THE INFLUENCE OF MINERAL AGGREGATES AND BINDER VOLUMETRICS ON BITUMEN AGEING

by

Jiantao Wu

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ABSTRACT

Age hardening of bitumen has long been perceived as one of the main factors that can significantly affect the durability of bituminous paving materials. When the bitumen is age hardened, the asphalt mixture will become brittle and its ability to support traffic-induced stresses and strains may significantly reduce. Deterioration of the pavement by readily-induced cracking may follow. In addition, excessive hardening can also weaken the adhesion between the bitumen and aggregate, resulting in loss of materials at the surface layer and generate weakening of the asphalt mixture.

It is generally agreed that ageing is primarily associated with bitumen oxidation and the loss of volatile/oily components from the bitumen to the air and/or aggregates during asphalt mixture production (short-term ageing) and in-place service period (long-term ageing). Both factors cause an increase in viscosity (or stiffness) of the bitumen and consequential stiffening of the asphalt mixture. However, in terms of the effects of mineral aggregates on bitumen ageing, studies have shown that it is not only the exudation part of bitumen ageing that appears to be of significance, the petrographic nature of aggregates may have added effects on the ageing of bitumen.

This thesis attempts to provide an improved understanding of the effects of different mineral aggregates on bitumen ageing. Asphalt mixtures comprising different aggregate types and bitumen-filler mastics containing different fillers were artificially aged in the laboratory and the stiffness of the mixtures, the rheological properties and chemical composition of recovered binders were determined after different durations of ageing. A pure bitumen ageing study, utilising two different ageing simulation methods, and a study on the effect of binder film thickness on asphalt ageing were carried out prior to the above experiments. This is so that the mechanism of bitumen oxidation, which is the main cause of bitumen age hardening, could be better understood and a suitable binder film thickness could be selected for asphalt mixtures to show the effects of aggregate on ageing more clearly.

Comparison between pure bitumen ageing using the standard Rolling Thin Film Oven Test (RTFOT) and that using the non-standard High-shear mixer indicated that bitumen age hardens following different mechanisms when it was aged in different ageing simulation techniques. Although the High-shear aged binder was observed to be with similar penetration and ring & ball (R&B) softening point to the RTFOT aged binder, the results from Fourier transform infrared spectroscopy (FTIR) tests showed that bitumen oxidation has played a more important role in the hardening of RTFOT aged binder than in that of High-shear aged binder.

Significant differences were observed between the ageing properties of asphalt mixtures with different binder film thicknesses (binder contents). In general, the amount of age hardening in the asphalt mixture increases with decrease in binder film thickness, which indicates that the effects of bitumen oxidation and mineral aggregates on bitumen ageing can be promoted by a thin binder film.

Studies on the influence of mineral materials (aggregates and/or fillers) on bitumen ageing showed that the acidic and basic mineral matters affect the bitumen ageing in differing ways due to their differently charged surface textures. The acidic minerals, e.g. granite and gritstone, were observed to be better in catalysing bitumen oxidation, which accelerated bitumen ageing, whereas the basic minerals, e.g. limestone, showed greater adsorbing effects, which decelerates bitumen ageing. In addition to these main findings, it was also found from these studies that the current binder recovery technique may not be suitable in the ageing study of bituminous materials and a bitumen ageing study utilising the modified dynamic shear rheometer (DSR) test is proposed at the end of this thesis.

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DECLARATION

The research described in this thesis was conducted at the University of Nottingham, Department of Civil Engineering between October 2005 and October 2008. I declare that the work is my own and has not been submitted for a degree of another university.

Jiantao Wu
Nottingham
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1 INTRODUCTION

1.1 Background

The term ‘bitumen’ is widely believed to originate in the ancient and sacred language of Hindus in India, Sanskrit, in which ‘jatu’ means pitch and ‘jatu-krit’ means pitch creating. These terms referred to the pitch produced by some resinous trees. The Latin equivalent is claimed to be originally ‘gwitu-men’ or ‘pixtu-men’, which was subsequently shortened to ‘bitumen’ when passing via French to English (Read and Whiteoak, 2003).

The earliest recorded use of bitumen was by Sumerians whose empire existed from around 3500 to 2000 B.C.. From then on, bitumens have been used for millennia as adhesives, waterproofing agents and in some cases, preservatives (Abraham, 1945). These early applications made use of ‘natural’ bitumens obtained from surface seepages such as the lake of natural bitumen in Trinidad. Although natural bitumens are still used, most present-day applications utilise bitumens manufactured from crude oils.

The manufacturing of bitumen from crude oil involves the processes of distillation, blowing and blending. After these processes, the components of the crude oil with the highest molecular weight and chemical complexity become concentrated in bitumen. The four principal crude oil producing areas in the world include the United States, the Middle East, the Caribbean countries and Russia. Crude oils from different sources differ in their physical and chemical properties and, as a consequence, so do the bitumens produced from the crudes. Bitumens are principally composed of organic compounds consisting of primarily hydrogen and carbon, referred to as hydrocarbons, but most also contain other atomic particles, e.g. sulphur or oxygen, which significantly influence the chemical and physical properties of the bitumen (Traxler, 1936; Romberg et al., 1959).

The use of bitumens in road construction dates back to the middle of the nineteenth century when attempts were made to utilise rock asphalt from European deposits for road surfacing and, from this, there was a slow development of the use of natural products for this purpose, followed by the advent of coal tar and later of bitumen manufactured from crude oil (refinery bitumen) (Read and Whiteoak, 2003). At present, the principal use of bitumens (mainly refinery bitumens) is for road construction and, to a lesser extent, airfield pavements. It is claimed that over 80% of the 100 million tonnes of worldwide annual bitumen consumption is used for paving applications in the construction and maintenance of roads (www.bp.com, 2009).

1.2 Problem Statement

Bitumens are widely used in road construction largely because they are relatively inexpensive and generally provide good durability in paving mixtures. In addition, bituminous pavements are generally characterised by their immediate serviceability, good riding quality and absence of joints. However, bitumen is not a panacea. As an organic substance, bitumen can age harden, i.e. increase in viscosity, which results in significant deterioration of the serviceability of bituminous paving materials. When the bitumen is age hardened, the asphalt mixture will become brittle and its ability to support traffic-induced stresses and strains may significantly reduce, leading to deterioration of the pavement by readily-induced cracking. In addition, excessive hardening can also weaken the adhesion between the bitumen and aggregate, resulting in loss of materials at the surface layer and generate weakening of the asphalt mixture.

Much effort has been afforded to the study of age hardening and many factors have been established to be capable of affecting bitumen ageing. It is generally agreed that bitumen ageing is primarily associated with bitumen oxidation and loss of volatiles from bitumen to air and/or mineral aggregates. However, in terms of the effects of aggregate on ageing, further researches showed that it is not only the exudation part of bitumen ageing that appears to be of significance; the petrographic nature of aggregates may have added effects on the ageing of bitumen. Firstly, some mineral components on the surface of aggregates are found to be able to catalyze bitumen oxidation (Petersen, 1974). Secondly, the aggregates can be electrically charged by the moisture present on their surface due to the ionisation of their minerals (Castano et al., 2004; Bagampadde et al., 2005). The charged and polarised aggregate surface can adsorb polar groups (either naturally occurring ones or the products of oxidation) within bitumen, which may decelerate the bitumen hardening process (Curtis et al., 1993).

The above mechanisms regarding the way mineral aggregates influence the bitumen ageing have been discovered by researchers during the last three decades. However, the exact mechanisms of ageing of bitumen when in contact with mineral aggregates in the real paving materials remain an enigma and require further research. This is because the ageing of bituminous mixtures is a result of bitumen oxidation, aggregate effects and many other minor factors, all of which are further affected by the bitumen and/or mineral aggregate type, aggregate gradation, binder and air void contents of the asphalt mixture. Therefore, it is extremely difficult to quantify the effect of every single factor on bitumen ageing.

1.3 Research Objectives and Scope

The main aim of this study is to develop a better understanding of the effects of mineral aggregates on bitumen ageing. Chapter 5 introduces a study on the ageing of asphalt mixtures containing the same binder but two different types of aggregates: a typical acidic aggregate of granite and a typical basic aggregate of limestone. In addition, it has been long recognised that it is the fine aggregate that contributes the major part of the contact area between aggregate and bitumen and affects bitumen ageing more significantly than other aggregates in an asphalt mixture. A study on the ageing of bitumen-filler mastic was, therefore, also conducted and is presented in Chapter 6.

As stated above, the ageing of bituminous materials is a result of various factors. Bitumen oxidation, as the main cause of age hardening, can significantly influence the effects of mineral aggregates on ageing, either the adsorbing or the catalytic effects. Therefore, a study on the effects of oxidation on pure bitumen ageing was carried out before the above two studies and is presented in Chapter 4. In addition, Chapter 4 also presents a study on the effect of binder content (bitumen film thickness) on the ageing of asphalt mixtures, because it is considered that the proportion of bitumen affected by oxidation and mineral aggregate is highly affected by how thick the binder is spread over the aggregate surface.

Prior to introducing the above experimental work, the principal findings of a literature review are summarised in Chapter 2 of this thesis, and the experimental techniques adopted in these studies are presented in Chapter 3.

2 LITERATURE REVIEW

2.1 Introduction

This chapter presents both specific areas pertaining to the fundamental properties of bituminous materials, and the principal findings from a review of selected literature that are strongly related to the current study – ageing of bituminous paving materials.

The literature review begins with a general introduction about the application of bituminous materials in pavement engineering, outlining the history, types and structures of bituminous pavements. In addition, the different failure modes for bituminous paving roads and their relations to bitumen ageing are also introduced. Subsequently, fundamental properties of the two main phases of bituminous materials, bitumen and aggregate, are presented in the second and third sections, where various means of measuring these properties are also introduced.

The final section of the literature review summarises principle previous findings on the physical and chemical mechanism associated with the ageing of bituminous materials. The different artificial ageing simulation methods developed by previous researchers are presented in this section also.

2.2 Binders in Road Construction

2.2.1 Use of bituminous binders in road building

The term ‘bituminous binder’ is generally taken to include ‘coal tar’, ‘natural asphalt’ and ‘refinery bitumen’ (which is obtained from petroleum crude). All of these three types have been used historically by paving industry; however it is the petroleum one that is now enjoying maximum use in this industry, although it was the last to be adopted.

In the United Kingdom (UK), before bituminous binders were used in road construction, the two main forms of pavements were Telford pavements, which have a likeness to today's asphalt pavements, and Macadam pavements, which are rudiments of modern DBM pavements (Smiles, 1904). Figures 2.1 and 2.2 show typical Telford and Macadam roads. Such roads, constructed without any binder medium to hold the stones together, proved to have serious shortcomings under the action of pneumatic tyres and the higher speeds of motor cars (Illston and Domone, 2001). In dry summer weather, a great deal of dust was generated from the road surface, which forced pavement engineers to consider new materials for road construction.

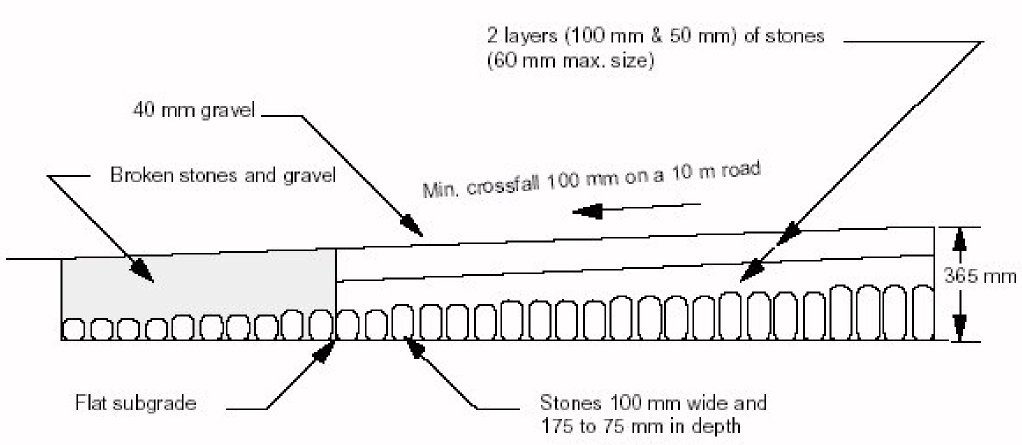


Figure 2.1 Typical Telford Road (Collins and Hart, 1936)

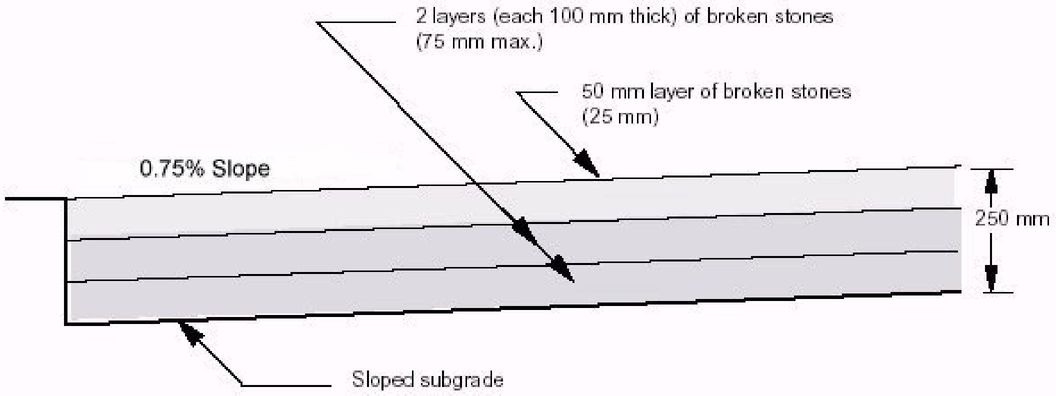


Figure 2.2 Typical Macadam Road (Collins and Hart, 1936)

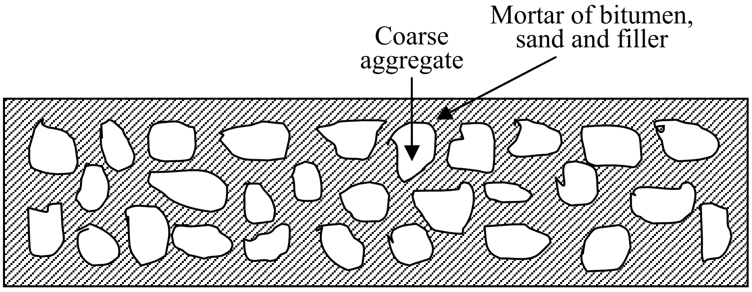
Coal tar, as a by-product from the coal-gas industry, had been abundantly available in the UK from about 1800. It was quickly recognised by road engineers as an appropriate dressing material to bind the road surface since it could become sufficiently fluid to be sprayed by the use of heat, but stiffened on cooling (Illston and Domone, 2001). In 1848, the world's first tar macadam pavement was placed outside of Nottingham (Lincoln Road) (Hubbard, 1910; Collins and Hart, 1936), which indicated the beginning of the 'Bituminous Pavement Era'.

Initially, the coal tar was simply poured onto the road surface in order to seal it and protect the road from water damage. After that, more and more benefits of using tar were realized by engineers and a range of 'coated stone' materials, or 'tarmacadam mixes', were developed (Illston and Domone, 2001). At the same time, other bituminous binders with similar properties as coal tar were gradually employed into the road construction.

In 1913, refinery bitumen was used in road building for the first time in the UK. Compared with coal tar, bitumen was found to be less temperature-susceptible, which makes it more resistant to deformation at high temperature, less brittle and more resistant to cracking at low temperature (Illston and Domone, 2001). Therefore, bitumen is now predominantly used in pavement engineering; the use of tar in road construction is limited to tar/bitumen blends for sealant use where its greater resistance to oil and diesel spillage is an advantage. This report is concerned only with bitumen.

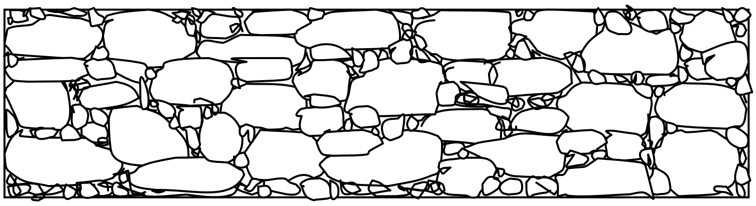
2.2.2 Types of bituminous paving mixtures

With the development of the bituminous paving industry, an extensive range of bituminous mixtures are now available for the wide variety of circumstances in which they are used. The mixture characteristics can vary significantly according to their bitumen content and grade as well as their aggregate size and grading. However, based on their aggregate gradings, they can all be generally classified into two groups: asphalts (gap graded materials) and coated macadams (continuously graded materials). Figure 2.3 shows the fundamental features of asphalts and macadams. Although it has been suggested by researchers (Read and Whiteoak, 2003; Illston and Domone, 2001) that this classification was never particularly scientific and somewhat inconsistent, it has implied the two main load-carrying mechanisms for bituminous materials: 'mortar mechanism' (in which the strength of mixtures is derived from the characteristics of bitumen/sand/filler mortar, such as UK 'hot rolled asphalt') and 'stone contact mechanism' (in which the strength of mixtures is derived from the interlock of the coated aggregate, such as UK 'dense bitumen macadam') (Jackson and Dhir, 1996).



