase angle values compared to the two laboratory aged bitumen samples. The master curves of protocol 1 and protocol 3 shows very similar results. The complex modulus curve for protocol 1 positioned slightly above the curve for protocol 3 and the reverse is true for phase angle curves.

The comparison of complex modulus and phase angle test results of laboratory and field aged specimens presented above confirm the fact that the laboratory ageing protocol 1 and 3 were not severe enough to simulate field ageing of porous asphalt.

The complex modulus and phase angle results for selected temperatures and frequencies are shown in Table 4.8.

Table 4.8: complex modulus and phase angle for selected temperature and frequency

Temperature (°C)	Frequency (Hz)	Sample name									
		Virgin		Protocol 1		Protocol 3		Field upper part		Field lower part	
		G* (Pa)	δ (degree)	G* (Pa)	δ (degree)	G* (Pa)	δ (degree	G* (Pa)	δ (degree)	G* (Pa)	δ (degree)
-10	1	2.01E+08	21.02	2.42E+08	15.97	2.38E+08	17.57			4.21E+07	20.52
-10	8	3.00E+08	14.93	3.33E+08	12.13	3.35E+08	13.05			5.53E+07	19.97
-10	20	3.45E+08	12.73	3.73E+08	10.59	3.77E+08	11.26			4.74E+07	24.2
0	1	6.69E+07	35.21	1.11E+08	23.55	9.06E+07	27.77	1.72E+08	22.03	5.29E+07	27.55
0	8	1.34E+08	26.71	1.80E+08	19.11	1.60E+08	22.16	2.67E+08	16.83	8.50E+07	21.93
0	20	1.72E+08	23.18	2.16E+08	17.24	1.98E+08	19.69	3.15E+08	14.79	1.02E+08	19.55
10	1	1.22E+07	53.24	2.94E+07	35.68	2.40E+07	40.7	5.73E+07	32.98	3.73E+07	37.89
10	8	3.69E+07	42.63	5.55E+07	30.66	5.61E+07	33.35	1.13E+08	26.62	8.23E+07	30.92
10	20	5.60E+07	38.37	7.65E+07	28.15	7.75E+07	30.34	1.48E+08	24.24	1.11E+08	27.92
20	1	1.39E+06	70.16	3.06E+06	54.77	4.39E+06	55.27	1.50E+07	43.85	8.56E+06	49.93
20	8	6.32E+06	60.53	9.38E+06	47.15	1.43E+07	46.68	3.82E+07	37.5	2.48E+07	42.57
20	20	1.15E+07	55.99	1.45E+07	44.08	2.25E+07	43.04	5.50E+07	34.59	3.77E+07	39.43

4.3.3 Infrared Spectroscopy

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing which infrared (IR) wavelengths are absorbed by the sample. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs.

The infrared spectrum of bitumen samples recovered from specimens aged in the laboratory under the proposed aging protocols (protocol 1 and 3) and bitumen recovered from field cored specimens are shown in Figure 4.11.

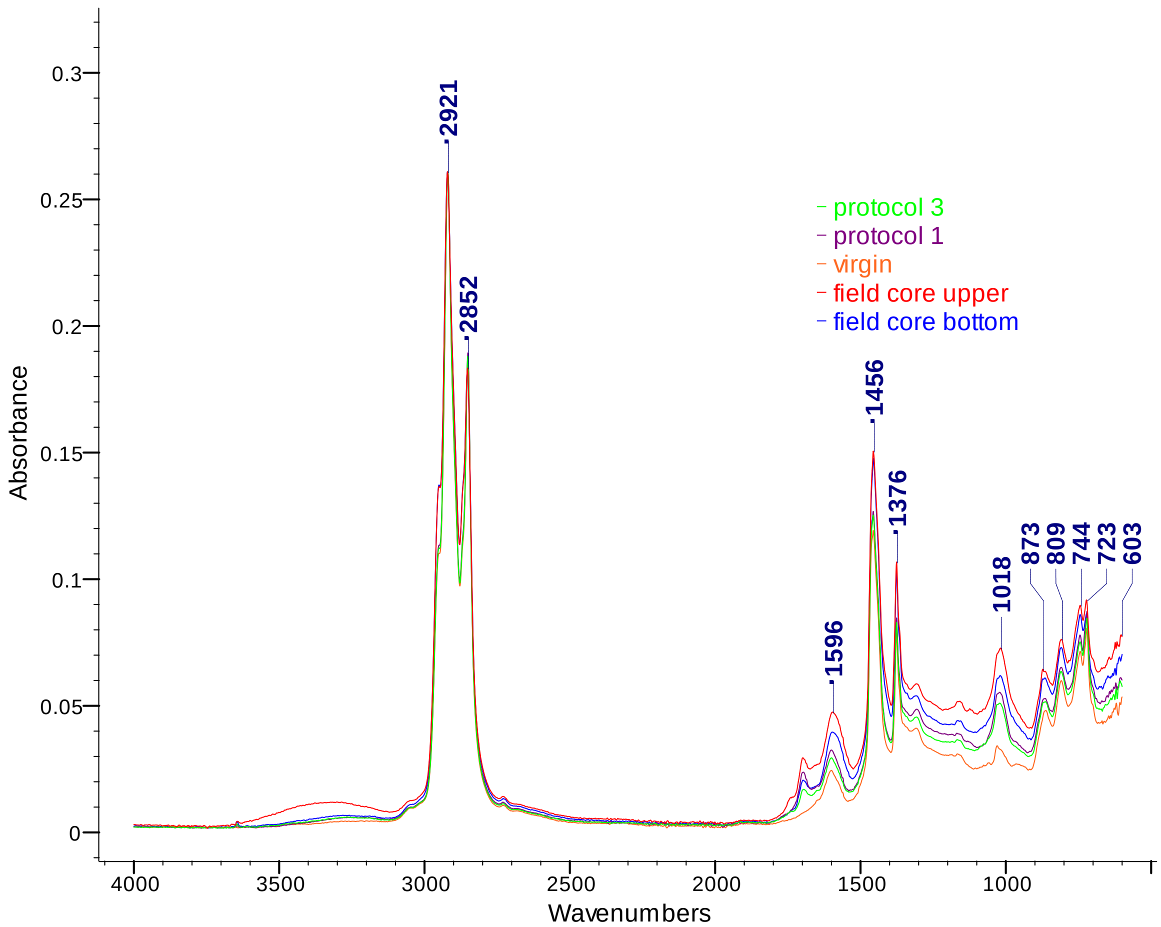


Figure 4.11: IR spectrum of bitumen samples from laboratory and field aged specimens

The quantitative analysis of the IR spectrum of binder samples was carried out based on a relative comparison of the absorption peaks characterizing the formation of aging products, especially ketones and sulfoxides. The aging indicators at 1700 cm^{-1} (ketones C=O) and 1030 cm^{-1} (Sulfoxides S=O) are the two characteristic bands at which the peak height and the area under the peak were used for the assessment of the effect of aging of the binder samples. For clarity, the zoomed in IR spectrum is presented in Figure 4.12 at the relevant range of wave numbers to determine the ketones and sulfoxides indices and area.

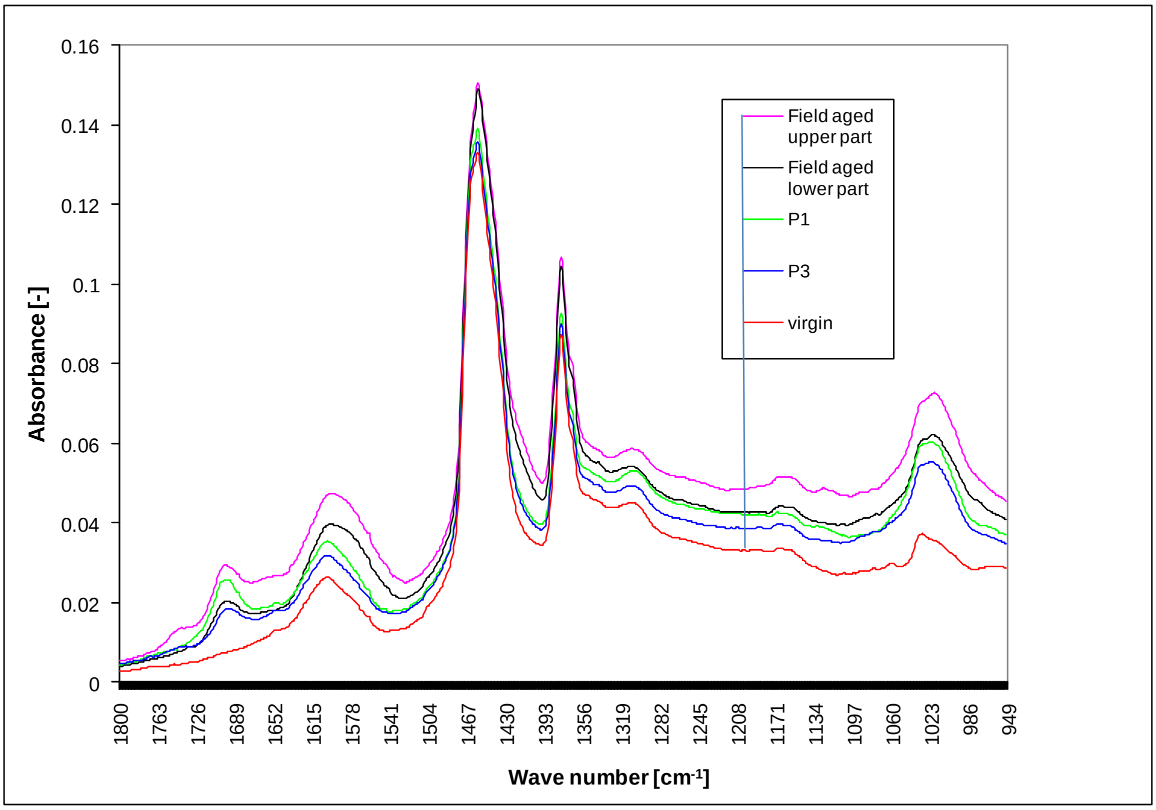


Figure 4.12: IR spectrum of bitumen samples from laboratory and field aged specimens only at the region relevant to determine ketones and sulfoxides peaks

The carbonyl and sulfoxides indices for all the bitumen samples were determined by using Equation (3.15) and (3.16) respectively. The peak indices (Ico and Iso) and peak heights of the laboratory-aged and field cored bitumen samples at the functional groups 1030 cm^{-1} (S=O), and 1700 cm^{-1} (C=O) are shown in Figure 4.13 and Figure 4.14 below.