Characteristics
- Dense Mortar providing strength and stiffness
- High bitumen content
- High filler fines content
- Low coarse aggregate content
- Load transmitted through mortar

a)



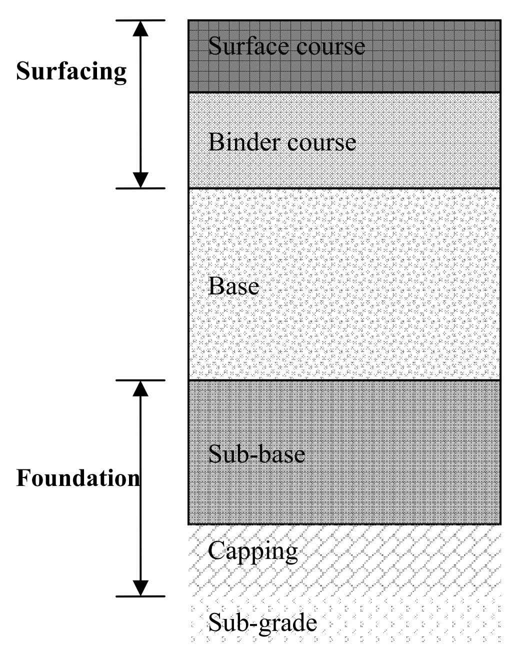
Characteristics
- Well graded aggregate giving a dense stable aggregate structure
- Low bitumen content
- Load transmitted through aggregate structure

b)

Figure 2.3 The fundamental features of asphalts (a) and macadams (b)

2.2.3 Bituminous pavement layers

In structural terms, the purpose of a pavement is to distribute the traffic load to a level which the underlying subgrade can bear (Illston and Domone, 2001). It is noticed that the stresses induced by traffic loads are high at the surface but reduce with depth. Therefore, from practical and economical considerations, bituminous pavements are normally constructed with multi-layers, using relatively weak materials below and progressively stronger ones above (Croney and Croney, 1998). Figure 2.4 shows typical layers of bituminous pavement structure. The functional and structural requirements of the layers, varying with position (depth), are also listed in the figure.



Layers for bituminous pavement	Requirements
Surface course Binder course	• skid-resistant • acceptable level of noise • acceptable level of spray • acceptable riding quality • prevent water infiltration
Base	• main structural element in pavement • permanent deformation resistant • cracking resistant • capable of withstanding stress induced by temperature gradients
Sub-base Capping	• well drained • adequate platform to place layers above • capable of transmitting the stresses induced by traffic loading to subgrade • provide frost protection if needed
Sub-grade	

Figure 2.4 Typical layers in a bituminous pavement (Read and Whiteoak, 2003)

2.2.4 Failure mechanisms of bituminous pavement

Under the effects from both the magnitude and number of traffic loads, roads deteriorate in a number of ways. These different modes, as shown in Figure 2.5, can be broadly divided into two forms: surface failure and structure failure.

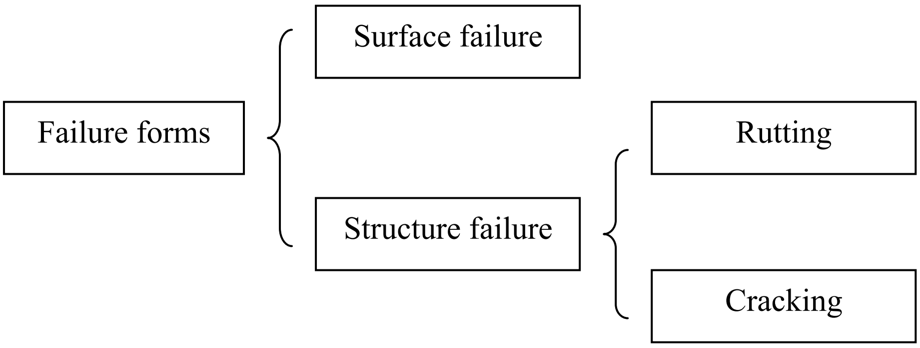


Figure 2.5 Failure forms for bituminous paving roads

As it can be seen in Figure 2.4, the surface layer is the only layer that is visible to the road user; failure of the surface can hence affect the road serviceability in a more distinct manner than the structure failure. This may be caused by breakdown of the surface material either generally (e.g. fretting or stone loss) or locally (e.g. a pot hole develops as a result of a local weakness). In addition, the skidding resistance may drop below an acceptable level, because of polishing or abrasion.

Brown and Brunton (1986) described the two principal structure failure mechanisms (rutting and cracking) for a bituminous paving road, as shown in Figure 2.6. Rutting is associated with permanent deformation of all the pavement layers, which is an accumulation of the small irrecoverable part of the deformation caused by each wheel load (Illston and Domone, 2001). It is a function of the viscoelastic nature of the bitumen, the mechanical support offered by the grading of the aggregate, and the supporting ability of the underlying subgrade also. Cracking of the asphaltic layers arises from the tensile strain developed in the bound layers as each wheel load passes. It is therefore a function of both the magnitude of tensile strain and the number of the load applications. In thinner pavements, cracking is commonly assumed to initiate at the bottom of the bound layer (as shown in Figure 2.6) where the maximum tensile stress and strain occur, and then propagate upwards under repeated load applications (Brown, 2000). However, cracking can initiate at the pavement surface and propagate toward the bottom of the layer for thicker pavements. Surface cracking is also possible at the shoulder of ruts.

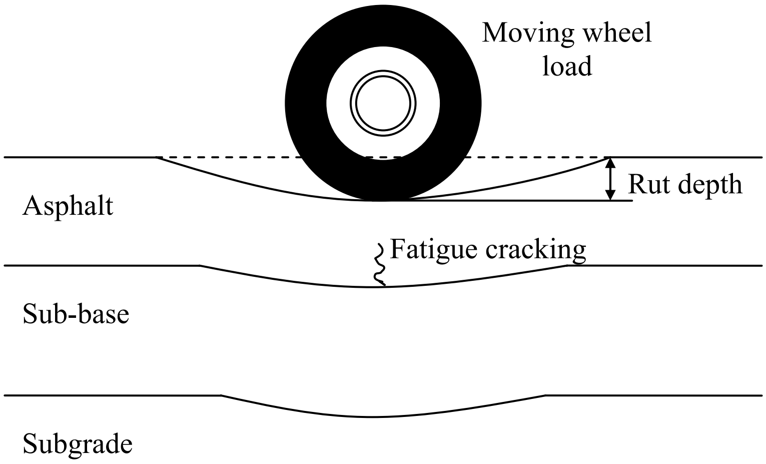


Figure 2.6 Failure mechanism for bituminous pavement structure

2.2.5 Age hardening in bituminous pavement

Many adverse environmental factors can accelerate the process of pavement failures that have been introduced above. However, for a pavement constructed strictly according to specification, it is commonly agreed that the two primary factors affecting the durability of the bituminous mixture are ageing hardening and moisture damage (Scholz, 1995). In this thesis, only the age hardening will be discussed and studied.

Bitumen, in common with many organic materials, can become age hardened (increases in viscosity) under the influences of oxygen, ultraviolet radiation and changes in temperature. A reasonable level of age hardening in pavement layers has been commonly viewed as being beneficial to the load spreading ability and the deformation and/or fatigue resistance of the structure. This hardening is known as ‘curing’ and is believed to extend the life of a pavement (Nunn et al., 1997). However, an excessive bitumen ageing will significantly influence the durability of bituminous mixtures. When the bitumen is excessively aged, the asphalt mixture will become brittle and its ability of supporting traffic-induced stresses and strains may significantly reduce, which can easily cause some cracking damage to the bound layer of a pavement (structure failure in Figure 2.5). Excessive hardening can also weaken the adhesion between the bitumen and aggregate, resulting in loss of materials at the surface layer (surface failure in Figure 2.5). Therefore, bitumen ageing is extremely important for the durability of bituminous pavements; and it is essential to have a good understanding of it.

2.3 Bitumen

Bituminous materials consist of a graded aggregate bound together with bitumen. Thus their properties, including ageing property, depend upon the properties of the individual phases as well as the mix proportions. Read and Whiteoak (2003) stated that the performance of an asphalt pavement in service is largely determined by the rheological (physical) properties and, to a lesser extent, the chemical composition of the bitumen. Therefore, prior to discussing the mechanism and/or the affecting factors of bitumen ageing, it is warranted to make a review on the chemical composition of bitumen.

2.3.1 Elemental composition of bitumen

The chemical composition of bitumen is extremely complex and it varies widely according to the source of the crude oil from which the bitumen originates (Read and Whiteoak, 2003). In general, bitumen is a complex chemical mixture that is mainly composed of a large amount of hydrocarbons with minor amounts of structurally analogous heterocyclic species, some functional groups (heteroatoms) containing sulphur, nitrogen and oxygen atoms (Traxler, 1936; Romberg et al., 1959) and trace quantities of metals such as vanadium, nickel, iron, magnesium and calcium, which occur in the form of inorganic salts and oxides or in porphyrine structures.

Although the heteroatoms are a minor component compared to the hydrocarbon moiety and their concentration can vary over a wide range depending on the source of bitumen, they can significantly impart functionality and polarity to the molecules and their presence may make a significant contribution to the differences in the rheological properties of bitumens from different crude sources (Petersen, 1984).

Elementary analysis of bitumens manufactured from a variety of crude oils shows that most bitumens contain:

•	Carbon	82% - 88%
•	Hydrogen	8% - 11%
•	Sulphur	0% - 6%

Oxygen	0% - 1.5%
Nitrogen	0% - 1%

Although the elemental analyses are important to note, they are average values of binders manufactured from different crude oil sources and reveal little information about how the atoms are composed in the molecules, which is necessary for a fundamental understanding of how composition of bitumen affects the physical properties and chemical reactivity (Petersen, 1984).

2.3.2 Molecular structure of bitumen

As stated above, the way in which the elements are incorporated into molecules and the type of molecular structure present is far more important than the total amount of each element present in bitumen. However, as the organic molecules comprising bitumens vary widely in composition from non-polar, non-aromatic hydrocarbons to highly polar, highly aromatic structures containing varying amounts of heteroatoms, such as oxygen, nitrogen and sulphur (Petersen, 1984); it is almost impossible to fully unravel the chemical structures of a single bitumen, at the present time, let alone the vast number of different bitumens that occur as a result of variable crude oil sources. Therefore, researchers generally gain an insight into bitumen chemical structures by examining the behaviour of some ‘typical’ functional groups.

Figure 2.7 presents the three principal types of molecules found in bitumen. The carbon atoms in the aliphatics are linked in straight or branched chains. In the naphthenics, or cyclics, they are linked in simple or complex (condensed) saturated rings, where ‘saturated’ means that all the available electron bonds of carbon atoms are occupied with hydrogen. Aromatics are materials characterized by the presence of one or more particularly stable six-atom rings (e.g. benzene, toluene, etc.).

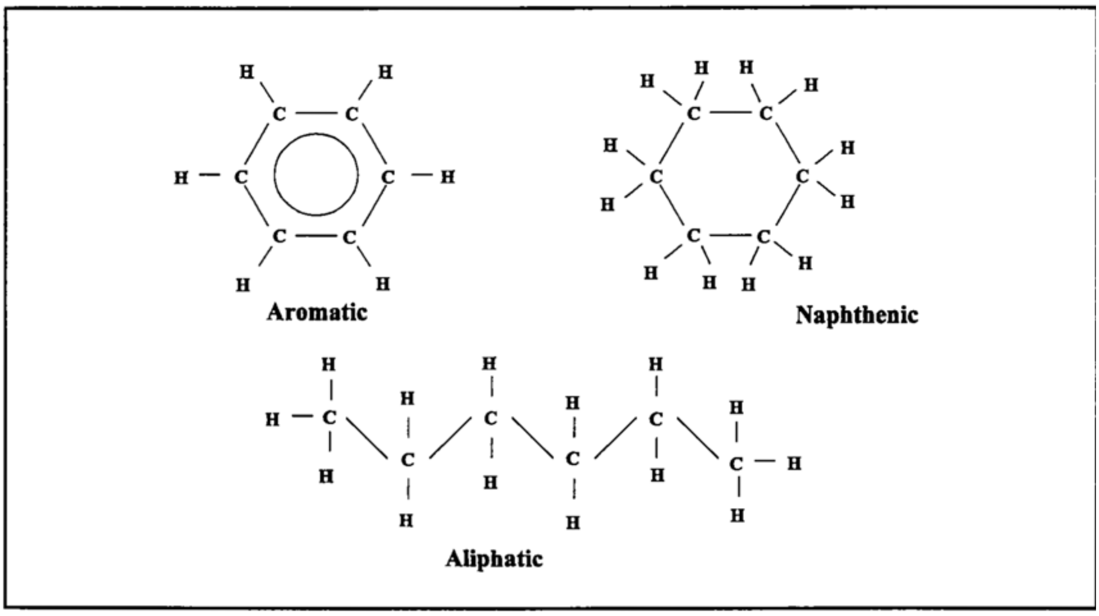


Figure 2.7 Typical types of molecules found in bitumen

The molecules with different structures are held together through chemical bonds which are relatively weak and can be broken by application of heat and/or shear loading. The physical and chemical behaviour of bitumens are affected by the various ways in which these molecules interact with each other.

2.3.3 Fractional composition of bitumen

The number of molecules with different chemical structures is astronomically large in every single bitumen. In addition, the precise composition of a bitumen is strongly dependent on its parent crude oil and the method of manufacture. Therefore, chemists have not attempted to separate and identify all the different molecules in bitumen (Petersen, 1984; Halstead, 1985). Instead, different techniques have been developed to separate bitumen into less complex and more homogenous fractions. Generally, these techniques divide the bitumen into groups or generic fractions based on molecular size, chemical reactivity and/or polarity. It is important to note that, with regard to chemical and physical characteristics, the fractions from one separation technique differ from those from another technique.

Among all the fractional separation techniques, the method developed by Corbett (Corbett, 1969) has probably been most widely employed to define bitumen constitution for research purposes. Figure 2.8 shows a schematic procedure for this method.

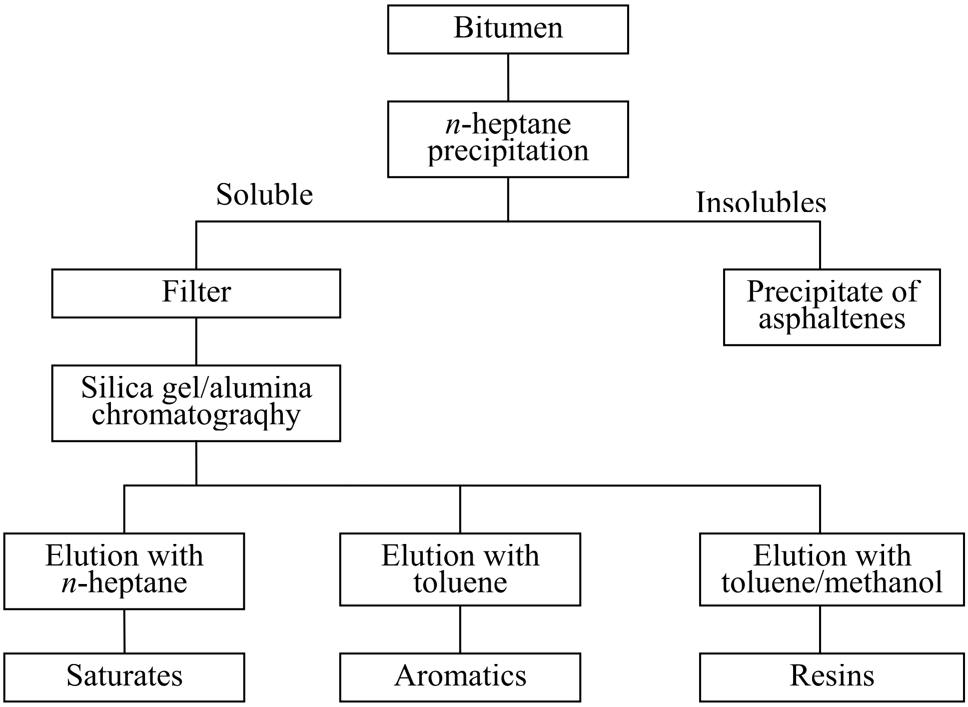


Figure 2.8 Corbett adsorption/desorption chromatography

In this method, asphaltenes are separated first based on their insolubility in n-heptane, they are found to be the most highly polar fraction in the bitumen. After the precipitate of asphaltenes, the fractions remaining in n-heptane, which are commonly called maltenes, are then adsorbed on a chromatographic column and sequentially desorbed with solvents of increasing polarity. After several cycles of selective adsorption-desorption treatment, maltenes are subdivided into three fractions with increasing polarity (Read and Whiteoak, 2003). As shown in Figure 2.8, these three fractions are usually called saturates, aromatics and resins. It is important to note that these four fractions are still complex mixtures and there is usually some overlap between them. The main characteristics of the four groups are as follows:

Asphaltenes

Asphaltenes are *n*-heptane insoluble black or brown amorphous solids containing, in addition to carbon and hydrogen, some nitrogen, sulphur and oxygen (Airey, 1997).

The significant differentiating feature of this fraction is the preponderance of molecules with highly condensed planar and polarizable aromatic ring systems together with a high concentration of polar, heteroatom-containing functional groups (Petersen, 1984). Because of this, molecules in this fraction are strongly attached and are difficult to disperse even in polar solvents. The asphaltenes have a large effect on the rheological properties of bitumen. The increase of the asphaltene content will lead to a harder, more viscous bitumen with a lower penetration, higher softening point and consequently higher viscosity. Asphaltenes constitute approximately 5% to 25% of the bitumen (Read and Whiteoak, 2003).

Resins

Resins are n-heptane soluble and are chemically similar to asphaltenes. They are dark brown solid or semi-solid and very polar in nature which makes them strongly adhesive. Resins are regarded as dispersing agents or peptisers for asphaltenes. Thus, the proportion of resins to asphaltenes can determine, to a degree, the solution (SOL) or gelatinous (GEL) character of the bitumen (Read and Whiteoak, 2003).

Aromatics

Aromatics comprise the lowest molecular weight naphthenic aromatic compounds in the bitumen. They are dark brown viscous liquids that usually contain condensed nonaromatic and aromatic ring systems and heteroatoms sulfur, oxygen and nitrogen. Aromatics constitute 40% to 65% of the total bitumen and they represent the major proportion of the dispersion medium for the peptised asphaltenes (Read and Whiteoak, 2003).

Saturates

Saturates are non-polar viscous oils with a similar molecular weight range to aromatics. The saturate fraction may contain saturated normal and branched-chain hydrocarbons, saturated cyclic hydrocarbons (naphthenic hydrocarbons). Sometimes, a small amount of mono-ring aromatic hydrocarbons may also be observed in this fraction; however, the properties of these mono-ring molecules are determined by attached saturated hydrocarbon side chains (Petersen, 1984). Saturates generally constitute 5% to 20% of the total bitumen.

2.3.4 Functionality and polarity

As previously stated, the heteroatoms (e.g. nitrogen, sulphur and oxygen) impart functionality and polarity to molecules present in bitumens. Although present only in small quantities, they are of importance to bitumen chemists because of their disproportionately large effect upon the physical properties and performance characteristics of bitumens. Functionality refers to the way in which bitumen molecules interact with each other as well as with the molecules and/or surfaces of other materials (e.g. mineral aggregate). Polarity refers to the way in which the electrochemical forces among the bitumen molecules are imbalanced, producing a dipole. Polar compounds (composed of carbon, hydrogen and heteroatoms) form associations that give bitumen its elastic properties. These compounds coexist with non-polar compounds (composed of carbon and hydrogen), and together give bitumen its viscous properties.

2.4 Aggregate

Aggregates constitute the biggest part of bituminous materials; the percentage by weight ranges from about 92 per cent for a wearing course asphalt to about 96 per cent for a continuously graded macadam. With such a big proportion in bituminous materials, the aggregate has important effects on the strength and stiffness of bituminous mixtures.

Most references about the aggregates within asphalt have paid attention to aggregate gradings, shapes, strength, roughness etc, all of which are important to the performance of asphalts. However, as the main purpose of this study is to investigate the effects of different mineral aggregates to bitumen ageing, only the mineral-related properties of aggregates are reviewed in this thesis.

2.4.1 Minerals and aggregates

A mineral is a naturally occurring solid with a definite chemical composition and a specific crystalline structure; and aggregates are made up of minerals, usually several, but sometimes only one or two. The common minerals in paving aggregates have been summarized and classified in different ways by different researchers (ASTM C

294, 1991; Roberts et al., 1991). Among these minerals, the groups of silicates and carbonates are always mostly studied and discussed.

The silicates are the largest, the most interesting and the most complicated class of minerals by far. Approximately 30% of all minerals are silicates and some geologists estimate that 90% of the Earth's crust is made up of silicates. They are composed largely of silicon and oxygen, with the addition of ions such as aluminium, magnesium, iron, and calcium. Great attention is also paid to the carbonate minerals because one of the most widely used paving aggregates, limestone, belongs to this category. In addition, limestone ($CaCO_3$) is a typical example of aggregate that is mainly composed of a single mineral.

2.4.2 Surface charge of aggregates

Aggregates, where water is always present, have an electrical charge in their surface due to the ionization of their minerals (Castano et al., 2004; Bagampadde et al., 2005). Aggregates containing different minerals can be charged differently and, the sign of the charge allows researchers to classify aggregates into two groups: acidic and basic. It is stated that acidic aggregates, e.g. quartzite, granite, porphyry, etc., are mainly silicates, which can be negatively charged when contact with moisture by forming SiO_3^{2-} ions; and basic aggregates (limestone) are mainly carbonates forming positively charged Ca^{2+} ions (Su, 1996). With such chemical charges, the aggregate surfaces will present different polar characteristics, as shown in Figure 2.9, which can lead to a variable affinity towards the polar compounds within the bitumen when they are mixed, see Figure 2.10.

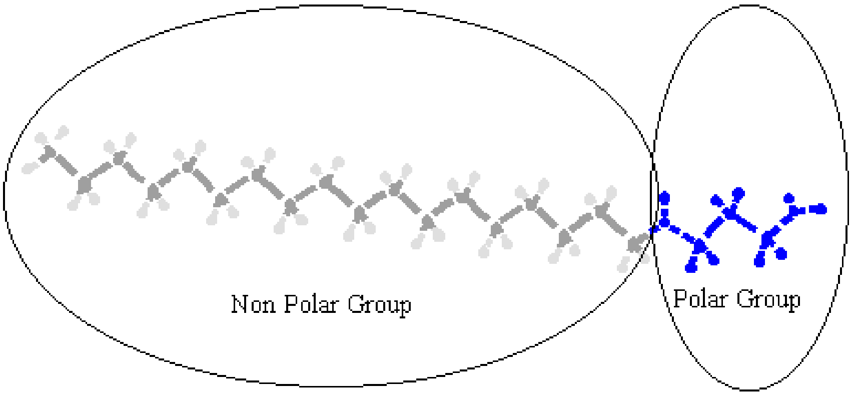


Figure 2.9 Typical surfactant chemical structure (Castano et al., 2004)

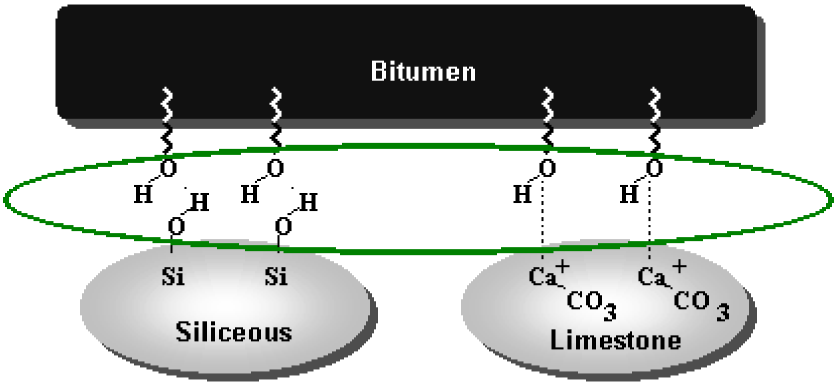


Figure 2.10 Adhesion mechanisms for different aggregates (Castano et al., 2004)

2.4.3 Mineral fillers

The term mineral filler has been generally applied to a special fraction of the mineral aggregate, most or all of which (at least 65% by ASTM and AASHO specifications) passes the No. 200 sieve (75 µm). As one of the ingredients in a bituminous mixture, the filler plays a major role in determining the properties and behaviour of the mixture and therefore, its role in the mixture has been studied extensively (Tunnicliff, 1967; Anderson and Coetz, 1973; Harris and Stuart, 1995; and Cooley et al., 1998) from the first time it was involved in asphalt paving mixtures, which, as recorded, may date back to 1890 (Tunnicliff, 1967).

Initially, the mineral filler fraction was commonly considered by many engineers as part of the aggregate system, whose main role is to fill the voids between coarser aggregate particles. However, further studies have shown that, because of its fineness and its surface characteristics, the importance of the filler in a bituminous material is much more than a role of ‘void filler’. This point is reinforced by the work being conducted at the Danish National Road Laboratory as part of a Strategic Highway Research Program (SHRP) Idea Project, SHRP AIIR-13, Microscopic Analysis of Asphalt Aggregate Mixtures Related to Performance (Larsen, 1991). In that study, researchers impregnated the HMA with a fluorescing polymer, and thin sections of this HMA were then photographed with optical transmission microscopy.

Based on the AIIR study, Anderson et al. (1992) made several observations as follows:

- A major part of the filler fraction is embedded in the bitumen in such a way that the binder in asphalt mixture is not the pure bitumen but instead a mastic consisting of mineral filler and bitumen.
- The fine fraction of aggregate contributes the majority of the surface area generated by the aggregate.
- The properties of the fine fraction should be dominant in terms of physical-chemical interaction between the binder and mineral aggregate.

2.5 Bitumen Ageing

As stated above, bitumen age hardening is one of the two main factors that can significantly affect the durability of asphalt mixtures, by causing both surface failure and structure failure to the bituminous paving road. In this section, factors affecting bitumen ageing will be introduced; major previous findings about ageing mechanisms will also be reviewed and discussed.

2.5.1 Factors affecting ageing

Traxler (1963) indentified 15 different factors which may affect the chemical, rheological and adhesion characteristics of bitumen (as shown in Table 2.1). Some of these effects were proved by Traxler with experimental data. However it is noted that some of those listed had not been given experimental consideration.

Table 2.1 Factors affecting bitumen ageing

	Influenced by					Occurring	
Factors	Time	Heat	Oxygen	Sun-light	Beta & gamma rays	At the surface	In mass
Oxidation (in dark)	√	√	√			√	
Photo-oxidation (direct light)	√	√	√	√		√	
Volatilisation	√	√				√	
Photo-oxidation (reflect light)	√	√	√	√		√	
Photo-chemical (direct light)	√	√		√		√	
Photo-chemical (reflected light)	√	√		√		√	√
Polymerization	√	√				√	√
Steric or physical	√					√	√
Exudation of oils	√	√				√	
Changes by nuclear energy	√	√			√	√	√
Action by water	√	√	√	√		√	
Absorption by solid	√	√				√	√
Absorption of components at a solid surface	√	√				√	
Chemical reactions	√	√				√	√
Microbiological deterioration	√	√	√			√	√

Petersen (1984) stated that the most important aspect of a durable bitumen is its resistance to chemical composition change while in service. He outlined three fundamental composition-related factors which govern the changes that could cause bitumen hardening in pavements as follows:

- Loss of oily components of bitumen by volatility or absorption by porous aggregates;
- Change in chemical composition of bitumen molecules from reaction with atmospheric oxygen, and
- Molecular structuring that produces thixotropic effects (steric hardening).

Petersen (1984) also pointed out that, “Irreversible adsorption of polar bitumen components by mineral aggregate surfaces, although not a factor that might be expected to harden bitumen, will produce compositional changes in the bitumen that may also significantly affect bitumen properties and ageing characteristics.” This point is well supported by some of Petersen’s other studies (Huang et al., 2002; Petersen et al., 1974 (a) and Petersen et al., 1974 (b)).

Based on Petersen’s statements above, it is concluded that most composition-related bitumen ageing happens on two interfaces: the air-bitumen interface and the bitumen-aggregate interface, as shown in Figure 2.11.

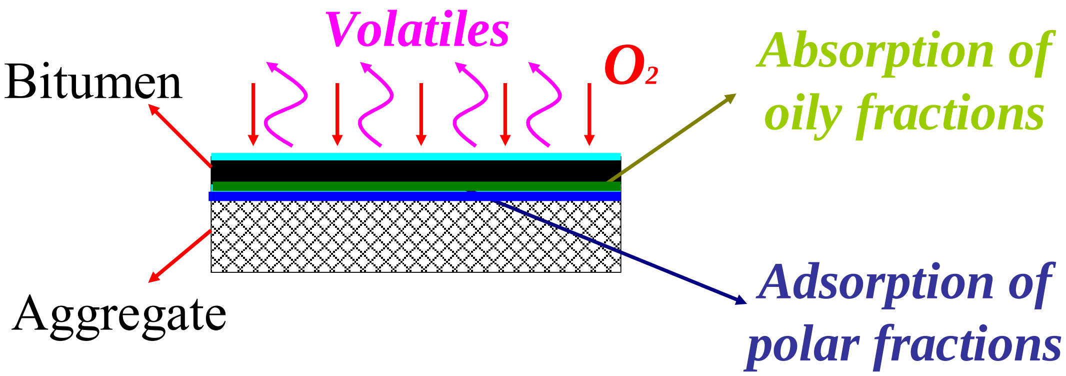


Figure 2.11 Major factors affecting bitumen ageing

2.5.2 Mechanism of bitumen oxidation

The oxidation of the hydrocarbon components in bitumen is generally accepted as a major factor contributing to the hardening and embrittlement of asphalt roads

(Petersen et al., 1974 (a)). Its chemical mechanism has been investigated for more than 50 years, and most of the studies can be generally divided into two groups: studies based on fractional change and studies based on typical molecular change.

Fractional changes in oxidation

The change in the amounts of fractional components of bitumen generally observed on oxidative ageing is a movement of components from the more nonpolar to the more polar fractions (Petersen, 1984). The changes in fractional chemical composition of bitumen associated with ageing are shown in Figure 2.12, from which, firstly, a continued increase in asphaltenes can be observed during progressively longer ageing, oxidation times and this increase is offset by a significant decrease in total amount of aromatic and resin fractions. Elemental Analysis of the asphaltenes implies that there is also an increase in the oxygen content during ageing (Tallafigo, 1993). Secondly, Figure 2.12 shows the resins increase during the initial stages of oxidation, up to a maximum and then decrease in content. The increase in this fraction coincides with the rapid reduction in the aromatics fraction and starts to decrease at the point where the decrease rate in aromatics starts slowing down considerably. Finally, the saturate fraction shows the least change on bitumen oxidation ageing and the slight decrease of this fraction during oxidation is probably a result of volatilisation of some of the saturate components.

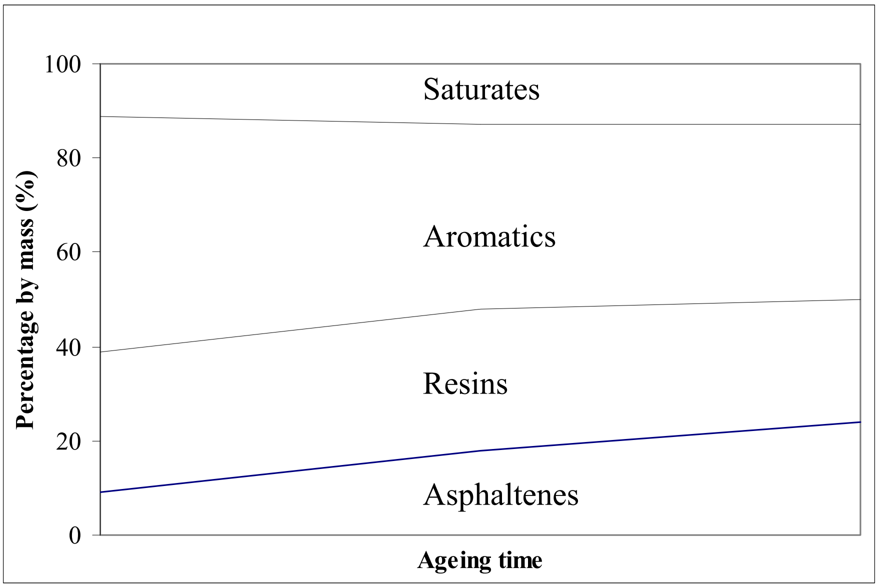


Figure 2.12 Changes in fractional chemical composition as a function of ageing (Chipperfield et al., 1970)

Figure 2.12 shows the fractional change situation when the fractions are aged together as a whole binder. Petersen et al. (1974) studied the oxidative properties of different fractions when they are oxidised separately. By directly measuring the formation of oxygen containing functional groups, they ranked the relative reactivity with atmospheric oxygen of the saturate, aromatic, polar aromatic (similar to resins), and asphaltene fractions (slightly different with the fraction division shown in Figure 2.8) as 1:7:32:40, respectively, for a Wilmington (California) bitumen when the fractions were oxidised separately at 130°C.