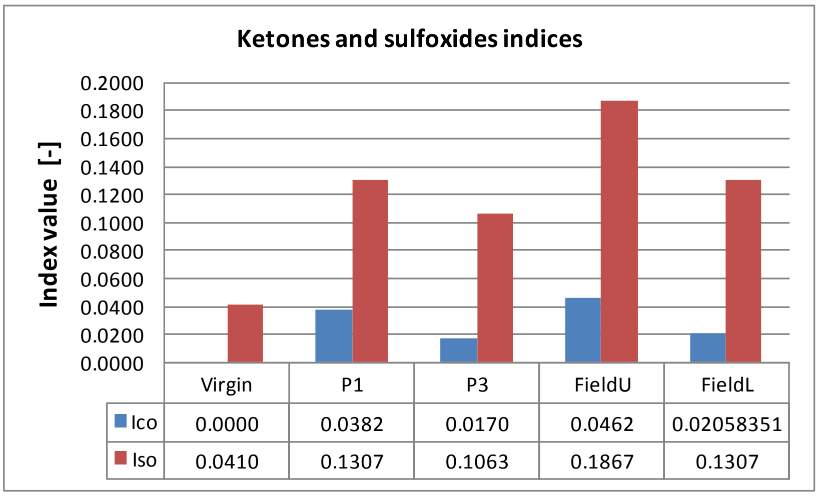


Figure 4.13: Ketones and sulfoxides indices for laboratory aged and field aged bitumen samples

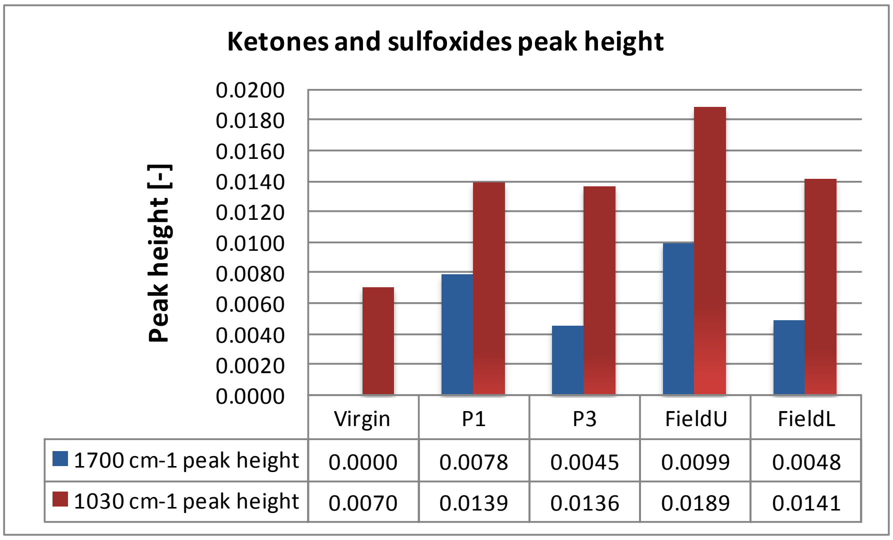


Figure 4.14: Ketones and sulfoxides peak heights

As it can be observed from the spectrum in Figure 4.12 and the computed indices and peak heights for C=O and S=O in Figure 4.13 and 4.14 above, the material from the upper part of the 10 year old pavement seems to have relatively higher peaks both at C=O and S=O band. P1 has the second highest peak and area at C=O band next to the upper part of field aged bitumen sample. The specimen from the lower part of the porous asphalt pavement have comparable peak at the S=O band with P1. The binder from P3 seems to have the lowest peak at 1030 cm^{-1} and 1700 cm^{-1} wave numbers next to the virgin bitumen. From the FTIR result in Figure 4.12, the change in C–C band (1600 cm^{-1}) is also apparent and field aged PA samples have the highest peaks. In general the spectrum line for field aged samples stays above the laboratory aged samples for the whole range of the finger print region except at 1700 cm^{-1} where P1 lies above the lower part of field PA. These results are in full agreement with the empirical and fundamental rheological test results explained in the previous sections.

The conclusion from the analysis given above is that, similar aging patterns as in the field is seen with P1 and P3 laboratory accelerated aging protocols apart from the variation at C=O band. Nonetheless, the laboratory mixture aging is not as severe as the field aging.

4.3.4 Wilhelmy plate test

To assess and compare adhesive property of bitumen, laboratory test has been carried out to determine surface energy components according to the test conditions mentioned in section 3.3.8. The surface energy components of bitumen samples both from laboratory aged specimen and from porous asphalt pavement (field aged specimens) are determined using the Wilhelmy Plate test (section 3.3.8.2). Three liquids with known surface energy parameters have been used to calculate the surface energy of bitumen samples i.e. distilled water, diiodomethane and glycerol. First the contact angle between these liquids and the bitumen sample has been determined directly from the tensiometer (Wilhelmy plate test) measurements (Equation 3.21). The bitumen coated glass plates used for test were selected, among many produced samples, based on smoothness and thickness of the bitumen film on the slides. The thicknesses of the bitumen coatings were determined by measuring the thickness on five points using a digital caliper. The computer attached to the tensiometer computes the contact angles by plotting the force against the immersion depth. For all the bitumen slides immersed in water it was found that the plots (example Figure 4.15) show more or less a straight line and the receding forces (red line) are larger than the advancing forces (blue line).

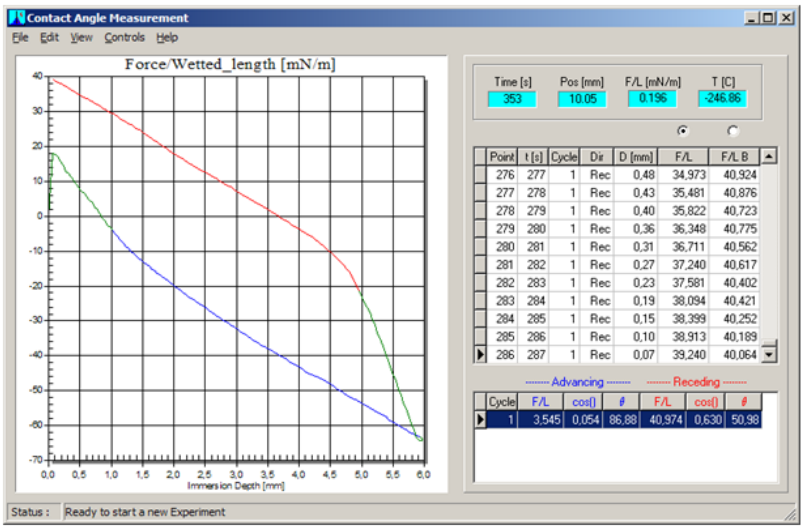


Figure 4.15: Plot of P1 bitumen sample immersing in water

For bitumen samples immersed in diiodomethane, the advancing and receding forces versus immersing depth graphs are straight and parallel to each other (Figure 4.16) and the receding force (red line) is larger than advancing force (blue line) with a small margin.

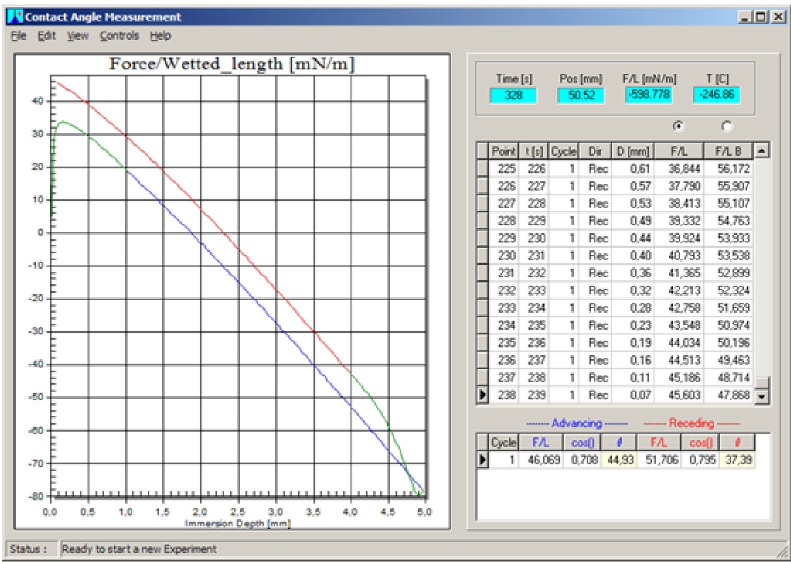


Figure 4.16: Plot of P1 bitumen sample immersing in diiodomethane

For all the bitumen slides immersed in glycerol (Figure 4.17) it was found that both the advancing and the receding force versus immersing depth lines are almost straight and the advancing forces are more or less the same as the receding forces. During the test, dissolving of bitumen in glycerol was observed; which might have an effect on the test results but the true consequence is not known. This phenomenon has been observed for all the bitumen samples.

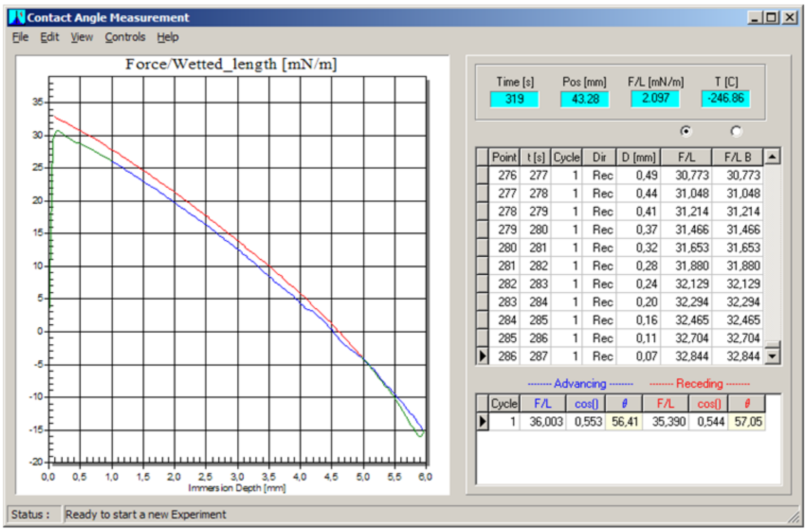


Figure 4.17: Plot of P1 bitumen sample immersing in glycerol

Data acquisition software connected to the test setup calculates automatically the contact angle of the reference liquids and the bitumen sample based on the change in force (Equation 3.21). The contact angles for the advancing and receding stages are shown in Table 4.8.

Table 4.9: Contact angle results from the tensiometer

Sample name	**measured contact angle (^{0})**					
	water		**glycerol**		**diiodomethane**	
	Advancing	**receding**	**Advancing**	**receding**	**Advancing**	**receding**
Virgin	87.70	37.27	58.74	58.36	54.13	32.05
Protocol 1	86.88	50.98	56.41	57.05	66.43	41.19
Protocol 3	89.74	42.93	58.86	58.53	57.77	34.45
Field upper	91.44	32.56	59.31	55.82	51.68	42.39
Field lower	88.67	25.81	66.24	61.18	44.93	37.39

It is clear from the above test result that there is a difference between advancing and receding angles. These differences are expected as there were differences in the advancing and receding force versus displacement graphs presented above. The difference between advancing and receding angles is that advancing angles interact with new, untouched surface of the bitumen, in contrast to receding angles, which interact with the wetted surface of the bitumen sample. This difference between advancing and receding angles (called hysteresis) is caused by surface roughness and/or chemical heterogeneity. The application of advancing or receding contact angles for computing the surface energy components is a discussion point among researchers (Little, 2005). Therefore, in this research surface energy components have been computed for both advancing and receding phases.

Based on the above contact angle measurements, the surface energy components of the bitumen samples are computed for the advancing and receding contact angles by using the relation in Equation 3.19. These results are given in Table 4.9.

Table 4.10: Computed surface energy components of the bitumen samples

Sample name	Advancing				Receding			
	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}
Virgin	33.06	31.94	3.97	0.08	43.35	43.35	0.00	27.56
Protocol 1	26.79	24.89	6.90	0.13	41.40	39.01	0.04	33.22
Protocol 3	29.86	29.86	4.79	0.00	42.28	42.28	0.00	29.70
Field cored upper	33.33	33.33	3.75	0.00	38.39	38.39	0.00	48.93
Field cored lower	38.50	37.04	1.13	0.47	40.90	40.90	0.00	26.21

It is clear from the above results that the total surface energy computed by using receding angles gives a higher value compared to the result from advancing angles. The same trend has been reported by other researchers (van Lent 2008, Hefer and Little 2005).