Molecular changes in oxidation

Many studies have also been done on the specific molecular changes that take place in binders on oxidation (Petersen et al., 1974 (a); Dorrence et al., 1974; Petersen, 1975). Figure 2.13 provides structural formulas of important chemical functionalities. The chemical functional groups formed on oxidative ageing include sulphoxides, anhydrides, carboxylic acids and ketones (anhydrides, carboxylic acids and ketones are normally classified into carbonyl functional group). Table 2.2 presents data from tests conducted on four bitumens from different crude oils that had been aged under identical conditions. The data shows that ketones and sulphoxides are the major oxidation products formed during oxidative ageing and, anhydrides and carboxylic acids are formed in smaller amounts. Therefore, special attention is paid to the formation of ketones and sulphoxides.

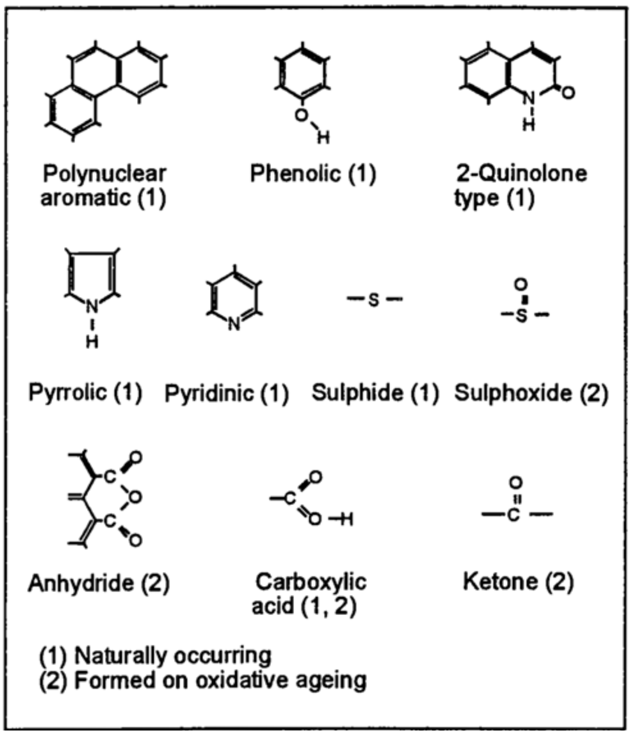


Figure 2.13 Chemical functionalities in bitumen molecules normally present or formed on oxidative ageing (Petersen, 1984)

Table 2.2 Chemical functional groups formed in bitumens during oxidative ageing (Plancher et al., 1976)

Bitumen	Concentration (moles per litre)				Average hardening index^b
	Ketone	Anhydride	Carboxylic Acid^a	Sulphoxide	
B-2959	0.50	0.014	0.008	0.30	38.0
B-3036	0.55	0.015	0.005	0.29	27.0
B-3051	0.58	0.020	0.009	0.29	132.0
B-3602	0.77	0.043	0.005	0.18	30.0

Note: Column oxidation, 130°C, 24 hours, 15μm film

[a] Naturally occurring acids have been subtracted from reported value.

[b] Ratio of viscosity after oxidative ageing to viscosity before oxidative ageing.

The data in Table 2.3 shows that the concentration of ketones formed on oxidative ageing is greatest in the asphaltene and polar aromatic fractions (resins); smaller concentrations are found in the aromatic and saturate fractions. Petersen (1984) explains that, this is because the polar aromatic and asphaltene fractions contain the highest concentrations of aromatic ring systems, which have the highest content of hydrocarbon types sensitive to air oxidation. It is generally agreed by organic chemists that, the most sensitive hydrocarbon moiety expected to be present in bitumen is the one that associates with the carbon atom adjacent to an aromatic ring system, commonly called a benzylic carbon (Petersen, 1984). The hydrogen attached to the carbon in this position is relatively easy to displace, forming a free radical on the carbon. Based on this, Petersen (1984) proposed a simplified ('admittedly oversimplified'- Petersen), generalized scheme for the oxidation of the hydrocarbon moieties in bitumen, which shows ketones as the major functional group formed (as shown in Figure 2.14). The details of this chemical process will not be explained in this review, as the main purpose of presenting this scheme is only to show the sensitivity of the benzylic carbon; additionally to demonstrate that oxidation of bitumen components is an extremely complicated process.

Table 2.3 Carbonyl functional groups formed in Wilmington bitumen fractions during column oxidation (Petersen, 1984)

Fraction	Concentration (moles per litre)		
	Ketone	Anhydride	Carboxylic acid
Saturate	0.045	0.010	Trace
Aromatic	0.32	0.017	-[a]
Polar aromatic	1.48	0.088	-[a]
Asphaltene	1.82	0.080	ND[b]
Whole Bitumen	1.02	0.052	0.007

[a] Some acids lost on alumina column during component fractionation.
[b] Not determined

The sulphoxides are shown to result from the oxidation of organic sulphides that exist in the complex bitumen molecules (Petersen, 1981). Although the formation of sulphoxides has been proved as the second most dominant bitumen oxidation product, their formation rate is much higher than ketones and their formation often precedes significant ketones formation. There are several reasons that can explain this. Firstly, the sulphoxides are mostly formed in the saturate fraction and the carbonyl functional groups are usually found to be in the more polar fractions (Petersen, 1984). In bitumen, the more polar fractions can be viewed to be dispersed (or buried) in the more nonpolar fractions (Petersen and Harnsberger, 1998); therefore, it is reasonable that the sulphides in the saturate fraction will be oxidised first. This is also probably because sulphides are hydroperoxide scavengers and are converted to sulphoxides by the scavenger reaction; Figure 2.15 shows the general principle for the sulphide hydroperoxide scavenger reaction (Petersen and Harnsberger, 1998).

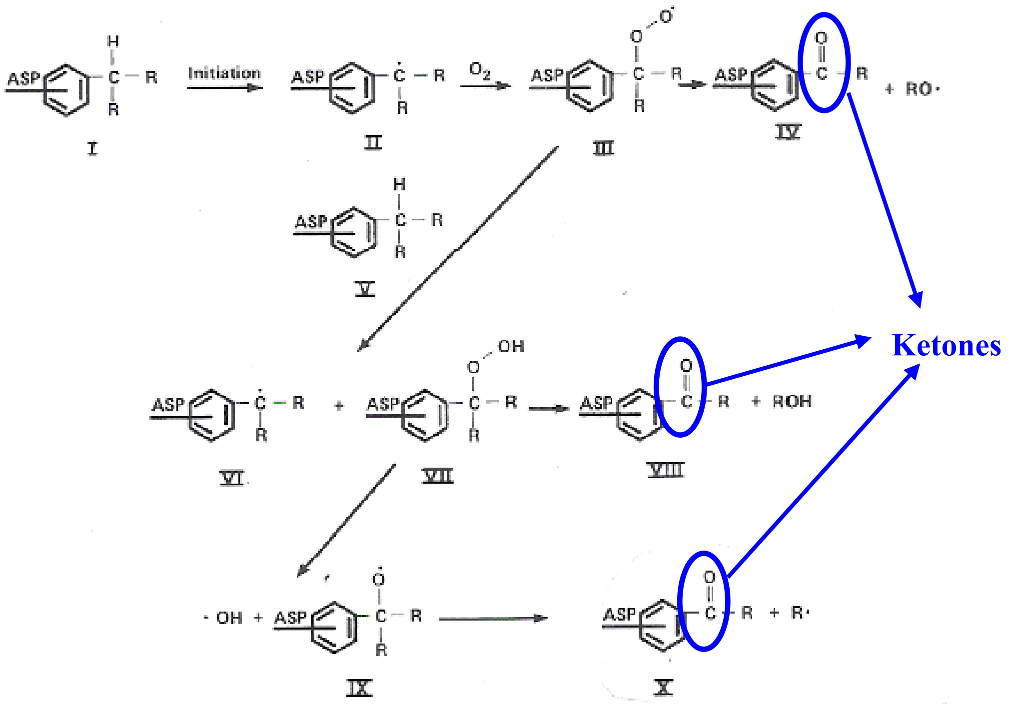


Figure 2.14 Suggested mechanism for the free-radical air oxidation of bitumen

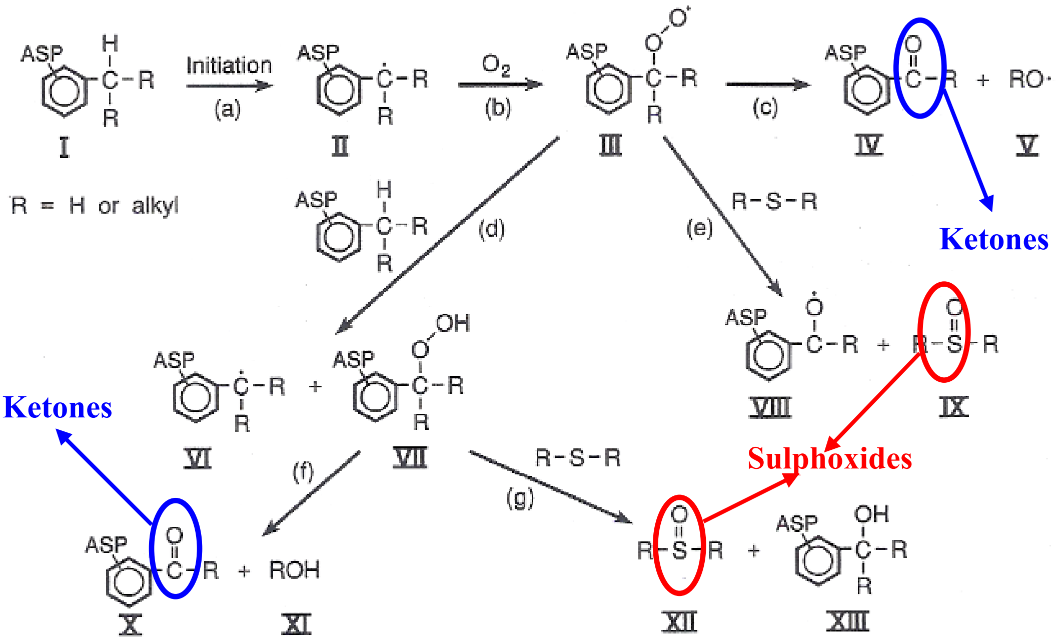


Figure 2.15 Possible reaction sequences for ketone and sulphoxides formation during oxidation of bitumen benzylic carbon

Although the oxidation products are an important factor in bitumen age hardening, it must be stressed that ageing is not directly related to concentration of oxidation products (Petersen et al., 1994). For instance, the non-polar components in the solvent moiety may be very effective in dispersing weakly associated polar species formed by oxidation resulting in a highly oxidised bitumen that does not show a large change in stiffness. Therefore, the degree of hardening is the result of:

- The total associating polarity formed in bitumen,
- The strength of the associations of the polar molecules and
- The dispersing capacity of the non-polar components in the solvent moiety (Branthaver et al., 1993).

2.5.3 Effects of mineral aggregate on bitumen ageing

Initially, in terms of the influence of aggregates on ageing it is only the exudation part of bitumen ageing that appears to be of any significance and for most aggregates this can be considered to be minimal. However, further studies have suggested that the petrographic nature of different aggregates may have some added effects on the age hardening of bitumen (Barbour et al., 1974; Petersen et al., 1974 (a); Petersen, et al., 1974 (b); Plancher et al., 1976; and Huang et al., 2002). It is noted that, besides absorbing oily components from bitumen, aggregates can affect binder ageing in two other ways. Firstly, the charged and polarised aggregate surface (as shown in Figure 2.9) can adsorb polar groups (either naturally occurring ones or the oxidation products) within bitumen, which may decelerate the bitumen hardening process. In addition, some mineral components on the surface of aggregates can catalyze bitumen oxidation (Petersen, 1974).

Adsorption and absorption

As stated above, mineral aggregates attract bitumen components following two mechanisms: adsorption and absorption (as shown in Figure 2.11). Adsorption is a surface phenomenon involving molecular forces on or between surfaces. Absorption is also a surface phenomenon, but the action is through, not on, the surface; space or volume must be available for the absorbed material to occupy after it goes through the surface (Osman, 2004).

Absorption of oily components by porous aggregates is classified by Petersen (1984) as one of the three fundamental composition-related factors that could cause bitumen hardening in pavements. Bitumen hardening in this form, which is named as "Exudative hardening" by researchers (Van et al., 1989), mainly results from the movement of oily components that exude from the bitumen into the mineral aggregate. It is a function of both the exudation tendency of the bitumen and the porosity of the aggregate.

The adsorption of bitumen polar groups by aggregate surface has also been studied extensively by different researchers (Petersen et al., 1974 (a); Plancher et al., 1977; Lesueur and Little, 1999; Huang et al., 2005; and Little and Petersen, 2005) with different approaches. It is generally agreed that the molecular interaction between aggregate and bitumen on their interface can mitigate age hardening effects to bitumen; this ageing-mitigating function of aggregates can be observed most intensively on hydrated lime (HL). The data in Table 2.4 show the effect of the lime treatment in reducing the hardening rate of the bitumens when subjected to a laboratory oxidation procedure during which the bitumens were supported as thin films on the surface of four different aggregates (Plancher et al., 1976). Petersen (1984) interprets this as the result of the adsorption of polar, strongly interacting groups on the aggregate surface, thus removing these hardening-building components from the bitumen matrix.

Table 2.4 Reduction of hardening rate of bitumen by treatment with hydrated lime (Plancher et al., 1976)

Sample	Hardening Index[a]		Reduction (%)
	Untreated	Lime treated	
Bitumen[b]			
B-2959	37	17	54
B-3036	27	10	63
B-3051	132	35	73
B-3602	29	18	39
Aggregate[c]			
Quartzite	57	22	61
Hol limestone	58	22	61
Riverton limestone	36	13	63
Granite	75	22	70

[a] Hardening index = viscosity after oxidative ageing divided by viscosity before oxidative ageing.
[b] Average for aggregates.
[c] Average for asphalts.

Petersen et al. (1974 (a), 1982) investigated the bitumen-aggregate interaction by using different solvents to desorb different bitumen components from an aggregate surface. From their studies, the specific chemical types found strongly adsorbed on aggregate surfaces are carboxylic acids, anhydrides, sulphoxides, 2-quinoline types, ketones, phenolics, and nitrogen compounds. In addition, it was found that carboxylic acid groups were more strongly absorbed on aggregate surfaces compared to other molecules; and this is especially true for limestone (which has been classified as basic aggregate above). They also found that quinoline, a pyridine-type nitrogen compound, has a significantly greater affinity for quartzite and granite than limestone. This was expected because quartzite and granite contain more acidic sites than limestone.

Catalysis of bitumen oxidation by aggregates

Knotnerus (1971) studied the uptake of oxygen by toluene solutions of bitumens and bitumen fractions and found that certain metal salts increased the rate of oxygen uptake. Traxler and Scrivner (1971) suggested a relationship between vanadium content and the hardening rate of bitumen. These two studies have implied that bitumen oxidation can be catalyzed by certain minerals and therefore, attracted great interest of researchers to the study of catalysis effects on bitumen ageing. After a series of studies, Petersen et al. (1974 (a)) suggested that aggregate surfaces can also catalyze the air oxidation of certain bitumen fractions.

In order to identify and quantify the catalytic effects of the aggregate surface to the air oxidation of bitumen fractions, Peterson et al. (1974(a)) aged the four fractions and the whole binder (130^{o}C, 24 hours) by coating them on both inert fluoropak and quartzite aggregate. The concentration of carbonyl groups (ketones, dicarboxylic anhydrides, carboxylic acids, and 2-quinolone types) in unoxidised samples and in samples oxidised on the above two bases were then tested using a differential infrared spectrometric technique combined with selective chemical reactions. In this technique, carboxylic acids and dicarboxylic anhydrides were converted to sodium salts by reaction with sodium hydroxide and were then differentiated from the ketone by using differential spectroscopy on sodium hydroxide-treated versus untreated samples. Reactions with silylating reagents and potassium bicarbonate were used to differentiate between carboxylic acids (reactive) and dicarboxylic anhydrides (unreactive). The 2-quinolone types were determined by selective silylation.