The results also show that the LW component (free energy of Lifshitz-Van der Waals forces) is the most significant contributor to the total surface energy of the asphalt binders, while the magnitudes of acid and base components are very small. This is in harmony with the fact that most asphalt binders are weakly polar materials.

From the above test results it was not possible to give a general trend for the surface energy in relation to the ageing of the bitumen with all the test samples. Since aging leads to the formation of weak bases and acids such as ketones and sulfoxides, the net effect on the surface energy components due to aging will depend on the initial chemical nature of the asphalt binder and the dynamics of various functional groups during the aging process. Other possible reasons for this may be a difference in bitumen type (difference between bitumen used in the laboratory ageing protocols and the one used to build the pavement from which the field samples were cored).

The purity of the chemicals (liquids) used for the test and the higher sensitivity of the test for the thickness and width measurement of the glass plate coated with bitumen might be additional reasons.

4.3.5 General discussion

As a recap the main findings from the test results of the three preliminary proposed ageing protocols in this study and the comparison of these results with the test results of specimens from field cores are presented in this section.

It seems that there is difference in the rheological (both empirical and fundamental) and chemical characteristics of the binders from the upper and lower parts of the field porous asphalt specimens. The upper part shows a higher ageing compared to the lower part of the porous asphalt pavement in the field. As raveling is a surface phenomenon, the characteristics of the upper part of the field specimen have been given special attention and targeted to be simulated in the laboratory.

In general the penetration, softening point, DSR and the FTIR test results for all the bitumen samples are in good agreement with each other. The analysis of the test results have shown clear differences in the rheological and chemical properties of the laboratory aged and field materials. It can be seen from the above result that protocol 1 and 3 are not severe enough to simulate 10 years of field ageing. Ageing protocol 2 was not a success at all; the asphalt mixture was damaged and bitumen has drained during ageing in the laboratory.

The materials recovered from specimens under aging protocol 1 and 3 were intended to simulate the aging of PA in the field. However, the outcome did not match the long term aging of bitumen in the field. Thus, it can be said that the laboratory aging methods adopted are not capable of simulating 10 years of PA aging in the field. Yet, both protocol 1 and 3 have a potential to be improved for the next trial to give a better result.

In the subsequent chapter the revised (improved) laboratory ageing protocol test results in comparison with the field porous asphalt test result will be discussed.

Chapter 5 Results and Analysis - Revised ageing protocols

As was discussed in the previous chapter, all the preliminary laboratory ageing protocols were not able to simulate field ageing of porous asphalt. It turned out that all the laboratory ageing protocols were less severe. On the other hand both protocol 1 and protocol 3 have the potential to be revised and become more severe so that they can mimic the ageing of porous asphalt in the field. Hence, in this chapter the revised protocols together with the test results of bitumen samples recovered from specimens aged by using these laboratory ageing protocols are discussed in comparison to the test results of field aged specimens.

5.1 Revision of protocol 1

In protocol 1 the pressure ageing vessel was used to age mortar. The rheological and chemical test results of the bitumen sample recovered from aged mortar by this protocol shows less ageing compared to test results of bitumen samples recovered from field cored specimens. Four revision options can be considered to make the protocol more severe:

1. To use oxygen instead of air to age the mortar but for safety reasons this option is not considered further.
2. Increasing the pressure is another option but the pressure might become unrealistically high and might also cause some safety concerns. The safety relief valve of the PAV also opens automatically and releases all the pressure when exceeding a pressure of 325 psi (2.24 MPa).
3. Increasing the ageing period is also not a real alternative. The objective of this research was to mimic field ageing of PA in the laboratory with utmost 7 days. In ageing protocol 1 specimen were aged already for ageing period of 7 days therefore there is no chance to further increase the ageing period.
4. The other option is to increase the ageing temperature. This option seems acceptable to be used to revise the ageing protocol. Thus, a test temperature of 100 °C was adopted instead of 80 °C.

In the next paragraphs the first revision of protocol 1 referred to as protocol 1A and the test results on bitumen samples recovered from mortar aged in this protocol are discussed.

5.1.1 Protocol 1A (first revision of protocol 1)

The only difference between ageing protocol 1 and protocol 1A is the change of temperature from 80 °C to 100 °C.

Test results of bitumen recovered from specimen aged in this protocol compared to field ageing of porous asphalt are discussed below.

5.1.1.1 Penetration and Softening Point

The penetration, softening point, and penetration index results for bitumen recovered from specimens aged in the laboratory by using the revised protocol and bitumen recovered from field specimens are given in Table 5.1.

Table 5.1: Penetration, softening point and penetration index values

Name	Penetration (0.1 mm)	Ring and Ball (°C)	Penetration Index (-)
Protocol 1A	9	73.6	-0.0
Field aged upper part	12	67.6	-0.5
Field aged lower part	17	63	-0.6

The above test results of laboratory and field aged materials reveals that protocol 1A gives higher ageing compared to the aging of top and lower part of porous asphalt layers in the field. Compared to the top part of the PA, the ageing protocol 1A shows 3 dmm lower penetration and a softening temperature of 6 °C higher. These differences are also reflected in the calculated penetration index shown in the above table.

5.1.1.2 Dynamic Shear Rheometer (DSR)

A frequency sweep test has been carried out on bitumen samples recovered from specimens aged under laboratory ageing protocol 1A and from field cored PA. The time-temperature superposition principle explained in section 3.3.6 was used to generate master curves of the complex modulus and phase angle at a reference temperature of 20 ºC (Figure 5.1).

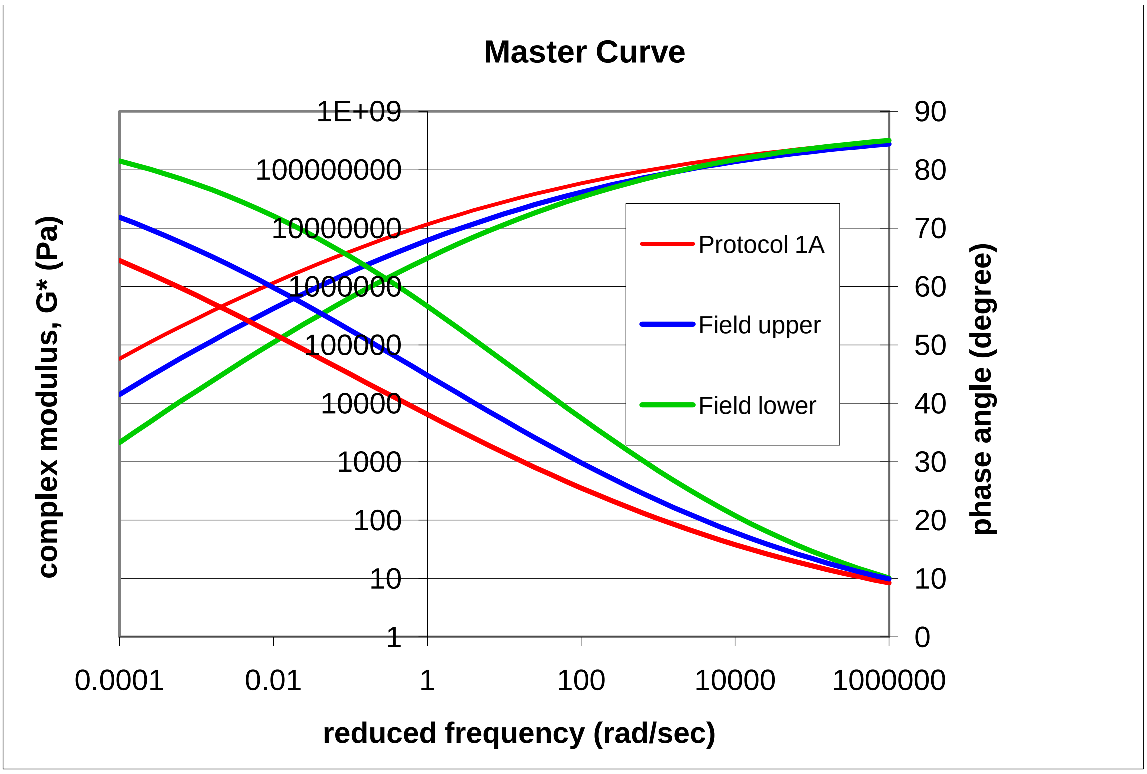


Figure 5.1: Master curves at a reference temperature of 20ºC

The model parameters and coefficient of determination of the master curves for both laboratory aged bitumen and field aged bitumen are shown in Table 5.2.

Table 5.2: WLF model parameters and coefficient of determination (R2) for the construction of mater curves

	Parameters	**Sample name**		
		Protocol 1A	Field aged upper part	Field aged lower part
WLF constants	C1	28	28.692	20.401
	C2	213	206.066	169.204
Coefficient of determination	R^2 (G*)	0.989	0.994	0.998
	R^2 (Phase angle)	0.916	0.984	0.954

The DSR results shown in Figure 5.1 above are well-matching the penetration and softening point test results explained previously. Bitumen recovered from specimen aged using ageing protocol 1A exhibit a higher complex modulus value and lower phase angle compared to the field PA (both the top and bottom part of field aged specimen).

A comparison of complex modulus and phase angle test results of laboratory and field aged specimens presented above shows that the laboratory ageing protocol 1A gives higher ageing compared to 10 years field ageing of PA.

5.1.1.3 Infrared Spectroscopy

To measure the chemical change in the laboratory and field aged specimens, Fourier Transform Infrared (FTIR) test has been carried out on bitumen samples. The test procedures and test conditions are mentioned in detail in section 3.3.7. The infrared spectrum of bitumen samples recovered from specimens aged in the laboratory using aging protocol 1A and bitumen recovered from field cored specimens are shown in Figure 5.2 below.

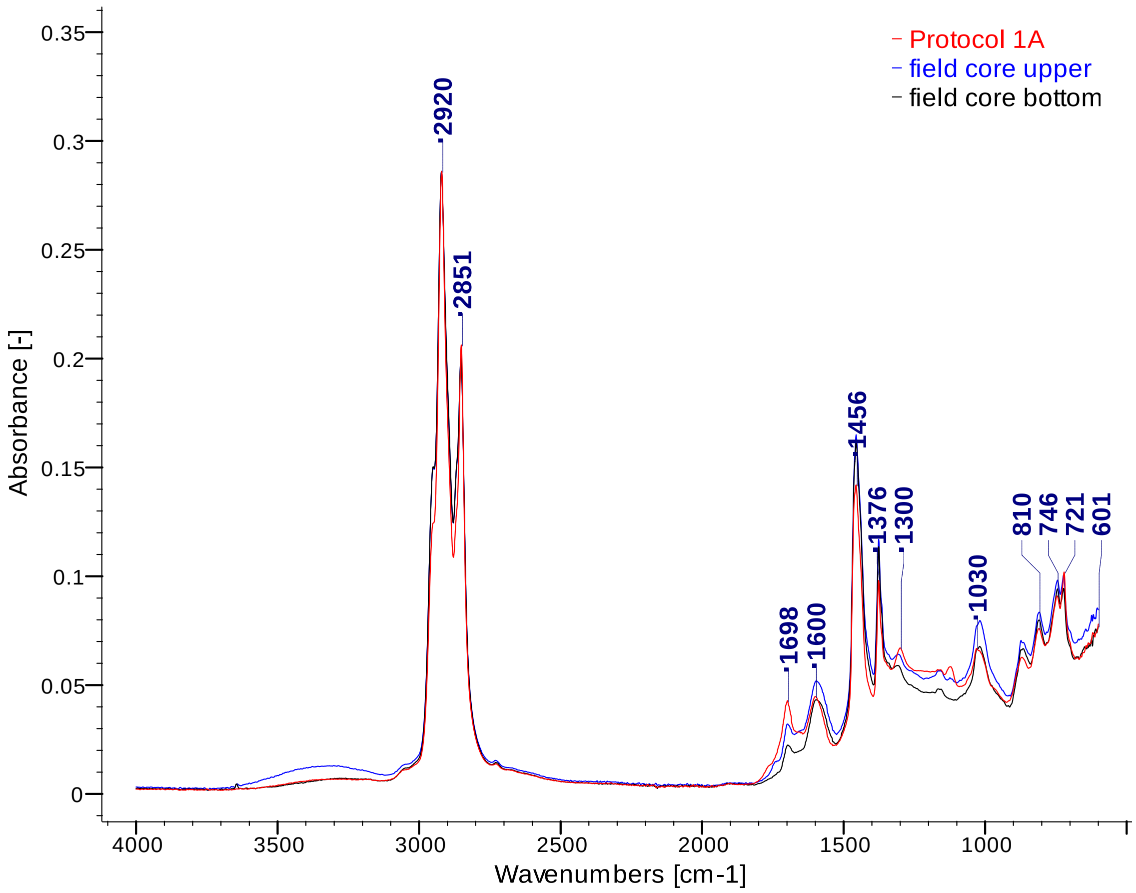


Figure 5.2: IR spectrum of bitumen samples from laboratory and field aged specimens

The change in characteristic peaks only in figure print region is shown in Figure 5.3. It is apparent that the spectrum graph for protocol 1A stays on top of the field cored specimens for the large part of the wavenumbers including the carbonyl peak (1700 cm^{-1}). However, the upper part of the field cored specimen shows higher sulfoxides index and sulfoxides peak height compared to protocol 1A. The bottom part of the field PA shows lower values for both characteristic peaks (ketones and sulfoxides peaks) compared to the upper part and protocol 1A.

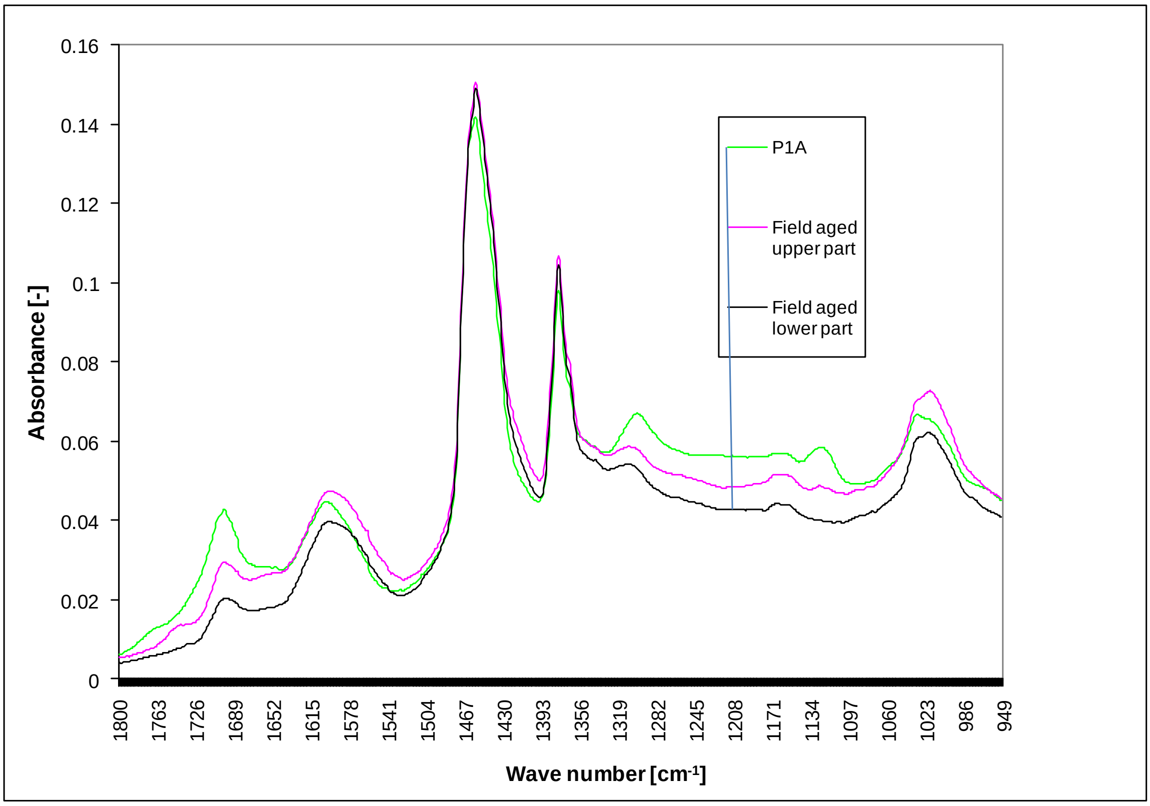


Figure 5.3: IR spectrum of bitumen samples in figure print region

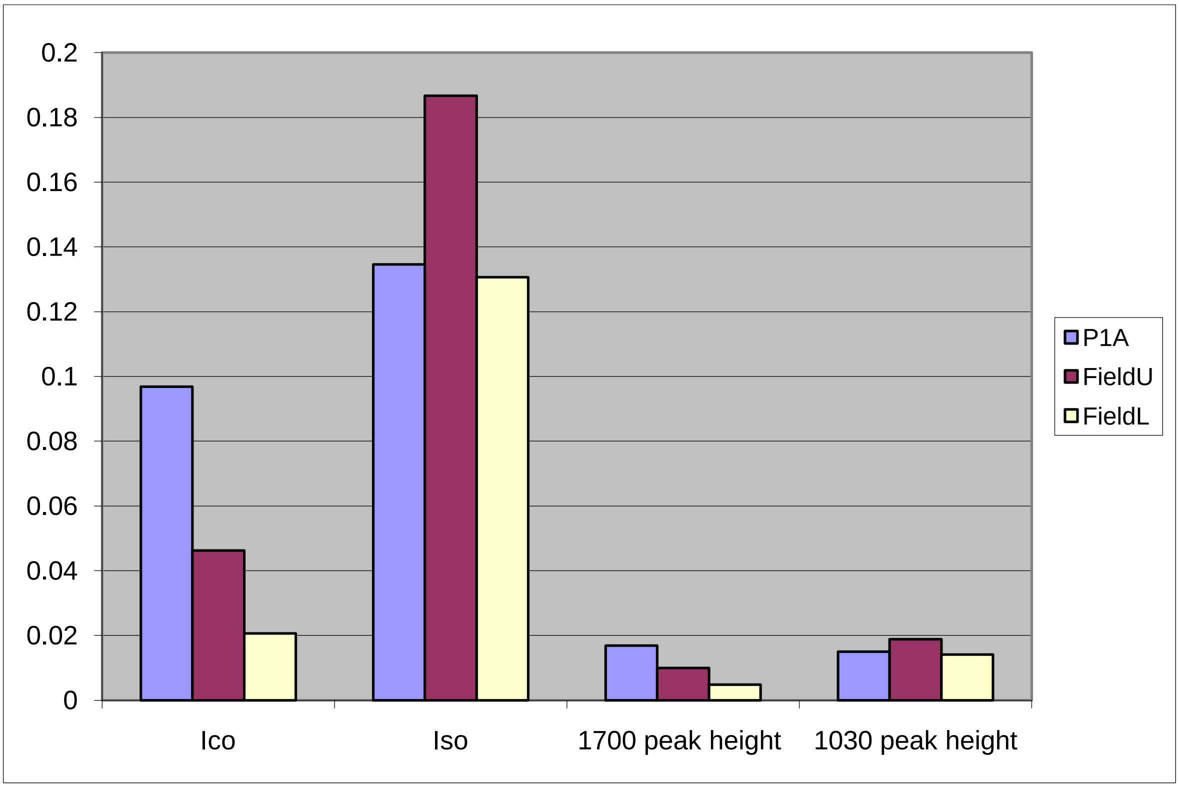


Figure 5.4: Ketones and sulfoxides indices and peak heights

The above FTIR results are in reasonably agreement with the rheological test results discussed in section 5.1.1.2 and section 5.1.1.1 above. Hence, from the FTIR test result it can be said that ageing protocol 1A gives higher ageing compared to the field ageing of PA for a period of 10 years.

5.1.1.4 Wilhelmy plate test

To assess the adhesive property, the Wilhelmy plate test has been carried out on bitumen samples recovered from field cored specimens and laboratory aged specimens under protocol 1A. The contact angle and the respective surface energy values computed from the Wilhelmy plate test are shown in the tables below:

Table 5.3: Tensiometer contact angle results for P1A and field PA bitumen samples

Sample name	measured contact angle (^{o})					
	water		glycerol		diiodomethane	
	Advancing	receding	Advancing	receding	Advancing	receding
Field upper	91.44	32.56	59.31	55.82	51.68	42.39
Field lower	88.67	25.81	66.24	61.18	44.93	37.39
P1A	83.06	61.55	55.44	59.09	48.71	40.07

Table 5.4: Computed surface energy components of P1A and field PA bitumen samples

	Advancing				Receding			
Sample name	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}
Field cored upper	33.33	33.33	3.75	0.00	38.39	38.39	0.00	48.93
Field cored lower	38.50	37.04	1.13	0.47	40.90	40.90	0.00	26.21
Protocol 1A	37.75	34.99	3.52	0.54	43.06	39.58	0.15	19.65

Here again the total surface energy computed by using receding angles are higher than the surface energy computed from advancing angles. The total surface energy of bitumen sample from protocol 1A is nearly similar to that of the bitumen of the field cored lower part. However, it was not possible to make conclusion from this result. As it is explained in section 4.3.4 a consistent trend was not found for the change in surface energy due to ageing of bitumen.

5.1.1.5 Conclusion protocol 1A

From all the above test results and comparisons between field and laboratory aged bitumen samples, it is clear that laboratory ageing protocol 1A gives higher ageing compared to 10 years of field ageing of porous asphalt. Protocol 1A shows lower penetration, higher softening point, higher complex modulus, low phase angle, and higher carbonyl index and carbonyl peak height. Nonetheless, the upper part of the field cored specimen shows higher sulfoxides index and sulfoxides peak height.

Generally, ageing protocol 1 (with ageing temperature of 80 ºC) resulted in less ageing while ageing protocol 1A (with ageing temperature of 100 ºC) gives higher ageing of bitumen compared to field ageing of PA. Thus, ageing protocol with ageing temperature somewhere between 80 ºC and 100 ºC will give comparable results to that of 10 years field ageing. Consequently, for the second revision of the ageing protocol the ageing temperature of protocol 1A has been decreased from 100 ºC to 90 ºC. In the following paragraphs the rheological, chemical and adhesive test results of the bitumen samples from this revised ageing protocol compared to the field ageing are presented and discussed.

5.1.2 Protocol 1B (second revision of protocol 1)

The only deviation of ageing protocol 1B from protocol 1 or protocol 1A is the ageing temperature used in pressure ageing vessel. Protocol 1B uses ageing temperature of 90 ºC while protocol 1 and protocol 1A uses 80 ºC and 100 ºC respectively.

The rheological, chemical and adhesion test results of bitumen samples recovered from specimens aged by using this ageing protocol and the comparison with field aged bitumen test results are presented in the following sections.

5.1.2.1 Penetration and Softening Point

Empirical rheological tests (penetration and softening point) have been conducted on bitumen samples recovered from laboratory aged (using protocol 1B) and field aged specimens. Penetration index of the bitumen samples are computed from penetration and softening point test results. These results are shown in Table 5.5 and Figure 5.5 below.