Table 2.5 presents the total carbonyl types formed during the oxidation on quartzite and those formed on fluoropak. From Table 2.5, it can be clearly seen that, the amount of oxidation products on the quartzite is larger than that on the fluoropak base, particularly for the less-polar fractions (saturates and aromatics). It can be concluded that the aggregate surface can significantly promote the oxidation of the saturate fraction and the promoting ability of the aggregate surface appears to decrease with the increase in the polarity of the fraction.

Table 2.5 Comparison of carbonyl compounds formed in samples after being oxidised on quartzite and fluoropak (Petersen et al, 1974 (a))

	Wt. Fraction of Total Bitumen	Prorate amount[a] of carbonyls formed on oxidation, mol/l		Ratio of total carbonyls: quartzite/ fluoropak 80
		On fluoropak 80	On quartzite	
Saturates	0.23	0.012	0.12	10
Aromatics	0.31	0.10	0.36	3.6
Polar Aromatics	0.33[b]	0.52	0.54	1.04
Asphaltenes	0.13	0.25	0.22	0.88
Sum of fractions	1.00	0.88	1.24	1.41
Whole bitumen	1.00	1.07	1.16	1.08

[a] Sum of ketones, acids and anhydrides in fraction, times weight fraction of total bitumen.
[b] Corrected by addition of a factor of 0.08 to adjust for material lost during preparation of fractions.

However, it is obvious that the decrease of the catalytic ability is not enough to explain the phenomenon that the amount of oxidation products obtained in the asphaltenes fraction oxidised on quartzite was even smaller than that obtained from the samples oxidised on the inert fluoropak. Petersen et al. (1974 (a)) explains this in several aspects. Firstly, as stated above, polar asphaltene molecules can be strongly adsorbed on the polar sites of the quartzite surface; in this immobilized state their ability to undergo oxidation reactions would be reduced. Secondly, small amounts of polar components in this fraction (initially present or formed on oxidation) may have been irreversibly adsorbed on the aggregate surface and most of these are not recoverable for subsequent determination. Thirdly, it is believed that these strong interactions of bitumen components with the aggregate surface reduce the surface catalytic activity in bitumen oxidation. Finally, it will be proved below that bitumen oxidation catalysts are naturally present in its more polar fractions; and Petersen et al.

(1974 (a)) believe that the oxidation catalysts present in the asphaltenes can also be adsorbed on, and inactivated by, the quartzite surface.

The catalytic effect on bitumen oxidation of components naturally present in bitumen can be demonstrated by comparing the amount of carbonyls summed for all the fractions on fluoropak with that for the whole bitumen on fluoropak. It is declared that the weight of each fraction in Table 2.5 was predetermined according to their proportions in the neat binder. Therefore, it is strange that the amount of oxidation products for the sum of fractions on fluoropak was less than that for the whole binder on fluoropak. In order to find the reason for this phenomenon, some additional experiments were conducted by Petersen and his co-workers. Firstly, it was observed that nearly half of the saturates were oxidised to polar, oxygen-containing compounds when the whole binder was oxidised on fluoropak. This is totally different with the situation when the saturate fraction was oxidised separately on fluoropak (as seen in Table 2.5). Researchers then oxidised the saturate fraction containing one percent of asphaltenes on fluoropak. The amount of oxidation products formed in saturates were found to be much higher than that formed when it was aged separately. Accordingly, Petersen et al. (1974 (a)) concluded that oxidation catalysts are present in the more polar fractions and can promote the air oxidation of the saturate fraction.

2.5.4 Effects of bitumen film thickness on ageing

Although the bitumen oxidation and the effects of mineral aggregates have been identified as two of the major factors that can influence bitumen age hardening, it is undeniable that, as shown in Figure 2.11, these two hardening mechanisms have their working range limits: oxidation works only in the limited range around the air – bitumen interface, and the effects of mineral aggregates apply only in the limited range around the bitumen – aggregate interface. Therefore, for a bituminous paving mixture where bitumen binder is coated on aggregate surface as a thin film, an adequate bitumen film thickness is essential to ensure reasonable durability of the mixture. When the bitumen film thickness is increased, the proportion of the binder that is affected by these hardening mechanisms will decrease. In addition, a thicker binder film can effectively separate the air and aggregate surface, so that the catalytic activity of the mineral aggregate surface can be limited. However, on the other hand, because the cost of the binder always constitutes the major part of the total expenditure of a pavement project, a thicker bitumen film thickness will significantly increase the road construction cost. Many efforts have been made by researchers to keep the binder content to a minimum while satisfying specification criteria (thick enough to ensure rational resistance to ageing).

Campen et al (1959) investigated the influence of voids, surface area and film thickness on the durability of dense grade asphalt mixtures. It was pointed out that thicker binder films produced flexible and durable mixtures, while thin films produced brittle asphalt mixtures, which tended to crack excessively, retarded pavement performance, and reduced its service life. According to their analysis, film thicknesses of the most desirable asphalt mixtures usually ranged from 6 to 8 microns. It was also concluded that, although the film thickness decreases as the surface area of the aggregate is increased, the bitumen requirement for an asphalt mixture is not linearly proportional to its surface area. This phenomenon can indicate that the relationship between binder content, aggregate surface area and the binder film thickness is much more complicated than a simple average.

Goode and Lufsey (1965) presented the relationship between voids, permeability, film thickness and asphalt hardening. The hardening of the asphalt binder was expressed as a function of air voids, film thickness, temperature and time in their study. In order to avoid the implication that all aggregate particles had the same thickness of binder coating, the authors introduced a new concept named ‘bitumen index’, which was defined as pounds of binder per square foot of aggregate surface area. Based on this concept, they concluded that a minimum bitumen index of 0.00123, which corresponds to a value of 6 microns of average film thickness, could be set as a control in the asphalt mixture design. It was also indicated that a combination factor of the ratio of air voids to the bitumen index could give a good prediction to the ageing characteristics of asphalt mixtures. Finally, they suggested that a maximum value of voids-‘bitumen index’ could be incorporated in the Marshall Mixture design method instead of a maximum value of air voids alone. To ensure a reasonable durability, a value of 4 was recommended as the maximum of this ratio (as shown in the following equation).

$$\frac{AirVoids(\%)}{BitumenIndex \times 103} = 4.0(\text{maximum}) \qquad (2\text{-}1)$$

Kumar and Goetz (1977) studied bitumen age hardening as related to the mixture permeability and bitumen film thickness. They stated that the best way for predicting the hardening resistance of bitumen in a single-sized asphalt paving mixture was to calculate the ratio of the film thickness factor to permeability. The film thickness factor was defined as the ratio of the percent binder content available for coating the aggregate to the surface area of the aggregate. In addition, they declared that for dense-graded asphalt mixtures, the concept of an average film thickness is at best dubious, if not totally erroneous. Permeability was stated to be the best measure of hardening resistance for dense-graded mixtures. However, at the design value of 4% air voids, which is common for most dense graded asphalt paving mixtures, the effects of permeability of the mix was determined to be insignificant.

Kandhal and Chakraborty (1996) also did some investigation to quantify the relationship between various binder film thicknesses and the ageing characteristics of asphalt mixtures. For the asphalt mixtures with 8% void content, a binder film thickness of 9-10 microns was recommended by the authors, below which the ageing rate of both the asphalt mixture and the bitumen in the mixture would accelerate significantly. Studies involving more aggregate – bitumen combinations were recommended, because it was believed by authors that the ageing phenomenon is influenced by the interaction between the aggregate and the bitumen; and the optimum bitumen film thickness may change when different materials are used.

2.6 Ageing Tests for Bituminous Materials

Since bitumen ageing is one of the main factors that can affect the durability of bituminous paving mixtures, it is clearly desirable that there should be artificial ageing tests that can quantitatively determine the resistance of bitumens to hardening at an accelerated rate. A number of tests already exist to measure the effect of age hardening on bituminous materials at various stages during the production process (e.g. short-term ageing during asphalt mixture construction, and long-term ageing during the in-place service period). All of these tests can be broadly divided into two categories:

- Tests performed on bituminous binder and,
- Tests performed on bituminous (asphalt) mixtures.

2.6.1 Ageing tests for bituminous binder

Numerous investigations have been done by researchers over the last seventy years to correlate accelerated laboratory ageing of neat bitumen with field performance. Most of these investigations have utilised thin film ovens to age the bitumen in an accelerated rate, which is commonly achieved by extended heating of the bitumen film. An extensive list of the various ageing regimes for pure bitumen, with their principal parameters, has been summarised by Airey (2003), and is presented in Table 2.6. Among these tests, the thin film oven test (TFOT), the rolling thin film oven test (RTFOT) and the rotating flask test (RFT) are most commonly used to control the short-term ageing of conventional, unmodified bitumen; the rotating cylinder ageing test (RCAT) and the pressure ageing vessel (PAV) test have shown the greatest potential in the simulation of long-term ageing.

Table 2.6 Bitumen ageing methods (Airey, 2003)

Test method	Temp (°C)	Time (h)	Size (g)	Film (mm)	Extra features
Thin film oven test (TFOT)	163	5	50	3.2	-
Modified thin film oven test (MTFOT)	163	24	-	0.1	-
Rolling thin film oven test (RTFOT)	163	1.25	35	1.25	Air flow-4000 ml/min
Extended rolling thin film oven test (ERTFOT)	163	8	35	1.25	Air flow-4000 ml/min
Nitrogen rolling thin film oven test (NRTFOT)	163	1.25	35	1.25	N2 flow-4000 ml/min
Rotating flask test (RFT)	165	2.5	100	-	Flask rotation-20 rpm
Shell microfilm test	107	2	-	0.005	-
Modified Shell microfilm test 1963	99	24	-	0.02	-
Modified Shell microfilm test 1961	107	2	-	0.015	-
Rolling microfilm oven test (RMFOT)	99	24	0.5	0.02	Benzene solvent
Modified RMFOT	99	48	0.5	0.02	1.04 mm ϕ opening
Tilt-oven durability test (TODT)	113	168	35	1.25	-
Alternative TODT	115	100	35	1.25	-
Thin film accelerated ageing test (TFAAT)	130/113	24/72	4	0.16	3 mm ϕ opening
Modified rolling thin film oven test (RTFOTM)	163	1.25	35	1.25	Steel rods
Iowa durability test (IDT)	65	1000	50^{a}	3.2	2.07 MPa-pure oxygen
Pressure oxidation bomb (POB)	65	96	$-^{b}$	0.03	2.07 MPa-pure oxygen
Accelerated aging test device/Rotating cylinder ageing test (RCAT)	70-110	144	500	2	4~5 l/h-pure oxygen
Pressure ageing vessel (PAV)	90-110	20	$50^{a/c}$	3.2	2.07 MPa-air
High pressure ageing test (HiPAT)	85	65	50^{c}	3.2	2.07 MPa-air

[a] TFOT residue
[b] ERTFOT residue
[c] RTFOT residue

Thin film oven test (TFOT)

The TFOT was firstly introduced by Lewis and Welborn (1940). In this test, a 50 ml sample of bitumen is stored in a TFOT oven (as shown in Figure 2.16) at 163°C for five hours in a layer of 3.2 mm thick. It is claimed that the amount of hardening that takes place in this test is similar to that which occurs in practice and therefore, the test was adopted by AASHTO in 1959 and by ASTM in 1969 (ASTM D1754, 1995a) as a means of evaluating the hardening of bitumen during the plant mixing. However, as the bitumen is not agitated or rotated during the test, there is a concern that ageing (primarily volatile loss) may be limited to the 'skin' of the bitumen sample (Airey, 2003). Accordingly, this test is far from ideal and numerous significant modifications to the test have been developed since its inception.

Figure 2.16 TFOT ageing oven

Rolling thin film oven test (RTFOT)

In 1963, the State of California Department of Public Works, Division of Highways, developed an ageing test method which is called the Rolling Thin Film Oven Test (RTFOT) (Hveem et al., 1963). This method is probably the most important modification or development of the TFOT. In the RTFOT, eight glass containers each containing 35 g of bitumen are fixed in a vertically rotating shelf. Hot air is blown into each sample bottle periodically (usually when at its lowest position). During the test, the bitumen flows continuously around the inner surface of each container in a relatively thin film at a temperature of 163^{o}C for a period of 75 minutes. The vertical circular shelf rotates at a rate of 15rpm and the air flow is set at a rate of 4000 ml/min. This method can ensure that all the bitumen is exposed to heat and air and continuous bitumen flow can prevent the presence of a skin that may protect the bitumen. Although the conditions in the RTFOT are not exactly the same as those found in practice, experience has shown that the amount of hardening in this test correlates well with that observed in a conventional batch mixer (Read and Whiteoak, 2003). The RTFOT was adopted by ASTM in 1970 as ASTM D2872 (1995b). A picture of the RTFOT oven is shown in Figure 2.17.

Figure 2.17 RTFOT ageing oven

Rotating flask test (RFT)

The RFT method consists of ageing a 100 g sample of bitumen in the flask of the rotary evaporator for a period of 150 min at a temperature of 165°C (hot air is blown into the flask at a rate of 500 ml/min during ageing), as shown in Figure 2.18. Rotation of the flask, at a speed of 20 rpm, means that the material forming the surface of the specimen is constantly replaced, thus preventing the formation of a skin on the surface of the bitumen (Airey, 2003).

Figure 2.18 RFT ageing apparatus

Accelerated ageing test device/RCAT

Although standard tests such as the RTFOT and RFT can adequately simulate construction (short-term) ageing, their high temperatures make them unsuitable for simulating field (long-term) ageing. This has lead to the development of the accelerated ageing device at the Belgium Road Research Centre (BRRC) (Verhasselt and Choquet, 1991), as shown in Figure 2.19.

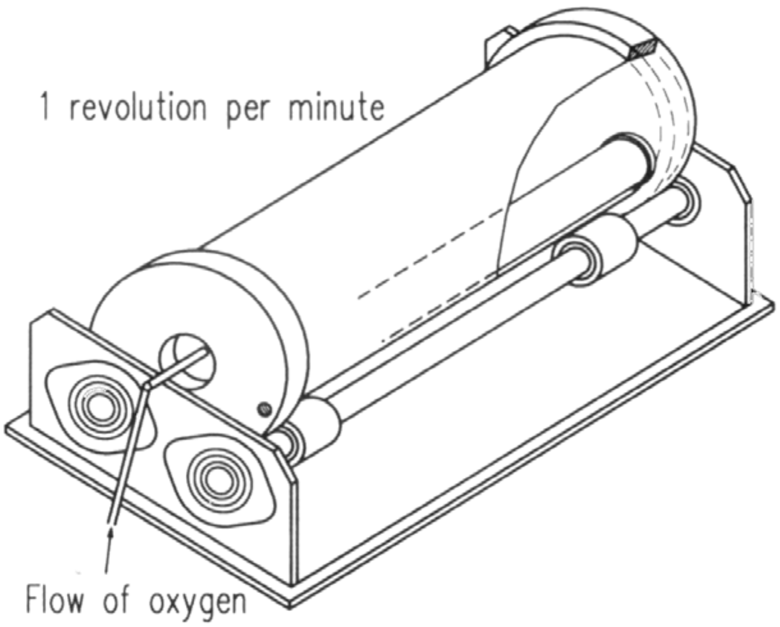


Figure 2.19 RCAT ageing apparatus (Verhasselt, 2000)

The accelerated ageing test device, now known as the rotating cylinder ageing test (RCAT), consists of a cylinder tube (with an internal diameter of 124 mm and a length of 300 mm), which is capped at both ends but with a 43 mm diameter aperture in the centre of one end, from which bitumen can be introduced and extracted (Verhasselt, 2000). After filling the binder (up to 500 g each time) into the cylinder, a stainless steel roller, with a length of 296 mm and a diameter of 34 mm, is placed in the cylinder. The cylinder is then placed in a frame capable of rotating the cylinder at 1 rpm, oxygen is introduced into the cylinder through the aperture at a rate of 4-5 l/h (75 ml/min). Rotation of the roller within the cylinder distributes the bitumen into an even 2mm thick film on the inner wall of the cylinder.

Choquet (1993) found that ageing bitumen at 85°C for 144 h with the RCAT test reflects field ageing with regard to the formation of asphaltenes. He also noted that, in order to produce chemical and rheological changes similar to those found in the field, temperatures less than 100°C are essential in accelerated ageing tests. Therefore, the RCAT tests are commonly conducted at temperatures between 70 and 110°C to simulate bitumen long-term ageing. However, a study carried out by Verhasselt (2003) showed that a RCAT test at relatively higher temperature can also simulate the bitumen short-term ageing. He found that 210-240 min of RCAT ageing (with a temperature of 163 ± 1°C, a cylinder rotation rate of 5.0 ± 0.2 rpm, an air flow rate of 4 ± 0.2 l/min and a sample size of 500-550 g) approximately corresponds to 75 min of RTFOT ageing. Accordingly, Verhasselt (2003) concluded that the RCAT apparatus appears to be a very practical method for both short- and long-term ageing simulation.