Table 5.5: Penetration and softening point test results of protocol 1B, field aged upper and lower part

Name	Penetration (0.1 mm)	Ring and Ball (°C)	Penetration Index (-)
Protocol 1B	14	65.4	-0.6
Field aged upper part	12	67.6	-0.5
Field aged lower part	17	63.0	-0.6

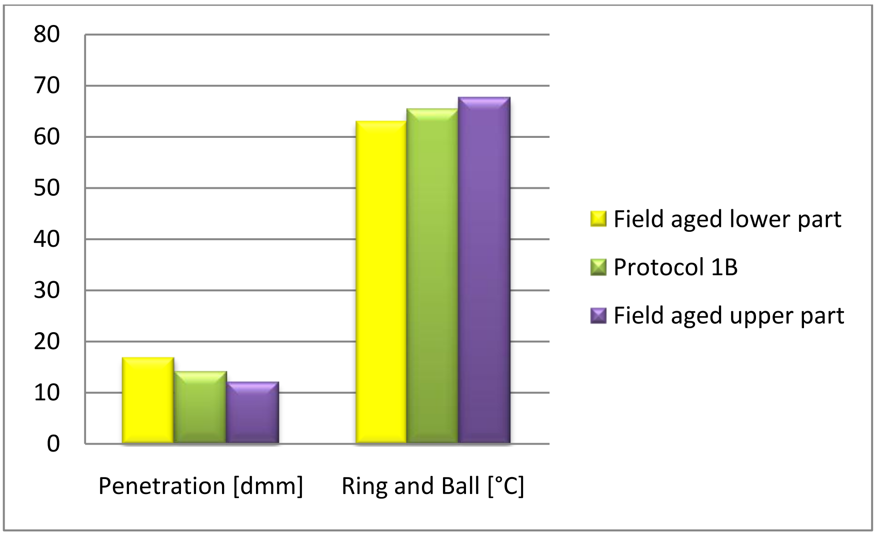


Figure 5.5: Penetration and softening point of protocol 1B, field aged upper and lower part

From the above results it is clear that the penetration and softening point of protocol 1B is comparable to the field porous asphalt results. Compared to the upper part of field aged material, protocol 1B deviates only with a penetration of 2 dmm and a softening temperature of 2.2 °C which resulted in a difference of penetration index of 0.1. These differences are very small and thus it is possible to say that protocol 1B is able to simulate penetration and softening point of 10 years of field aged porous asphalt.

5.1.2.2 Dynamic Shear Rheometer (DSR)

DSR frequency sweep test were conducted according to the test conditions mentioned in section 3.3.5 on bitumen samples recovered from laboratory aged (by using protocol 1B) and field cored specimens. Consequently, the complex modulus and phase angle at different temperatures and loading frequencies were determined for these bitumen samples.

From Figure 5.6 below it is apparent that the binders recovered from aging protocol 1B have shown similar characteristics as the top part of 10 years old field material both in terms of the complex modulus and the phase angle master curves. As the aim of this research is to mimic the top part of the field porous asphalt, these results are prominent. Therefore, it can be said that protocol 1B is able to simulate fundamental rheological characteristics of bitumen samples from field aged porous asphalt.

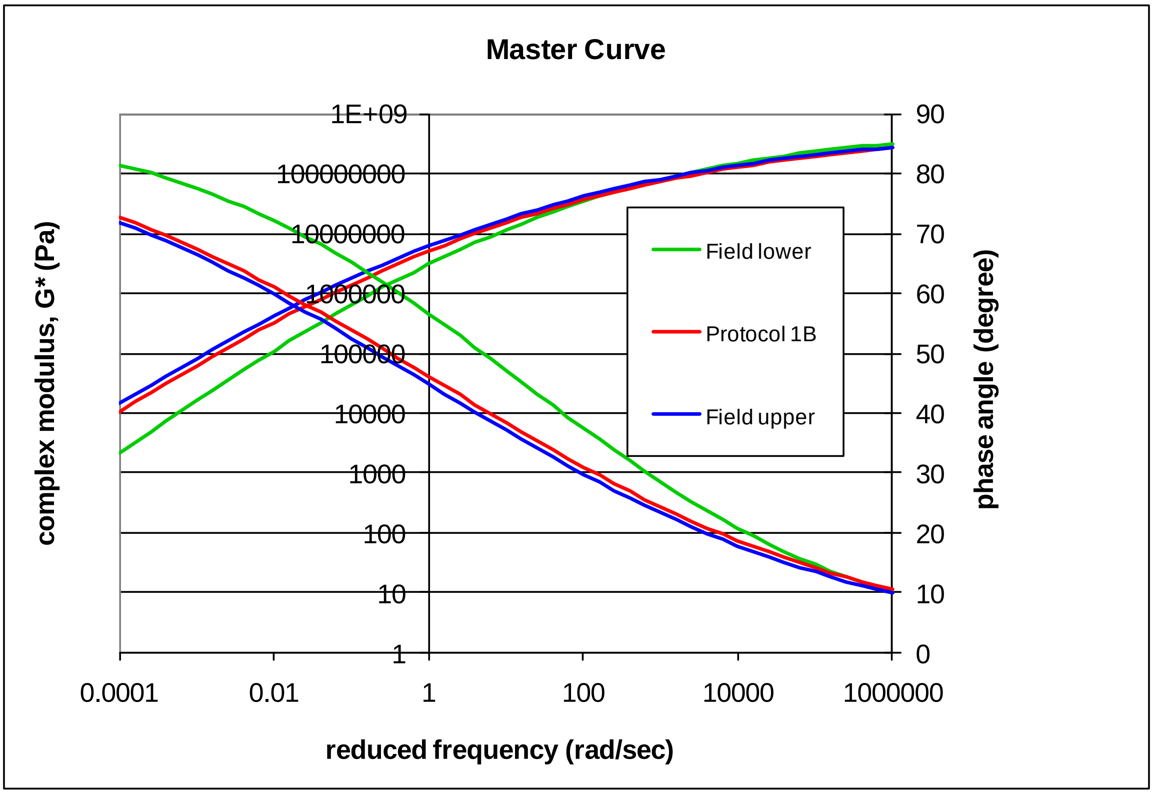


Figure 5.6: Master curves of bitumen sample from protocol 1B and field aged PA at a reference temperature of 20°C

The model parameters and coefficient of determination for the construction of the master curves for both laboratory and field aged bitumen are shown in Table 5.6.

Table 5.6: WLF model parameters and coefficient of determination (R^2) for the construction of master curves

	Parameters	Sample name		
		Protocol 1B	Field aged upper part	Field aged lower part
WLF constants	C1	28.0	28.692	20.401
	C2	205.0	206.066	169.204
Coefficient of determination	R^2 G*	0.995	0.994	0.998
	R^2 Phase angle	0.982	0.984	0.954

The complex modulus and phase angle results of protocol 1A and 1B for selected temperatures and frequencies are shown in Table 5.7

Table 5.7: Complex modulus and phase angle for selected temperatures and frequencies

Temperature (°C)	Frequency (Hz)	sample name			
		Protocol 1A		Protocol 1B	
		G* (Pa)	δ (degree)	G* (Pa)	δ (degree)
-10	1	2.06E+08	14.52	2.38E+08	15.44
-10	8	2.74E+08	11.9	3.26E+08	11.94
-10	20	3.06E+08	10.99	3.65E+08	10.51
0	1	1.33E+08	17.61	1.19E+08	21.61
0	8	1.92E+08	15.01	1.87E+08	17.77
0	20	2.23E+08	13.53	2.23E+08	16.11
10	1	6.33E+07	23.18	4.46E+07	29.82
10	8	1.04E+08	20.04	8.31E+07	25.2
10	20	1.27E+08	19.04	1.06E+08	23.32
20	1	2.34E+07	29.95	1.21E+07	40.17
20	8	4.45E+07	26.42	2.83E+07	34.4
20	20	5.78E+07	24.9	3.96E+07	32.03

5.1.2.3 Infrared Spectroscopy

To asses and compare the chemical evolution of laboratory (protocol 1B) and field aged bitumen samples, FTIR test has been carried out on these bitumen samples according to the test conditions mentioned in section 3.3.7. The obtained FTIR spectrum possesses absorption bands characteristic of bitumen. The functional indexes are calculated from the band areas measured from valley to valley. The infrared spectrum is shown in Figure 5.7 below.

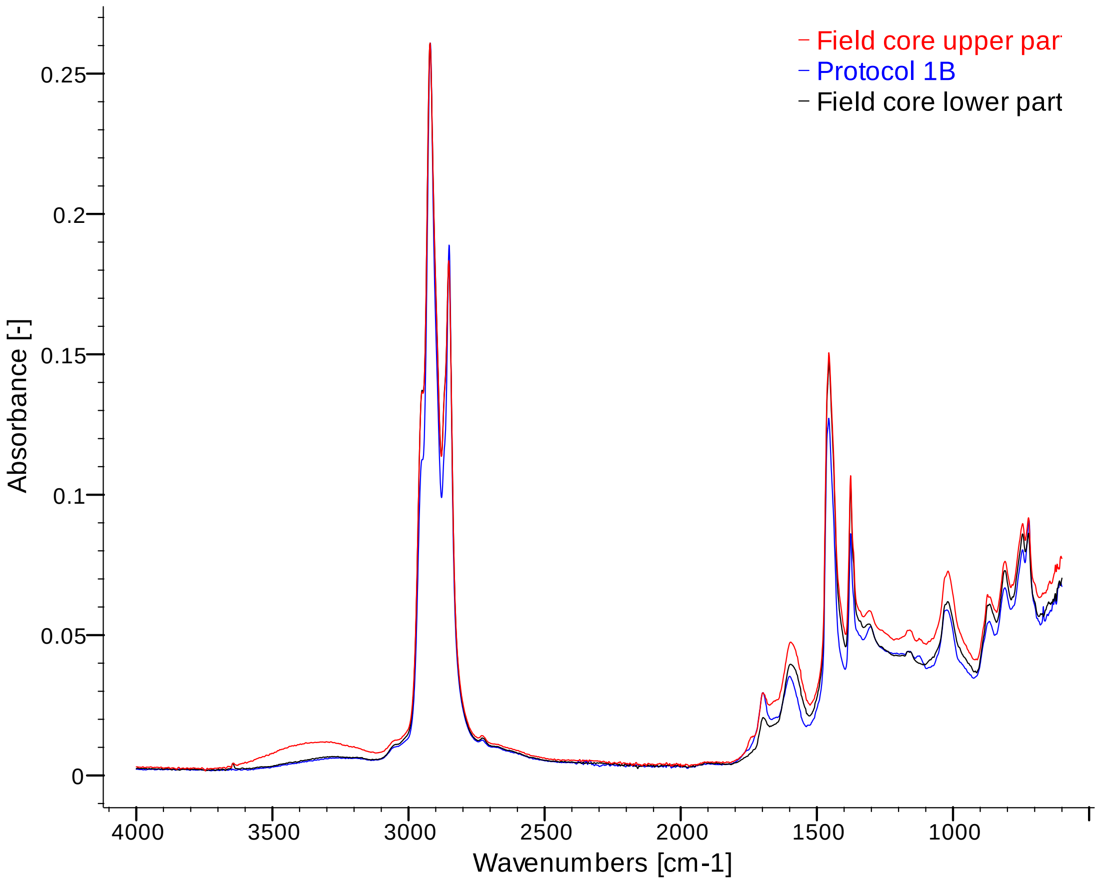


Figure 5.7: IR spectrum of bitumen samples from protocol 1B and field aged specimens

More interestingly the infrared spectrum result reveals that the laboratory ageing protocol 1B shows comparable result with 10 years field aged porous asphalt. This can be seen more clearly in Figure 5.8 below, which only shows the finger print region. The carbonyl and sulfoxides indices for the bitumen samples were determined by using Equation (3.15) and (3.16) respectively. The indices (Ico and

Iso) and peak heights of the laboratory-aged and field cored bitumen samples at the functional groups 1030 cm^{-1} (S=O), and 1700 cm^{-1} (C=O) are shown in Figure 5.9.