Pressure ageing vessel (PAV)

The SHRP-A-002A research team developed a method using the PAV to simulate the long-term, in-place oxidative ageing of bitumen in the field (Christensen and Anderson, 1992; and Petersen et al., 1994). The method involves hardening of bitumen in the RTFOT or TFOT followed by oxidation of the residue in a pressurised ageing vessel. The PAV procedure entails ageing 50 g of bitumen in a 140 mm diameter pan (3.2 mm binder film) within the heated vessel, pressurised with air to 2070 kPa for 20h at temperatures between 90 and 110°C. Figure 2.20 shows the PAV apparatus.

Figure 2.20 PAV ageing apparatus

Migliori and Corte (1999) investigated the possibility of simulating RTFOT (short-term ageing) and RTFOT+PAV (long-term ageing) simply by means of PAV tesing for unmodified penetration grade bitumens. It was found that 5 hours of PAV ageing at 100°C and 2070 kPa was equivalent to standard RTFOT ageing, and that 25 hours of PAV ageing at 100°C and 2070 kPa was equivalent to standard RTFOT+PAV ageing.

Verhaselt and Vanelstraete (2000) made a comparison using the PAV at 100°C and the RCAT at 85°C for a range of unmodified and polymer modified binders. It was found that the changes observed (rheological properties, IR spectra) and reaction mechanisms involved are quite similar for both techniques. They established an equivalency between the two methods such that 20 hours of PAV ageing approximately corresponds to 178 hours of RCAT ageing.

2.6.2 Ageing tests for bituminous (asphalt) mixtures

In addition to artificially ageing pure binders, a number of methods also exist for artificially ageing the bituminous (asphalt) mixtures. The earliest effort on the asphalt mixture artificial ageing can date back to 1903 when Dow (1903) proposed a durability test whereby the recovered bitumen from aged and unaged mixtures were tested in the penetrometer to determine the change in consistency due to age hardening. In this test, the aged mixture was heated in an oven at 149°C for 30 minutes prior to recovering the bitumen. Although there was no evidence that this method was used in specifications, it did give some indication of the relative durability of bitumens supplied at the time (Welborn, 1984). In addition, this proposal has implied the basic procedure for asphalt mixture ageing study, which is to artificially age the mixture and then assess the effect of ageing on key material parameters (e.g. stiffness, viscosity, strength etc.). The development of a standard method for recovering bitumen from bituminous mixtures (Abson, 1933) led to several subsequent studies of bitumen-aggregate mixtures (as presented in Table 2.7). These studies can broadly be divided into four categories: 1) Extended heating procedures; 2) Oxidation tests; 3) Ultraviolet/Infrared treatment; 4) Steric hardening (Bell, 1989). In this report, only the extended heating procedures and oxidation tests will be reviewed.

Table 2.7 Asphalt mixture ageing methods (Airey, 2003)

Test method	Temp. (^{o}C)	Duration	Size	Extra features
Production ageing (Von Quintas et al., 1988)	135	8,16,24,36 h	Loose	-
SHRP short-term oven aging (STOA)	135	4 h	Loose	-
Bitutest protocol (Scholz, 1995)	135	2 h	Loose	-
Ottawa sand mixtures (Pauls and Welborn, 1995)	163	Various	50×50 mm^2	-
Plancher et al. (1976)	150	5 h	25×40 mm^{2}φ	-
Ottawa sand mixtures (Kemp and Prodoehl 1981)	60	1200 h	-	-
Hugo and Kennedy (1985)	100	4 / 7 days	-	80% relative humidity
Long-term ageing (Von Quintas et al., 1988)	60	2 days	Compacted	-
	107	3 days		
SHRP long-term oven ageing (LTOA)	85	5 days	Compacted	-
Bitutest protocol (Scholz, 1995)	85	5 days	Compacted	-
Kumar and Geotz (1977)	60	1,2,4,6,10 days	Compacted	Air at 0.5 mm of water
Long-term ageing (Von Quintas et al. 1988)	60	5 to 10 days	Compacted	0.7 MPa-air
Oregon mixtures (Kim et al., 1986)	60	0,1,2,3,5 days	Compacted	0.7 MPa-air
SHRP low pressure oxidation(LPO)	60 / 85	5 days	Compacted	Oxygen-1.9 l/min
Khalid and Walsh (2000)	60	Up to 25 days	Compacted	Air-3 l/min
PAV mixtures (Korsgaard,1996)	100	72 h	Compacted	2.07 MPa-air

Extended Heating Procedures

Pauls and Welborn (1952) exposed 50×50 mm^2 cylinders of Ottawa sand mixture to a temperature of 163^{o}C for various periods. The compressive strength of the mixture cylinders, as well as the consistency of the recovered binder, were determined and then compared to that of the original materials. Bitumens representing major sources produced in the 1930s were used in this study. The test results from this study indicated that the hardening properties of bitumens can be assessed either by tests on bitumen recovered from the laboratory-aged specimens or by the TFOT. However it was noted that there is no suggestion that the TFOT was suitable for predicting in-service (long-term) hardening.

Plancher et al. (1976) used a similar oven ageing procedure to age 25 mm thick by 40 mm diameter samples (at 150^{o}C for 5 h) as part of a study to evaluate the effect of lime on oxidative ageing of bitumen. By comparing the resilient modulus of the samples both before and after ageing, it was found that the lime-treated mixtures changed less in resilient modulus than non-treated mixtures.

Hugo and Kennedy (1985) oven aged asphalt specimens that had been cored from laboratory compacted slabs at 100°C. They note that this procedure is similar to an Australian standard (Standards Association of Australia, 1980). This procedure was carried out for either 4 or 7 days under either dry atmosphere or an atmosphere of 80% relative humidity, due to the need to assess a project located near the ocean. Bitumen recovered from core samples was subjected to viscosity testing. In addition, the masses of samples were tested before and after ageing so that the volatile loss can be indicated by mass loss.

Most of the initial methods used for laboratory ageing of asphalt mixtures involve the ageing of compacted asphalt specimens. However, Von Quintas et al. (1988) investigated the use of forced-draft oven ageing to simulate ‘production hardening’, that is, hardening due to short-term ageing. In this method, loose asphalt mixtures were heated for periods of 8, 16, 24 and 36 h in a forced-draft oven at a temperature of 135°C. Although this method showed similar levels of ageing to those found in the field, it is noted by researchers (Bell, 1989; and Airey, 2003) that there is considerable scatter in the laboratory data.

Based on the work done by Von Quintas et al. (1988), the SHRP short-term oven ageing (STOA) procedure was developed under the SHRP-A-003A project. The procedure requires loose mixtures, prior to compaction, to be aged in a forced-draft oven for 4 h at 135°C. This process was found to represent the ageing that occurs during mixing and placing and also represents pavements of less than two years (Bell et al., 1994; and Monismith et al., 1994).

Scholz (1995) developed a similar short-term ageing procedure to simulate the ageing occurring during the construction process for both continuously graded (DBM) and gap graded (HRA) mixtures. The procedure is similar to the SHRP STOA procedure except that the ageing temperature is either 135°C or the desired compaction temperature, whichever is higher, and that the conditioning time is limited to 2 h for DBM. He also suggested that no conditioning period is required for HRA mixtures (Brown and Scholz, 2000).

Von Quintas et al. (1988) also investigated the use of a forced-draft oven for a ‘long-term environmental ageing’ study where compacted asphalt mixture specimens were aged for 2 days at 60°C followed by an additional 5 days at 107°C. However, Bell (1989) notes that the higher conditioning temperature in the second stage may cause specimen disruption, particularly for high void content and/or high penetration grade asphalt mixtures.

The SHRP long-term oven ageing (LTOA) procedure was also developed under the SHRP-A-003A project. It requires that after STOA, the loose material should be compacted and placed in a forced-draft oven for 5 days at 85°C (Harrigan et al., 1994). It is declared that the parameters used for SHRP LTOA are meant to represent 15 years field ageing in a Wet-No-Freeze climate and 7 years in a Dry-Freeze climate. Further field validation of the LTOA indicates that 8 days at 85°C is equivalent to over 9 years for Dry-Freeze and over 18 years for Wet-No-Freeze; 2 days at 85°C is equivalent to 2-6 years for both Dry-Freeze and Wet-No-Freeze; and 4 days at 85°C is equivalent to 15 years of field ageing in a Wet-No-Freeze climate and 7 years in a Dry-Freeze climate (Bell et al., 1994; and Monismith et al., 1994).

In addition to his short-term ageing simulation procedure, Scholz (1995) also developed a long-term oven ageing procedure for compacted asphalt mixture specimens. The procedure is identical to the SHRP LTOA procedure, and consists of forced-draft oven ageing of compacted specimens at 85°C for 5 days (Brown and Scholz, 2000).

Oxidation tests

Kumar and Goetz (1977) described a procedure consisting of ageing specimens at 60°C for periods of 1, 2, 4, 6 and 10 days while ‘pulling’ air through a set of compacted specimens at a constant head of 0.5 mm of water. The low head was used to avoid turbulence in the air flow through the specimen. Von Quintas et al. (1988) also used a pressure oxidation treatment, which involves conditioning compacted specimens at 60°C at a pressure of 0.7 MPa for 5-10 days.

Kim et al. (1986) utilised pressure oxidation to age compacted specimens representative of Oregon mixtures. Specimens were aged in oxygen at a pressure of 0.7 MPa and a temperature of 60°C for 0, 1, 2, 3 and 5 days and the effects of ageing were evaluated by indirect tensile stiffness and indirect tensile fatigue. Although the stiffness results generally increased with ageing, some mixtures showed an initial decrease in stiffness in the early part of the ageing procedure. Similar results were found by Von Quintas et al. (1988).

Another long-term ageing procedure that was developed under the SHRP-A-003A project was a low pressure oxidation (LPO) procedure, which is also carried out on compacted specimens after they had been short-term aged. The procedure consists of passing oxygen through a confined triaxial specimen at 1.9 l/min at either 60 or 85°C for 5 days.

Khalid and Walsh (2002) developed a LPO test for accelerated ageing of porous asphalt mixtures. The method consists of feeding compressed air (at a flow rate of 3 l/min) through a series of heat exchange coils placed in an oven and then through a number of porous asphalt samples (as shown in Figure 2.21). A test temperature of 60°C was used and a rubber membrane was fitted over the samples to ensure that air flowed through but not around the samples. The system has been shown to recreate the ageing effect produced by the SHRP LTOA procedure, although longer ageing times are required due to its lower testing temperature.

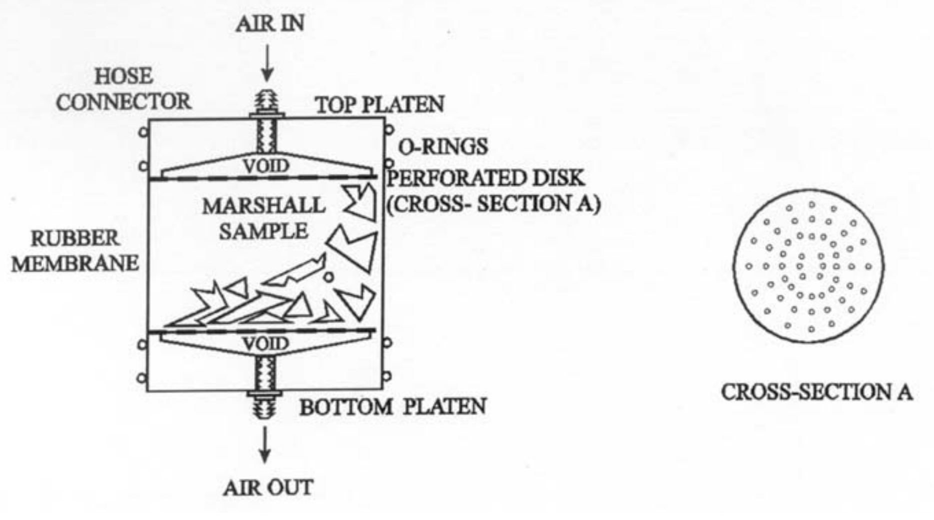


Figure 2.21 Low pressure oxidation technique for porous asphalt (Khalid and Walsh, 2002)

Korsgaad et al. (1996) used the PAV to age gyratory compacted dense asphalt mixture specimens rather than bitumen. Based on recovered binder properties they determined an optimum ageing procedure which consists of PAV ageing for 72 hours at 2.07 MPa and 100^{o}C. However, they conceded that 60 hours may be more appropriate for more porous mixture.

2.6.3 Ageing studies on in-service materials

While age hardening of bituminous materials have been studied extensively in the laboratory and various artificial ageing simulation methods (as introduced above) have been developed by researchers to investigate ageing properties of bitumen, ageing of binders in pavements is still much less well understood because of a number of complications for the real paving asphalt mixtures. Such complications include uncontrolled variables and unknowns such as mixture characteristics, maintenance treatments, traffic, and climate; sustaining a research effort over an appropriate time frame (in excess of one decade); and cost.

Al-Azri et al. (2005) introduced an ongoing research effort that had studied fifteen pavements across Texas with respect to binder oxidative hardening. These pavements included two test sections that were placed with multiple binders in 1983, one Texas highway that was taken under study at the beginning of its construction in 1987, two pavements sampled late in their life, and 10 Strategic Highway Research Program (SHRP) long-term pavement performance (LTPP) general pavement study (GPS) pavements that were cored from 1989 to 1990.

In their study, binders were recovered from samples cored from different depths of different pavements. These recovered binders were then subjected to DSR and Fourier Transform Infrared (FTIR) (which will be introduced in Chapter 3) tests. The testing results were compared to laboratory ageing of the same binders that were obtained during construction.

Based on their study, it was found that the Superpave RTFOT plus PAV procedure aged binders at Texas conditions to a level that is approximately equal to hot-mix ageing plus four years on the road. In addition, one month of ageing of bitumen with a binder film of 1 mm in the 60^{o}C environmental room was equivalent to approximately 15 months on the Texas highway after initial oxidation during construction is past. It should be noted that, these calibrations, as stated by Al-Azri et al. (2005), would vary with climate, binder composition and air voids.

An important finding from this study was that binders in pavements could oxidize at surprisingly uniform rates with depth once early oxidation occurs, even for dense-graded mixtures, and these rates might continue for an extended period of time. This indicates that the affected depth of asphalt hardening on pavements is not limited as much as might be expected.

2.6.4 Ageing index

The ageing of bituminous materials is commonly expressed by means of an ageing index. The following equation shows the generic form of the ageing index:

$$AgeingIndex = \frac{P_{AGED}}{P_{UNAGED}} \tag{2-2}$$

where:

P_{UNAGED} = some physical property (e.g. viscosity, Softening Point of binder and/or stiffness of the asphalt mixture) measured on the unaged bituminous materials;

P_{AGED} = the same physical property as measured on the unaged bituminous materials but performed after the materials have been aged.

2.7 Summary

Bitumen has been used as cement in road building for almost 100 years in the UK. Long-term studies have shown that, for a pavement constructed strictly according to specifications, embrittlement of the bitumen due to age hardening is one of the two primary factors that can adversely affect the durability of bituminous mixtures. When the bitumen is excessively aged, the asphalt mixture will become brittle and its ability of supporting traffic-induced stresses and strains may significantly reduce, which can easily cause some cracking damage to the bound layer of a pavement. Excessive hardening can also weaken the adhesion between the bitumen and aggregate, resulting in loss of materials at the surface layer.

Age hardening of the binder is the result of compositional changes in the bitumen. Petersen (1984) outlined three fundamental composition-related factors which govern the changes that could cause bitumen hardening in pavements: 1) Loss of oily components of bitumen by volatility or absorption by porous aggregates; 2) Change in chemical composition of bitumen molecules from reaction with atmospheric oxygen; and 3) Molecular structuring that produces thixotropic effects (steric hardening).

The atmospheric oxidation of certain bitumen components has long been held as the main cause of age hardening; and the oxidation products (e.g. ketones, sulphoxides and to a lesser extent, carboxylic acids) are widely regarded by researchers as an important factor in bitumen ageing. However, it must be asserted that ageing is not directly related to concentration of oxidation products. The degree of hardening is the result of the total associating polarity formed in bitumen, the strength of the associations of the polar molecules and the dispersing capacity of the non-polar components in the solvent moiety.

With regard to the effects of aggregate to bitumen ageing, further studies have suggested that besides absorbing oily components from bitumen, the petrographic nature of different aggregates may have some added effects on the age hardening of bitumen. Firstly, the charged and polarised aggregate surface can adsorb polar groups (either naturally occurring ones or the oxidation products) within bitumen, which may decelerate the bitumen hardening process. In addition, some mineral components on the surface of aggregates can catalyze bitumen oxidation. However, the catalytic activity of the aggregate surface can be retained by the adsorption of polar components from bitumen to aggregates.