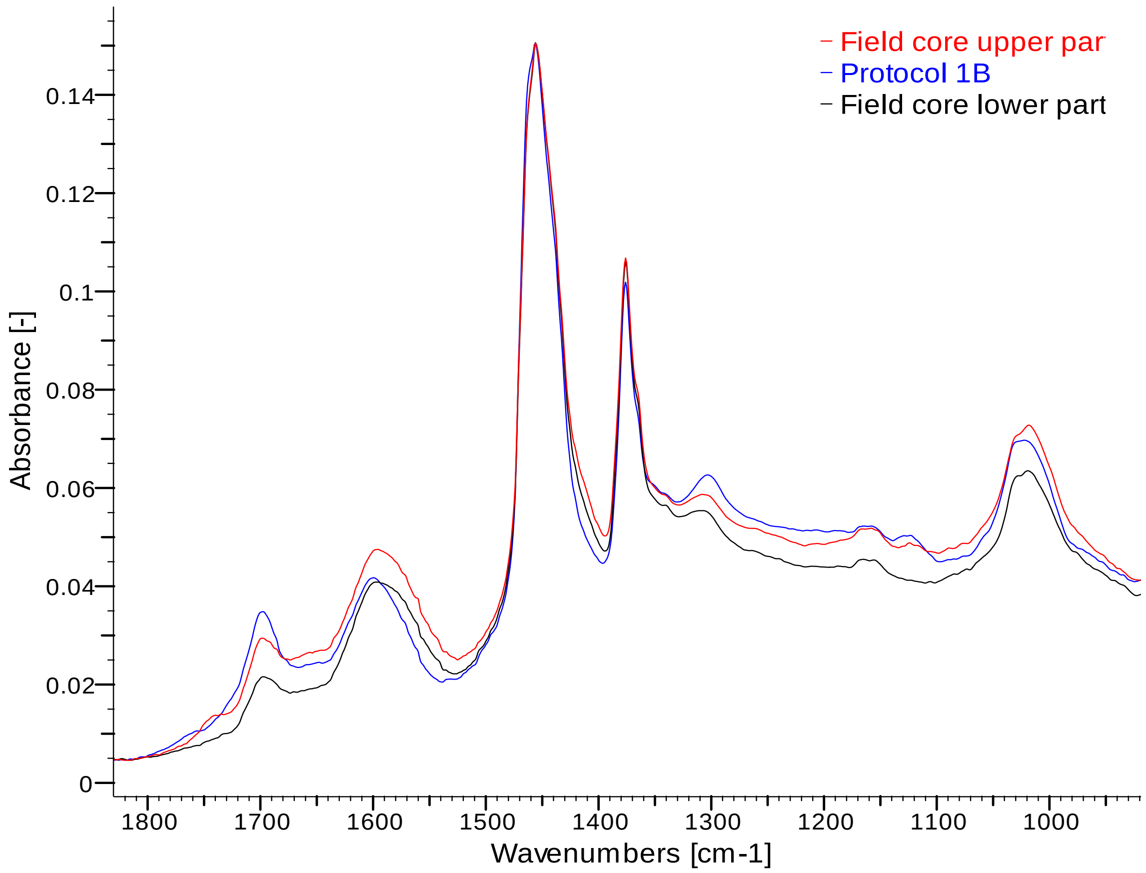


Figure 5.8: IR spectrum of bitumen samples from protocol 1B and field aged specimens in figure print region

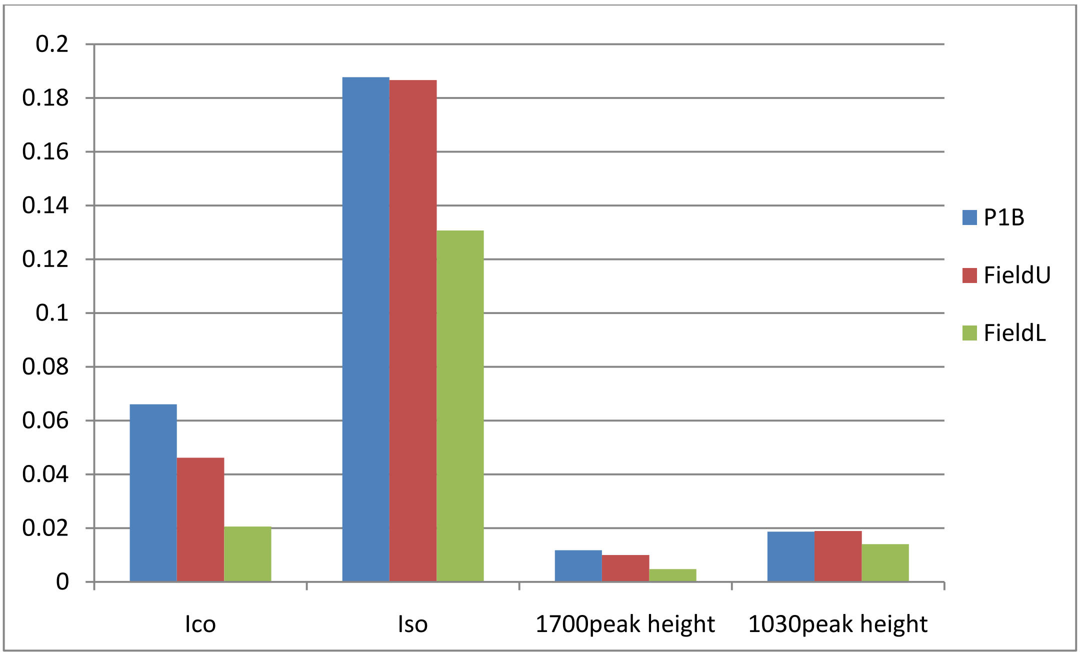


Figure 5.9: Ketones and sulfoxides indices and peak heights for P1B and field specimens

It is clear from the above quantitative analysis of the IR spectrum that protocol 1B and the top part of the field cored PA show similar results in sulfoxides index (Iso), the 1030 cm^{-1} and 1700 cm^{-1} peak heights. However, the laboratory aged bitumen sample showed slightly higher carbonyl index. In general it can be said that both bitumen samples have comparable infrared spectrum test results, which means that the ageing protocol 1B can simulate chemical characteristics of 10 years field ageing of porous asphalt.

5.1.2.4 Wilhelmy plate test

The total surface energy of the bitumen samples from protocol 1B and field cored specimens are calculated from the contact angles measured by means of the Wilhelmy plate test. The contact angle and the respective surface energy values computed from the Wilhelmy plate test are shown in the tables below.

Table 5.8: Tensiometer contact angle results for P1B and field PA bitumen samples

Sample name	measured contact angle (°)					
	water		glycerol		diiodomethane	
	Advancing	receding	Advancing	receding	Advancing	receding
Field upper	91.44	32.56	59.31	55.82	51.68	42.39
Field lower	88.67	25.81	66.24	61.18	44.93	37.39
P1B	95.01	66.52	58.78	59.02	52.79	33.18

Table 5.9: Computed surface energy components of P1B and field PA bitumen samples

	Advancing				Receding			
Sample name	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}	γ^{Total}	γ^{LW}	γ^{+}	γ^{-}
Field cored upper	33.33	33.33	3.75	0.00	38.39	38.39	0.00	48.93
Field cored lower	38.50	37.04	1.13	0.47	40.90	40.90	0.00	26.21
Protocol 1B	32.70	32.70	4.05	0.00	45.48	42.85	0.17	13.00

The total surface energies computed by using the receding angles are higher than those computed by using the advancing contact angles. It seems the surface energy for protocol 1B computed by using the advancing contact angle is in the same order of magnitude with the upper part of the field aged porous asphalt. However, it was not possible to link the change in surface energy of bitumen samples with the ageing results. Hence, the surface energy results are not taken to draw conclusions in the comparison of laboratory and field ageing of bitumen.

From the analysis of all the test results mentioned in the previous paragraphs, it can be seen that the upper part of field aged PA specimen and laboratory aged specimen (using protocol 1B) shows pretty well similar results. The penetration, softening point, DSR as well as the FTIR test results of protocol 1B and the upper part of field aged porous asphalt cores show comparable results. In other words, the bitumen recovered from protocol 1B exhibit similar rheological (both empirical and fundamental) and chemical characteristics compared to bitumen recovered from the top part of 10 years field aged porous asphalt. Therefore, it can be concluded that ageing protocol 1B can reasonably mimic binder properties from 10 years field aged porous asphalt.

5.2 Revision of protocol 3

In chapter 4 it has been shown that ageing protocol 1 and 3 were not able to mimic field ageing of porous asphalt. However, there was room for improvement of these two ageing protocols so that they can simulate field ageing of porous asphalt. As a result, ageing protocol 1 has been revised and achieved a remarkable result in simulating 10 years of field ageing of porous asphalt. It is believed that the same can be attained by improving Protocol 3.

In ageing protocol 3, loose porous asphalt mixture has been aged in an oven at a temperature of 85°C for 7 days. It is apparent from all the ageing indicator test results that field specimens appeared to have a much higher ageing compared to laboratory ageing (by using protocol 3). Simply ageing protocol 3 was not severe enough to simulate field ageing. Two options were considered to make this ageing method more severe:

1. To increase the ageing period. However, the maximum ageing period set in the objective of this research is 7 days and this has been used already in ageing protocol 3.
2. The other option is to increase the ageing temperature. Accordingly, for the revision of the protocol the ageing temperature has been increased from 85°C to 135°C.

The following paragraph explains briefly the revised ageing protocol (Protocol 3A) proposed to be examined:

5.2.1 Protocol 3A (first revision of protocol 3)

In this protocol, the aging procedure in protocol 3 has been modified. Loose porous asphalt mixture in a steel box has been aged by using an air ventilated oven. The loose mixture was kept at a uniform thickness (height) of 5 cm during ageing. The protocol is described below:

- The asphalt mixture has been prepared according to NEN-EN-12697-35+A1 (the percentage composition of materials and detailed explanation on preparation of test samples are explained in chapter 3).
- Then the loose asphalt mixture was placed in an air ventilated oven at a temperature of 135°C for duration of 7 days. During this ageing period, every time 3 kg of sample was taken after 1, 2, 3, 6 and 7 days of ageing. Bitumen has been recovered and penetration and softening point were determined for all bitumen samples. Each time the samples were taken, the rest of the

material was stirred for 1 minute and the height of the loose mixture was kept at 5 cm.

The penetration and softening point test results were used to determine the required ageing period of the protocol which can give comparable results with field ageing. The penetration results versus the ageing period was drawn in a graph. Then by using the penetration results from field specimens the corresponding ageing period can be read from this graph. Table 5.9 presents the penetration and softening point test results of bitumen samples aged by using the above ageing protocol.