Numerous attempts have been made by researchers to predict the ageing characteristics of bitumens in bituminous pavements. Tests related to ageing of bituminous materials can be broadly divided into tests performed on the bitumen and tests performed on the bituminous (asphalt) mixture. The most commonly used short-term binder ageing tests are the high temperature TFOT, RTFOT and RFT used to simulate the hardening occurring during asphalt mixture production. In terms of long-term binder ageing, no one test seems to be satisfactory for all cases and the RCAT method is probably the most acceptable. In addition, the PAV test has also shown great potential in the simulation of long-term ageing. With regard to the ageing tests for mixtures, the most promising methods for short-term ageing are extended heating of the loose materials. The most promising methods for long-term ageing of mixtures include extended oven ageing, such as the SHRP LTOA, and pressure oxidation, using low pressure oxidation as well as pressurised procedures.

3 EXPERIMENTAL TECHNIQUES

3.1 Introduction

This part reviews several specific experimental techniques that have been used in this ageing study. These techniques include bitumen film thickness calculation methods, indirect tensile stiffness modulus (ITSM) test, dynamic shear rheometer (DSR) test, Fourier transform infrared spectroscopy (FTIR) test and the bitumen recovery techniques. A section on DSR modification is also included, because significant work has been done in this area as part of this project (see Appendix B). Although no results are yet available, use of a modified DSR will be recommended in Chapter 7.

3.2 Bitumen Film Thickness Calculation

When mixed with aggregates, bitumen will be spread into thin films on the surface of both aggregates and fillers with a thickness of 5 to 15 μm, and this will lead to a very large contact area between binder and air, which is ideal for the bitumen ageing (Read and Whiteoak, 2003). Therefore, it is very important to choose a proper film thickness when designing the bituminous material in pavement engineering. Many investigations have been conducted with respect to theoretical calculation of binder film thickness and the influences of thicknesses to ageing properties of bitumen. However, most of these studies are based on assumption that all the aggregate particles, ranging from coarse aggregate down to very fine mineral fillers, are coated with uniform binder films and any differences in particle specific gravity, shape and texture can be ignored (Zaniewski and Reyes, 2003). This problem significantly limited the use of film thickness for evaluating the potential durability of the asphalt mixtures. Therefore, besides two of the traditional binder film thickness calculation methods, a new method developed by Heitzman (2006) will also be introduced in this part.

3.2.1 Traditional methods

The concept of average binder film thickness was first introduced by Campen and others in the 1950s (Heitzman, 2006). In their study, it was assumed that "all the binder exists in the form of uniform films as long as appreciable air voids exist" (Campen et al, 1959). By its definition, the film thickness value is calculated simply by dividing the total surface area of the aggregate by the effective binder content, as shown in Figure 3.1. It is highly unlikely that all the aggregate particles in an asphalt mixture have the same film thickness of binder coating. Some very fine fillers, which might simply be embedded in the binder, may have a much thicker coating as compared to the coarse aggregate particles. However, researchers thought that the value of the average binder film thickness is adequate for the purpose of predicting the durability of asphalt, although it is an approximate index.

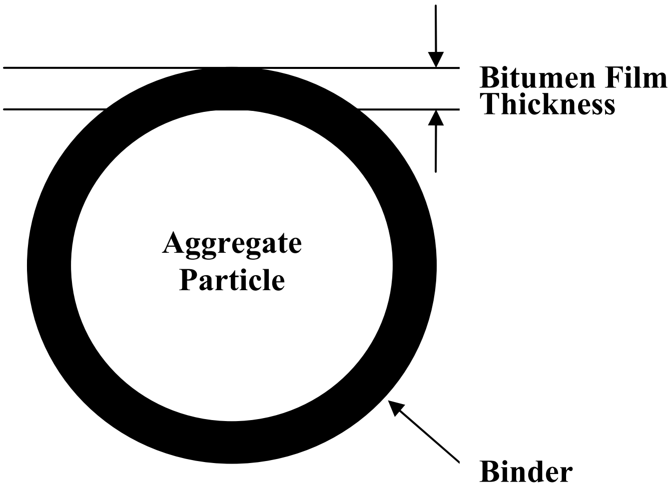


Figure 3.1 Asphalt film thickness

Campen's method

As illustrated in Figure 3.1, based on the traditional definition, the binder film thickness can be calculated by dividing the effective volume of binder by the total estimated surface area of the aggregate. Obviously, the key to the calculation is the estimation of the surface area of the aggregate. It is possible to estimate the surface area of an aggregate sample by coating it with oil and measuring the quantity of oil required for complete coating. Alternatively, the surface area of an aggregate can be calculated by assuming a specific aggregate particle shape. Hveem (1942) developed a simple but relatively accurate calculation method to determine aggregate surface area factors, which was further adopted in Campen's film thickness equation (Eq 3-1). Although some studies questioned the accuracy of this method, it is still the most widely used.

Hveem calculated surface area factors with two assumptions. Firstly, the aggregate particle shape is assumed to be spherical and, secondly, the specific gravity of aggregate is set to be 2.65. Typical surface area factors are shown in Table 3.1.

Table 3.1 Typical surface area factors (Read and Whiteoak, 2003)

Sieve size: mm	Surface area factor: m^2/kg
0.075	32.77
0.150	12.99
0.300	6.14
0.600	2.87
1.18	1.64
2.36	0.82
>4.75	0.41

The surface area of the aggregate is calculated by multiplying the total mass expressed as a percentage passing each sieve size by the appropriate surface area factor and adding the resultant products together. Different factors are necessary if different sieves are used (Read and Whiteoak, 2003). The theoretical bitumen film thickness is then calculated as:

$$T_f = \frac{b}{100-b} \times \frac{1}{\rho} \times \frac{1}{\alpha} \qquad (3\text{-}1)$$

where:

T_f = bitumen film thickness (m);

ρ = density of bitumen (kg/m^3);

α = surface area factor (m^2/kg);

b = bitumen content (in %).

Another expression for the above formula is as follows:

$$T_f = \frac{P_{be}}{SA \times P_s \times G_b} \times (1000) \qquad (3\text{-}2)$$

where:

T_f = average thin film (microns, 0.001 mm);

P_{be} = percent (by mix weight) of effective bitumen binder;

SA = surface area of the aggregate (m^2/kg);

P_s = percent (by mix weight) of aggregate;

G_b = specific gravity of the bitumen binder.

French method

Another method, developed in France, gives an approximation of the binder film thickness using the formula (Norme, 1991):

$$T = \frac{b}{a \times \sqrt[5]{\sum}} \tag{3-3}$$

where:

T = bitumen film thickness (in mm);

b = bitumen content expressed as the percentage by total mass of the mixture;

a is a correction coefficient taking into account the density of the aggregate and is given by

$$a = \frac{2650}{SGa}$$

where:

SGa = density of the aggregate (in kg/m^3);

$\sum$ is the specific surface area of the aggregate and is given by

$$\sum = 0.25G + 2.3S + 12s + 135f$$

where:

G = proportion by mass of aggregate over 6.3 mm;

S = proportion by mass of aggregate between 6.3 mm and 3.15 mm;

s = proportion by mass of aggregate between 3.15 mm and 0.80 mm;

f = proportion by mass of aggregate smaller than 0.80 mm.

3.2.2 Heitzman's New Method

In Campen's method, the surface area factors are multiplied by the total mass expressed as a percentage passing each sieve size. Using the gradation in terms of the total percent passing means that each value represents all aggregate particles smaller than that sieve and, therefore, the surface area values are not a direct expression of total surface area for aggregate particles on a specific sieve (Heitzman, 2006). Another critical limitation of Campen's method is that the differences in the specific gravity of the aggregate are ignored in the surface area calculation. This means that, when Campen's method is used to compare two mixtures, the resulting film thickness values only express differences based on the gradation but not on the specific gravity. A new film thickness calculation method, named the Index Model, was then developed by Heitzman (2006) to avoid this limitation. By comparing with Campen's Model, it is proved that the Index Model is a better two-dimensional approach, although it is still based on the simplification that the surface area coated by the binder is a flat surface and each particle is separately and equally coated.

The Index Model is an extension of the traditional calculation method and is a simple procedure to develop based on equation 3-2. After a matrix of gradations is established for each of the individual aggregate sources in an asphalt mixture, the procedure determines the retained weight of particles from each source on each sieve based on a 1000 gram total aggregate batch weight. After that, the retained weight is converted to a total retained volume by dividing by the specific gravity for that source. The retained volume on each sieve in the matrix is then converted to the number of particles using an average particle volume, which is based on the upper and lower sieve dimensions and the nominal particle shape. Once the number of particles is determined, it is multiplied by the surface area of each average particle to establish the total surface area of aggregate particles retained on each sieve for each source. These values are then all combined into the total surface area for the 1000 gram aggregate blend. A constant coefficient is used to adjust the combined surface area value to square metre of surface area per one kilogram of aggregate. The equations to step through the Index Model are shown below:

To determine the volume retained on each sieve for a 1000 gram batch:

$$V_{s(i)(n)} = \frac{\frac{P_{c(i)}}{100} \times \frac{(P_{s(i)(n-1)} - P_{s(i)(n)})}{100}}{G_{sb(i)}} \times 1000 \text{ (cm}^3\text{)} \tag{3-4}$$

To establish the volume of each average particle:

$$V_{p(n)} = \frac{\frac{4}{3}\pi((\frac{D_{(n-1)} + D_{(n)}}{2})/2)^3 \times VF_{(i)(n)}}{1000} \text{ (cm}^3\text{)} \tag{3-5}$$

To establish the surface area of each average particle:

$$SA_{p(n)} = 4\pi((\frac{D_{(n-1)} + D_{(n)}}{2})/2)^2 \times SAF_{(i)(n)} \text{ (mm}^2\text{)} \tag{3-6}$$

By combining equations 3-4, 3-5 and 3-6, the surface area of the particles retained on a specific sieve for each source can be calculated by the equation below:

$$SA_{(i)(n)} = \frac{0.0012 \times P_{c(i)} \times (P_{s(i)(n-1)} - P_{s(i)(n)}) \times SAF_{(i)(n)}}{G_{sb(i)} \times (D_{(n-1)} + D_{(n)}) \times VF_{(i)(n)}} \text{ (m}^2\text{/kg)} \tag{3-7}$$

After this, the film thickness can be calculated by inserting the new surface area equation into the traditional equation (equation 3-2):

$$T_I = \frac{P_{be}}{\sum SA_{(i)(n)} \times P_s \times G_b} \times 1000 \text{ (microns)} \tag{3-8}$$

where:

$V_{s(i)(n)}$ = total volume of aggregate of the ith source retained on the nth sieve;

$P_{c(i)}$ = the percent (by aggregate weight) of the ith source;

$P_{s(i)(n)}$ = the percent (by source weight) of the ith source passing the nth sieve;

$G_{sb(i)}$ = the bulk specific gravity of the aggregate from the ith source;

$V_{p(n)}$ = the volume of an average particle on the nth sieve;

$D_{(n)}$ = nominal opening of the nth sieve in millimeters;

$VF_{(i)(n)}$ = volume factor for particles from the ith source on the nth sieve;

$SA_{p(n)}$ = surface area of the average particle on the nth sieve;

$SAF_{(i)(n)}$ = surface area factor for particles from the ith source on the nth sieve;

$SA_{(i)(n)}$ = total surface area of the particles from the ith source on the nth sieve;

T_I = film thickness of the mixture from the Index Model;

P_{be} = percent (by mix weight) of effective bitumen binder;

P_s = percent (by mix weight) of aggregate;

G_b = specific gravity of the bitumen binder.

The shape factors (*VF* and *SAF*) are used to convert the volume and surface area from a uniform sphere to the desired particle shape. Their values are dependent on the nominal particle shape of the aggregate source. Table 3.2 gives some typical shape factors:

Table 3.2 Particle shape factors (Heitzman, 2006)

Particle Shape	Volume Factor	Surface Area Factor
Sphere●	1.0	1.0
Sphere 2:1 ◖■◗	2.5	2.0
Sphere 3:1 ◖■■◗	4.0	3.0
Cube ■	1.0	1.2
Cube 2:1 ■■	2.0	2.1
Cube 3:1 ■■■	3.0	2.9

Special attention should be paid to the selection of mineral filler, which can significantly impact the film thickness value. Heitzman (2006) suggests that the very small particles (less than 10 micron size) should be treated as a binder extender. However, in the Index Model, the mineral filler extender volume is not added to the effective binder volume.

3.3 ITSM Test

In the UK, much work has been done to develop an economic and practical means of measuring the structural and performance related properties of asphalts. The stiffness modulus is now commonly recognized as a very important performance property of bituminous paving materials. It can be used as a measure of the load-spreading ability of bituminous paving layers, and it is strongly related to the levels of traffic induced tensile strain at the bottom of the base which is regarded to be responsible for fatigue. In addition, it controls the levels of stresses and strains in the subgrade that can lead to structural deformation. Therefore, there is growing interest in developing a practical means of measuring the stiffness.

For many years the measuring of stiffness modulus of bituminous materials was conducted with sophisticated tests such as 3-point bending tests and bending or push-pull tests. These tests were capable of measuring the complex modulus of an asphalt beam over a range of frequencies and temperatures. However these methods are very expensive and time-consuming. For instance, it can take one day to test only one specimen with the 3-point bending test. In order to simplify the means of measuring stiffness modulus, a form of the indirect tensile test, the Indirect Tensile Stiffness Modulus (ITSM) test, became available in the late 1980's (Cooper and Brown, 1989). This test was identified to be a convenient and economic method and the measurements correlated well with those from the traditional sophisticated tests.

3.3.1 The principle of ITSM test

The ITSM test is the most commonly used test method in the Nottingham Asphalt Tester (NAT). Compared with the traditional sophisticated tests, this method is simple and can be completed quickly. Before the test is conducted, in order to avoid causing damage to the specimen during the test, the target horizontal deformation and the target load pulse rise time should be selected. A number of conditioning pulses are applied to the specimen to make any minor adjustments to the magnitude of the force needed to generate the specified horizontal deformation and to seat the loading strips correctly on the specimen. After that, five load pulses will be applied to the specimen. This causes an indirect deformation on the horizontal diameter and, since the diameter of the specimen is known beforehand, the strain can be calculated. In addition, the applied stress can also be calculated since the cross-sectional area is known and the force applied can be measured (Read and Whiteoak, 2003). With the calculated stress and strain, the stiffness modulus of the material can be calculated using the following equation:

$$S_m = \frac{L}{(D \times t)} \times (v + 0.27) \tag{3-9}$$

where:

S_m = indirect tensile stiffness modulus (MPa);

L = the peak value of the applied vertical load (N);

D = the peak horizontal diametral deformation resulting from the applied load (mm);

t = the mean thickness of the test specimen (mm);

v = the value of Poisson's ratio for the bituminous mixture at the temperature of test.

Standard test conditions and requirements for the ITSM test are listed in Table 3.3.

Table 3.3 Standard test conditions and requirements for the ITSM test

Horizontal strain	0.005% of the specimen diameter
Rise time	124ms
Specimen diameter	100mm, 150mm and 200mm
Specimen thickness	Between 30mm and 70mm
Test temperature	20^{o}C

3.3.2 Instrument description

In general, the ITSM system consists of the following three main devices: loading system, deformation measurement system and recording system.

Loading system

The loading system of the NAT incorporates a pneumatic load actuator (as shown in Figure 3.2), by which a load can be applied vertically across the diameter of the test specimen via the loading platens. The load actuator is capable of applying a load pulse to the test specimen. The rise-time, measured from when the load pulse commences and which is the time taken for the applied load to increase from zero to the maximum value, shall be 124 ± 4 ms. The peak load value shall be adjusted to achieve a peak transient horizontal diametral deformation of at least 5μm (UK experience indicates suitable values of peak horizontal deformation are 7 ± 2 μm for a 150 mm nominal diameter specimen and 5 ± 2 μm for a 100 mm nominal diameter specimen).