Table 5.10: Penetration and softening test result for loose asphalt mixture aged under revised ageing protocol 3

Type of test	test number	before mixing (virgin)	0 days (right after mixing)	1 day after mixing (22.5 h)	2 days after mixing (46.5 h)	3 days after mixing (70.5 h)	6 days after mixing (142.5 h)	7 days after mixing (166.5 h)
pen 25 °C [dmm]	1	86	55	20	10	4	0.2	0.4
	2	85	53	20	10	4	0.3	0.5
	3	84	50	19	11	4	0.2	0.5
mean		**85**	**53**	**20**	**10**	**4**	**0.2**	**0.5**
Determined using		water	water	water	water	glycerol	glycerol	glycerol
Tr&b [°C]	Left ball	44.8	49.0	63.7	76.3	97.4	132.8	128.8
	Right ball	44.6	49.1	63.7	76.5	97.9	133.0	129.2
mean		**44.7**	**49.1**	**63.7**	**76.4**	**97.7**	**132.9**	**129.0**
Penetration Index [-]		**-1.37**	**-1.3**	**-0.23**	**0.52**	**1.62**	**1.24**	**1.81**

In the above table the ageing period is expressed in days and the exact duration is also included in parenthesis in hours. It was found difficult to recover bitumen from the 6 days aged sample. Extra heating has been used to get the bitumen from the flask of the rotary evaporator. The effect is apparent from the discrepancies of the test results from 6 days aged bitumen and the other test results in the above table. Therefore, the test result form 6 days was discarded from further analysis.

The above test results are presented graphically in Figure 5.10 below. In this figure, hours are used instead of days to represent the duration of ageing. For a penetration of 12 dmm (penetration value for field aged specimen), the corresponding ageing period can be read from Figure 5.10 which gives approximately 42 hours of ageing (the red arrow in Figure 5.10). Therefore, a new loose asphalt mixture sample has been aged in the oven with a temperature of 135 °C for the duration of 42 hours. The rheological and chemical test results of bitumen recovered from specimen aged with this procedure compared to test results from field aged material are presented in the subsequent sections.

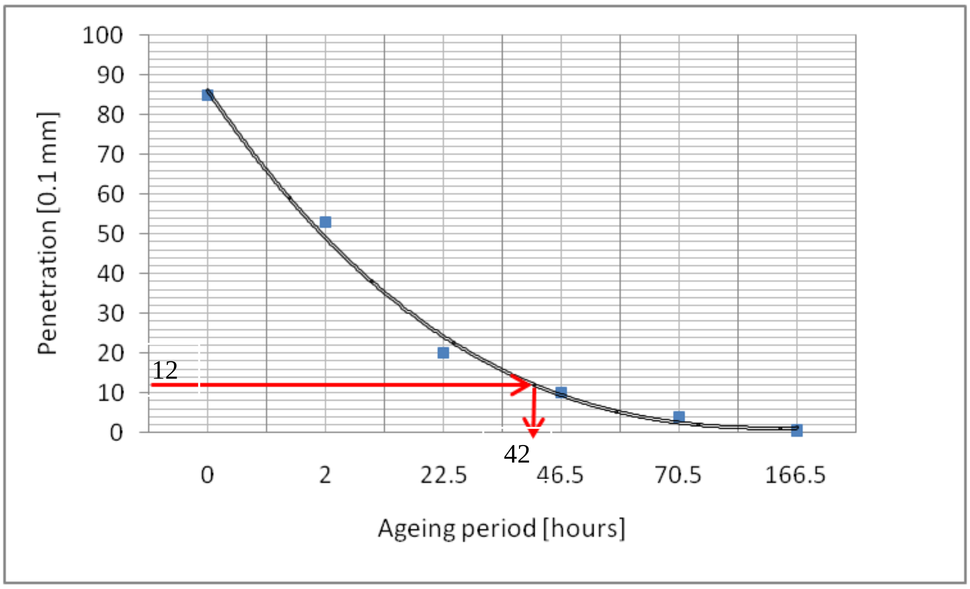


Figure 5.10: Penetration versus ageing period

5.2.1.1 Penetration and Softening Point

The materials presented in this section are bitumen recovered from specimens aged in the laboratory (using protocol 3A for duration of 42 and 46.5 hours) and bitumen recovered from field specimens. The penetration and softening point results for all the materials including penetration index (PI) values are given in Table 5.10.

Table 5.11: Penetration, softening point and penetration index value for protocol 3A and field aged bitumen samples

	Penetration [dmm]	Ring and Ball [°C]	Penetration Index [-]
Protocol 3A_42h	19	63.4	-0.4
Protocol 3A_46.5h	10	76.4	0.5
Field aged upper part	12	67.6	-0.5
Field aged lower part	17	63	-0.6

It is evident from the above table that protocol 3A with ageing period of 2 days (46.5 hours) gives a lower penetration and a considerably higher softening point compared to the top part of the field aged sample. On the other hand, bitumen sample aged using protocol 3A for duration of 42 hours shows less ageing (higher penetration and lower softening point values). From these results it can be concluded that protocol 3A with ageing period somewhere between 42 and 46.5 hours can give empirical rheological results comparable to the top part of field aged porous asphalt.

5.2.1.2 Dynamic Shear Rheometer (DSR)

DSR frequency sweep tests were conducted on bitumen recovered both from laboratory aged using protocol 3A and field cored specimens. The complex modulus and phase angle at different temperatures and loading frequencies were determined. The test conditions are mentioned in section 3.3.5.

A master curve has been constructed at a reference temperature of 20 ºC. In Figure 5.11, the master curves of recovered bitumen from laboratory aged and field cored specimens are shown.

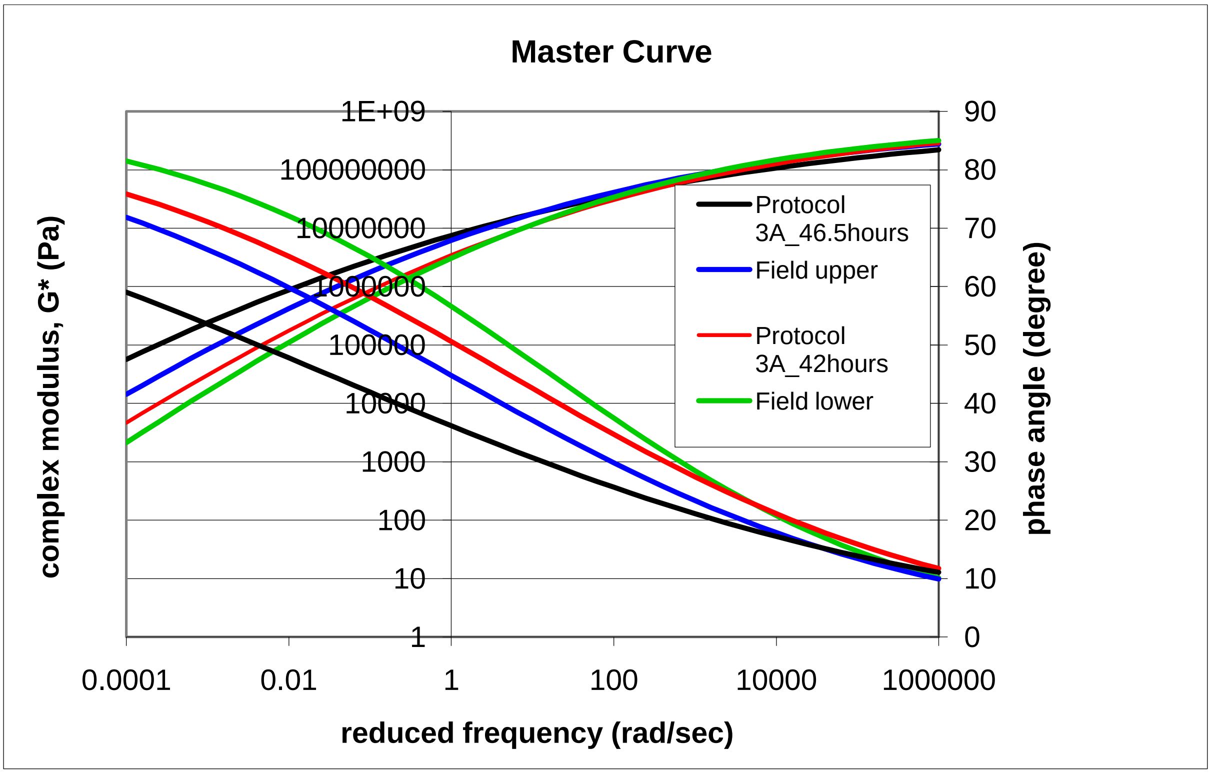


Figure 5.11: Master curves for recovered bitumen from field and protocol 3A aged specimens

As anticipated, based on the penetration and softening test results, the bitumen from protocol 3A_46.5hours has a higher modulus than the corresponding bitumen sample from protocol 3A_42hours, and the lower and upper part of field aged specimens. Figure 5.11 clearly shows the effect of aging on the rheological behavior of the materials. The increase in complex modulus due to aging is accompanied by a decrease in the phase angle. The difference observed in the phase angle is higher than the difference in complex modulus for all the bitumen samples. In the higher frequency region the complex modulus master curves seem to have comparable results. They show difference in results at the lower frequency region. The master curve (both the complex modulus and phase angle) for the top part of the field material is between protocol 3A_42hours and protocol 3A_46.5hours master curves. It follows that, when using protocol 3A, the right ageing period to simulate rheological properties of field ageing is somewhere between 42 and 46.5 hours.

The model parameters and coefficient of determination for the construction of the master curves for both laboratory aged bitumen and field aged bitumen are shown in Table 5.11.

Table 5.12: WLF model parameters and coefficient of determination (R^2) for the construction of master curves

		Sample name			
	Parameters	Protocol 3A_46.5hours	protocol 3A_42hours	Field aged upper part	Field aged lower part
WLF constants	C1	31	28	28.692	20.401
	C2	220	219	206.066	169.204
Coefficient of determination	R^2 G*	0.996	0.999	0.994	0.998
	R^2 Phase angle	0.976	0.992	0.984	0.954

Complex modulus and phase angle results of protocol 3A with ageing period of 42 and 46.5 hours for selected temperatures and frequencies are shown in Table 5.13.

Table 5.13: Complex modulus and phase angle for protocol 3A at ageing period of 42 and 46.5 hours

Temperature (°C)	Frequency (Hz)	sample name			
		Protocol 3A_42hours		Protocol 3A_46.5hours	
		G* (Pa)	δ (degree)	G* (Pa)	δ (degree)
-10	1	2.39E+08	16.46	2.36E+08	14.61
-10	8	3.31E+08	12.79	3.18E+08	11.53
-10	20	3.72E+08	11.18	3.54E+08	10.07
0	1	1.11E+08	23.83	1.21E+08	20.06
0	8	1.82E+08	19.28	1.85E+08	16.79
0	20	2.20E+08	17.28	2.19E+08	15.17
10	1	3.82E+07	32.83	4.93E+07	26.12
10	8	7.61E+07	27.87	8.67E+07	22.99
10	20	1.01E+08	25.54	1.09E+08	21.63
20	1	9.09E+06	44.44	1.61E+07	33.45
20	8	2.31E+07	37.71	3.33E+07	29.65
20	20	3.37E+07	35.7	4.47E+07	28.17

5.2.1.3 Infrared Spectroscopy

The chemical analysis of the bitumen samples has been carried out by using Fourier Transform Infrared (FTIR) test. The infrared spectrum of bitumen samples recovered from specimens aged in the laboratory under protocol 3A with aging period of 42 and 46.5 hours and bitumen recovered from field cored specimens are shown in Figure 5.12.

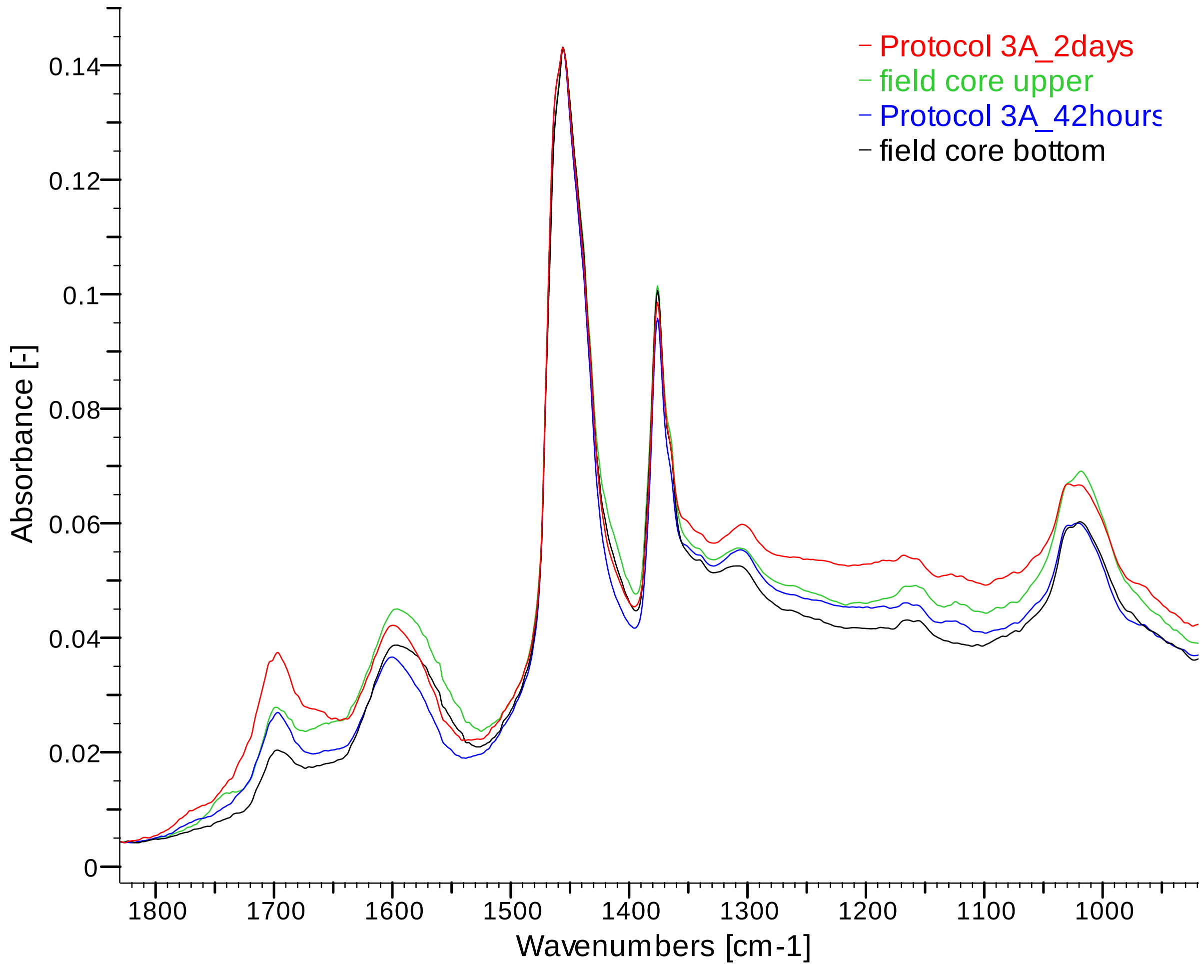


Figure 5.12: IR spectrum of bitumen samples from protocol 3A and field aged specimens at figure print region

It is clear from the above figure that the spectrum for protocol 3A_46.5hours is on top of all other spectra for a wide range of wavenumbers. Protocol 3A_46.5hours has higher ketones peak compared to all the other samples. The upper part of field PA has similar ketones index and height with protocol 3A_42hours while protocol 3A_42hours has comparable sulfoxides result with the lower part of field PA. In general, the upper part of field PA spectrum curve is between protocol 3A_42hours and protocol 3A_46.5hours spectrum curves. This is in agreement with the rheological test results explained in the previous sections. The carbonyl and sulfoxides indices (Ico and Iso) and peak heights of all the bitumen samples are shown in Table 5.12 below.

Table 5.14: Ketones and sulfoxides indices and peak heights

	Sample name			
	Field upper	Field lower	Protocol 3A_42h	Protocol 3A_2days
Ico	0.0462	0.0206	0.0351	0.0646
Iso	0.1867	0.1307	0.1285	0.1598
1700 peak height	0.0099	0.0048	0.0069	0.0106
1030 peak height	0.0189	0.0141	0.0137	0.0152

Based on the chemical test results it can be concluded that when compared to the top part of field aged porous asphalt, protocol 3A with ageing period of 2 days (46.5 hours) gives higher ageing while the same protocol with ageing duration of 42 hours gives less ageing. Which means, in order to get an ageing result comparable to field ageing, the ageing period for protocol 3A should be somewhere between 42 and 46.5 hours.

5.2.2 General discussion

Due to time constrain, Wilhelmy plate tests on recovered bitumen and mechanical tests (stiffness and strength test) on compacted specimens from laboratory aged (by using protocol 3A) were not conducted. Therefore, the following discussion of protocol 3A compared to field ageing are based only on the recovered bitumen rheological and chemical test results presented above.

All the test (penetration, softening point, DSR and FTIR tests) results are concurrent to each other. They all revealed that laboratory ageing of porous asphalt mixture by using protocol 3A at duration of 46.5 hours gives higher ageing compared to the field ageing of PA while with the same ageing protocol but with ageing period of 42 hours results in a lower ageing than the field ageing. In other words, the right ageing period when using protocol 3A to simulate field ageing of porous asphalt can be found somewhere between 42 and 46.5 hours. This ageing period can be determined easily by running some additional ageing tests using protocol 3A. Additional samples can be taken for example at 43, 44, and 45 hours of ageing and the rheological and chemical test results of recovered bitumen from these samples can be compared to the same test results of bitumen recovered from field specimens. Then the ageing period which gives a comparable result with field materials can be taken as the right ageing duration. However, due to time constrain, it was not possible in this study to run additional ageing tests to determine the right ageing period for protocol 3A.

In reality field ageing occurs at a much lower temperatures and using as low as possible ageing temperature in the laboratory is always recommended to best simulate field ageing. As explained before, higher ageing compared to field ageing has been found at a temperature of 135 ºC and an ageing period of 2 days. The ageing temperature can be lowered say to 115 ºC and the duration of ageing can be increased. The ageing period can be determined with the same procedure explained earlier.

Chapter 6 Conclusions and Recommendations

The main aim of this research was to develop an accelerated laboratory ageing method which is able to mimic long term field ageing of porous asphalt by using only standard road laboratory equipments and with a maximum ageing period of 7 days (1 week) in the laboratory. To realize this objective, different ageing protocols have been examined by comparing the rheological and chemical test results of bitumen recovered from laboratory and field aged specimens. In this way a useful laboratory ageing method has been developed to simulate long term field ageing of binder in PA. In the previous chapters the different ageing protocols and their test results compared to field aged PA were discussed. This chapter presents the major conclusions in this research and gives recommendations for further studies.

6.1 Main conclusions

The main conclusions of the research are presented below.

- It was found that the standard binder extraction and recovery procedure using Methylene chloride has trivial effect on rheological (both empirical and fundamental) and chemical properties of the recovered bitumen. Penetration, softening point, DSR and FTIR test results on bitumen sample which went through the recovery process showed no notable change compared to the test result of a bitumen sample which is not exposed to the recovery process. All the test results demonstrate that the effect of binder recovery on recovered bitumen property is insignificant. Consequently, the standard binder recovery method was deployed in this research.
- The field cored porous asphalt specimens have shown differences in the aging property of the binder in the upper and lower part. Rheological and chemical test results on binder recovered from the top and bottom part of field cores reveals this fact. The top part showed higher ageing compared to the lower part. This can be due to the fact that the top part is exposed to UV light and other environmental factors. As raveling is a surface phenomenon, the laboratory simulation of ageing in this research has targeted the properties of the top part of the porous asphalt specimen.

- Laboratory ageing protocol 2, consisting of ageing of a compacted porous asphalt mixture with pressure ageing vessel at a pressure of 2.1 MPa and a step by step increase of temperature (70 ºC for the first 3 days then 80 ºC for the next four days), was not a success. The specimens were highly deformed/damaged and bitumen has drained to the bottom of the plate. The mix was not able to sustain the 2.1 MPa pressure. It was possible to prevent the deformation by supporting the specimens laterally. However this will not avoid drainage of bitumen. The only option to stop drainage of bitumen was to decrease the ageing temperature below softening point which means then to achieve long term ageing of PA it will take unacceptably longer ageing period. Therefore, this ageing protocol was not further developed.
- In this study it was not possible to find a general trend for the adhesive properties of bitumen with change in ageing. The surface energy results determined with the Wilhelmy plate test for bitumen samples at different level of ageing show no consistent trend. The reasons are not know at this time however it might be due to the sensitivity of the Wilhelmy plate test to the thickness measurement of the bitumen samples and/or may be due to the integrity of the test liquids used. Hence, the surface energy test results could not be used in this research to draw any conclusions from the comparison of laboratory and field aged specimens.
- Accelerated laboratory ageing method which is able to mimic 10 years of field ageing of porous asphalt has been developed in this research. It is shown that ageing protocol 1B can very well mimic 10 years of field ageing of porous asphalt. The penetration, softening point, DSR as well as the FTIR test results of protocol 1B and field aged porous asphalt specimens show comparable results. In other words, the bitumen recovered from protocol 1B exhibit similar rheological (both empirical and fundamental) and chemical characteristics compared to bitumen recovered from the top part of 10 years field aged porous asphalt specimens. This ageing protocol (protocol 1B) uses standard ageing laboratory equipment, pressure ageing vessel (PAV), and ageing period of 7 days; which means the primary objective of this research has been successfully achieved.

6.2 Recommendations

Regarding future research work, the following main recommendations are forwarded:

- The ageing protocol developed in this study is able to simulate long term field ageing of porous asphalt. The laboratory ageing procedure is valid for the type of asphalt mixture examined in this research. The sort of porous asphalt mixture studied in this research is rather an old fashion mix. These days, new types of porous asphalt mixtures are being in use for pavement construction. Therefore, there is no guarantee that the accelerated laboratory ageing protocol give the same results for all kind of porous asphalt mixtures. For example a new PA mixture type has a higher percentage of bitumen (about 1%) and fibers are added to decrease binder drainage. Which means then, the binder thickness increases and in effect it delays the development of ageing. Hence, the ageing protocol developed in this research might be severe to such mixtures. Therefore, it is highly recommended to verify the ageing protocol results before use for asphalt mixtures different than the one studied in this research.
- Further studies need to be done to investigate the possible change in adhesive property of bitumen due to change in ageing. Surface energy has been used in this research to assess and compare the adhesive property of field and laboratory aged bitumen samples. As mentioned in the previous chapters, it was not possible to fully use the test results of the surface energy to compare laboratory and field aged samples. The reason was that the surface energy results don't show a specific trend with change in ageing. It is not possible for the time being to give explanation for the question why but possible hypothesis can be: it might be due to the sensitivity of the Wilhelmy plate test on the accuracy of sample preparation and measurement of the sample thickness and width. The other reason might be the integrity of the test liquids used. Hence, for future studies it is highly recommended to determine the surface energy with the use of sessile drop test method instead or in addition to Wilhelmy plate test.
- To assess and measure the simulation of laboratory binder aging with the binder aging in the field, a chemical analysis was done by using Infrared spectrum characteristic peak heights and peak areas. In addition to this

method, however, it is highly recommended in future studies to perform SARA (saturates, aromatics, resins and asphaltenes) classification by using elemental analysis of bitumen samples for a comprehensive qualitative and quantitative chemical investigation.

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