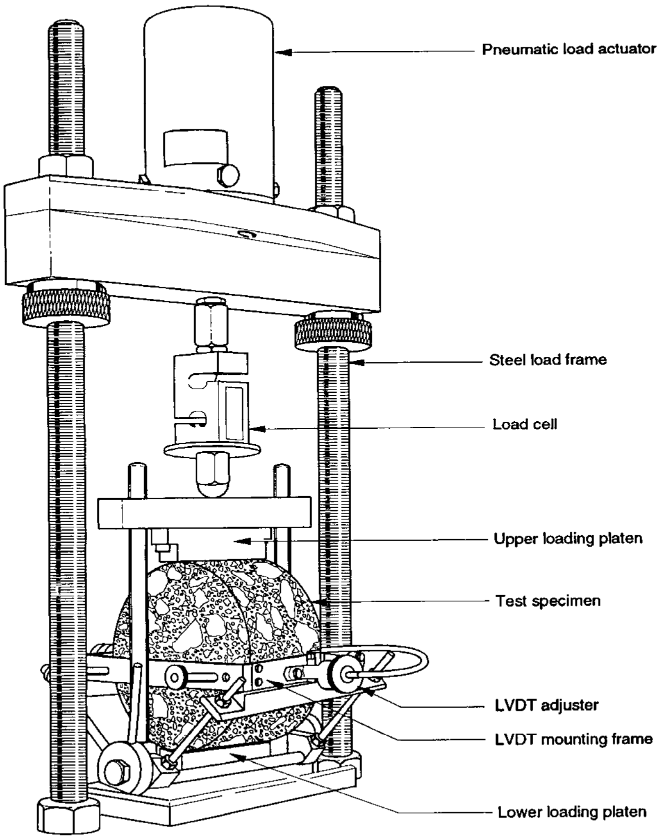


Figure 3.2 Test equipment for determination of indirect tensile stiffness

Deformation measurement system

This system is capable of measuring the peak transient horizontal diametral deformation of the test specimen, which is caused by the load pulse across a diameter of the specimen, perpendicular to the direction of load pulse application.

The accuracy of measurement shall be better than 1μm over the range of ± 0.1 mm. The recorded peak transient horizontal diametral deformation shall be the change in horizontal diameter of the specimen due to the applied load pulse.

The arrangement for measuring horizontal diametral deformation is shown in Figure 3.3. Two linear variable differential transducers (LVDTs) are mounted diametrically opposite one another in a rigid frame clamped to the test specimen. The frame shall not distort when the clamps are applied to the specimen and it shall not be supported during the test.

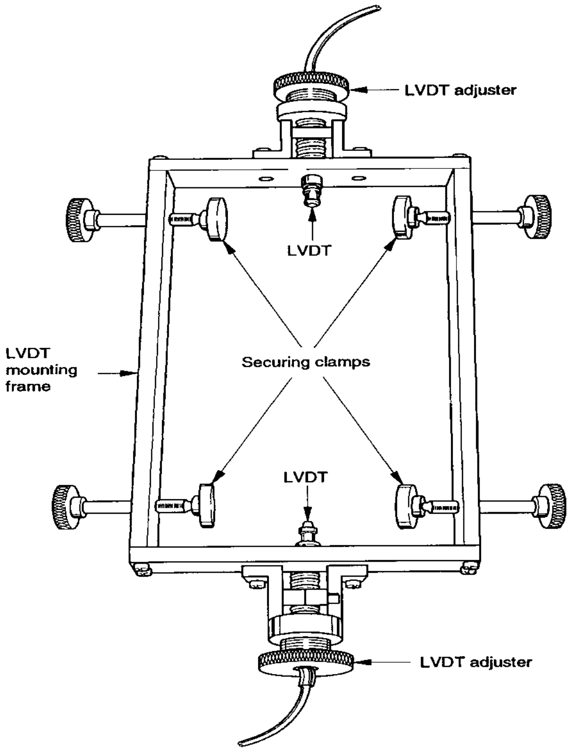


Figure 3.3 Arrangement for measuring horizontal diametral deformation

Recording system

The recording system comprises a digital interface unit connected to a computer that is used to monitor and record the electrical signals from the load actuator and LVDTs. The load pulse and the resulting transient peak horizontal diametral deformation shall be recorded by this system for the duration of each load pulse at a frequency such that the rise-time can be determined.

3.3.3 Test procedure

The ITSM test in this study is performed in accordance with BS DD 213:1993.

In order to ensure that the specimens had attained the test temperature (typically 20 ± 0.5°C), when they are subjected to the ITSM test, all the specimens are placed at the test temperature ± 1°C or better for at least 4 hours before the test.

Before the tests, the two platens should be wiped clean and inspected to check whether they are damaged or not. After that, the specimen is placed centrally in position on the lower platen and the deformation measurement system is secured to the specimen to make sure that it is located symmetrically about an axis through the centroid of the specimen and perpendicular to the direction of loading and the axis of symmetry of the specimen. The upper loading platen is then placed centrally on the top of the test specimen together with the assembly that is centrally placed beneath the load actuator. In addition, the deformation measuring devices should be adjusted to about the middle portion of their operating ranges to provide adequate travel on the transducers in either direction.

Five conditioning pulses are applied to the specimen to make any minor adjustments to the magnitude of the force needed to generate the specified horizontal deformation and to seat the loading strips correctly on the specimen. Then, the deformation measuring devices are adjusted again and a further five load pulses are applied to the specimen. For each load pulse application, the peak load, peak horizontal diametral deformation and rise time are measured and recorded and the stiffness modulus for each pulse load is calculated using equation 3-9. After all of these procedures, the specimen is rotated through $90^o \pm 10^o$ and the stiffness modulus is tested and calculated again at this position.

If the difference between the two results is within 10%, the mean for the two tests will be calculated and recorded as the stiffness modulus of the specimen. If the difference between the two values is greater than 10 %, the test should be repeated on the same specimen along the same diameters. If the difference persisted, the mean result for each diameter would be reported individually.

3.4 DSR Test

Bitumen is a visco-elastic material that behaves as an elastic solid at low temperatures and/or short loading times and as a viscous fluid at high temperatures and/or long loading times. At intermediate temperatures and loading times, bitumens exhibit visco-elastic behaviour that is a combination of both elastic and viscous components and display both a temperature and time dependent relationship between applied stresses and resultant strains. Therefore, in the measurement of the physical properties of bitumen, primary emphasis should be given to the characterisation of the rheological behaviour, which is defined as a study of the deformation or flow properties of materials whether in liquid, melted or solid form, in terms of the materials' elasticity and viscosity. Numerous methods have been used to characterize the flow properties of bitumen, and the Dynamic Shear Rheometer (DSR) has been proved to be one of the most complex and powerful.

3.4.1 Disadvantages of previous methods

Historically, some conventional methods have been used to characterise the rheological properties of bitumen (e.g. penetration and softening point). However, such completely empirical parameters are proved unable to describe the visco-elastic properties needed to relate fundamental physical binder properties to pavement performance and hence unsuitable to characterise the rheological properties of bitumen. Although the viscosity test is a more fundamental method of determining the rheological performance of bitumens, it does not provide information on the time dependence of bitumen.

Several more advanced methods exist to test the rheological properties of bitumens such as transient (creep) shear test methods using sliding plate rheometer, capillary forced flow rheometer and cone and plate viscometer. However, all of these three methods are frequently conducted in the non-linear flow region and are therefore difficult to characterize in the laboratory or to correlate to practical performance (Airey, 2005).

3.4.2 Principles of DSR Test

The DSR test provides a powerful means of characterising the rheological properties of bitumens in the region of linear response. The principle of the DSR test is to apply an oscillatory shear force to a bitumen sample, which is sandwiched between two parallel plates. As depicted in Figure 3.4, the typical arrangement of DSR is of an oscillating upper plate through which the shear force is applied to the specimen and a base plate that is fixed. Normally there are two plate geometries used in the DSR test, namely 8 mm diameter spindle with 2 mm testing gap and a 25 mm diameter spindle with 1 mm gap. The 8 mm plate geometry is generally used at low temperatures (-5°C to 20°C) and the 25 mm at intermediate to high temperatures (20°C to 80°C). Sometimes the 8 mm geometry can be used between -5°C and 60°C, although the precision of the results at high temperatures may be reduced.

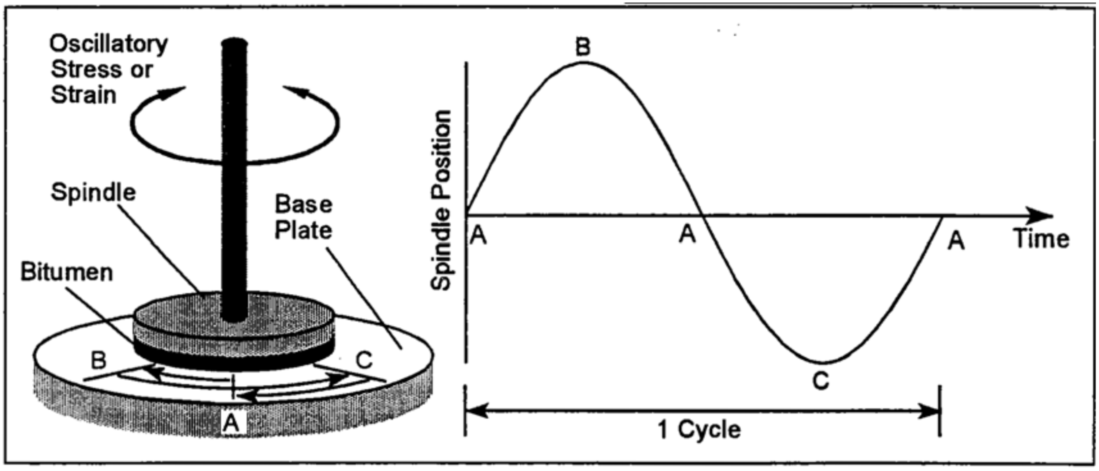
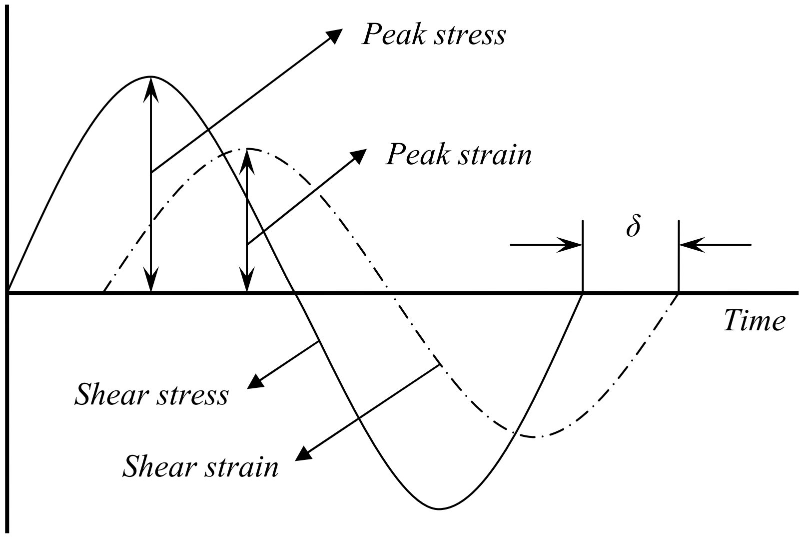


Figure 3.4 Schematic of dynamic shear rheometer testing configuration

DSR tests can be conducted in controlled stress and controlled strain modes. In a controlled stress test, a fixed torque is applied to the upper plate and an oscillatory motion will be generated. Because the magnitude of the torque is fixed, the distance the plate moves on its oscillatory path may vary between cycles. In controlled strain test, the upper plate moves between two fixed points on the oscillatory path at specified frequency and the torque to maintain the oscillation is record in the machine (Read and Whiteoak, 2003). In order to keep the rheological response of the bitumen within its linear region, DSR tests are normally conducted with a relatively small strain, which is usually achieved by adopting strain or stress limits.

Normally DSR tests are conducted over a range of temperatures and loading frequencies to provide a full characterization of the visco-elastic properties of bitumens. From a single test run, two principal visco-elastic parameters can be obtained from the DSR test to characterize the bitumen rheological properties. These two parameters are the complex shear modulus, G^*, and the phase angle, δ (as shown in Figure 3.5). G^* is defined as the ratio of maximum shear stress to maximum strain. It is composed of a loss modulus (viscous components, G'') and a storage modulus (elastic components, G'). δ is defined as the phase difference between stress and strain in the oscillatory test.



$$|G^*| = \frac{Peakstress}{Peakstrain} = \textit{Complex shear modulus}$$

$$G' = |G^*|\cos\delta = \textit{Storage (Elastic) modulus}$$

$$G'' = |G^*|\sin\delta = \textit{Loss (Viscous) Modulus}$$

$$\tan\delta = \frac{G''}{G'} = \textit{Loss tangent}$$

$$|\eta^*| = \frac{|G^*|}{\omega} = \textit{Dynamic viscosity}$$

where:

δ = phase angle

ω = angular frequency

Figure 3.5 Definitions of modulus obtained from DSR test

3.4.3 Sample preparation

Although most work of this test is done automatically by the DSR machine, bitumen samples have to be installed manually and this is widely regarded as one of the integral factors that can significantly affect the accuracy and repeatability of the measured rheological parameters (Airey and Hunter, 2003). Although various sample preparation methods and procedures exist, they can generally be reduced to three types: the hot pour method, the silicone mould method and the mass method (Airey and Hunter, 2003). The preparation methods used in this study are hot pour method and silicone mould method.

In hot pour method, firstly, the gap between the upper and lower plates was set to a height of 50 μm plus the required testing gap at the mid-point of the proposed testing temperature range. That is, the plate gap for the 25 mm geometry system was set to 1.05mm at 45°C and for 8mm geometry was set to 2.05 mm at around 20°C. Once the gap is set, a sufficient quantity of hot bitumen (typically at 100 to 150°C) is poured onto the lower plate of the DSR to ensure a slight excess of material appropriate to the chosen testing geometry. The upper plate is then gradually lowered to the required testing gap plus 50 μm. The bitumen that had been squeezed out between the plates is then trimmed flush to the edge of the plate by using a hot spatula. After trimming, the plate gap is closed by a further 50 μm to achieve the required testing gap.

The silicone mould method consists of pouring hot bitumen (typically at 100-150°C) into either an 8 mm or 25 mm diameter silicone mould of height approximately 1.5 times the recommended testing gap for the two geometries, namely 3 mm for 8 mm geometry and 1.5 mm for 25 mm geometry respectively. Similar with the hot pour method, the testing gap is set at a height of 50 μm plus 1 mm or 2 mm. Once the bitumen has cooled, either by means of short-term refrigeration or by natural cooling, the bitumen disc (typically at ambient temperatures) is removed from the mould and centred on the lower plate of the DSR. The upper plate is then lowered to the required gap plus 50 μm, the excess bitumen is trimmed with a hot spatula and the gap is further closed to its final testing height.

3.4.4 Typical presentation and analysis methods of DSR results

As stated above, in order to completely describe the rheological properties of bitumens, the DSR tests are conducted over a wide range of temperatures and loading times (frequencies) and the number of parameters obtained from the test is quite large. Therefore, in order to present the flow properties of bitumens more clearly, two typical forms are usually adopted: isochronal and isothermal plots (rheological parameters versus temperature at fixed frequencies and versus frequency at specific temperatures respectively). The region of the testing temperatures is dependent upon the geometries of the plates adopted in the test. With regards to the analysis methods, one of the primary analytical techniques is the construction of master curves using the interrelationship between temperature and frequency to produce a continuous rheological parameter curve at a reduced frequency or time scale (Ferry, 1971). Black Diagrams are a further method often adopted by researchers to identify and quantify inconsistencies in rheological data caused by ageing, polymer modification, non-linear effects and incorrect selection of sample geometries.

Construction of master curves

After years of investigation, researchers have found an interesting phenomenon; there is an interrelationship between temperature and frequency which, by using shift factors, can bring measurements obtained at different temperatures to fit one overall continuous curve at a reduced frequency or time scale (Airey, 2005). This means that, if the DSR test is conducted within the linear visco-elastic (LVE) region, rheological parameters obtained at higher and lower temperatures can be transposed simply and graphically into lower and higher frequencies respectively. In that case, a continuous curve that can represent the binder behaviour at a given temperature for a large range of frequencies will be obtained. Obviously, it will also work in the converse way.

The principle that is used to relate the equivalency between frequency and temperature and then produce the master curve is called the time-temperature superposition principle (TTSP) (Ferry, 1971). Materials to which this principle may be applied to construct continuous master curves are termed, or classified, as “thermo-rheologically simple” materials. Researchers have shown that most bituminous binders can be characterized as “thermo-rheologically simple” materials; therefore, TTSP can be used for binders to generate master curves and shift factor relationships (Airey, 2005). To produce a master curve using TTSP, the dynamic parameters over a range of temperatures and frequencies should be collected first. Then a standard reference temperature needs to be selected and the parameters at all other temperatures will be shifted with respect to frequency until a smooth function is obtained. It should be noted that the master curves are only valid for the standard reference temperature that is selected before curve construction.

Black Diagrams

Black Diagrams are now usually adopted by researchers to identify and quantify inconsistencies in the DSR results that are caused by ageing, polymer modification, non-linear effects and incorrect selection of sample geometries (Airey, 2002). It is generally plotted with the magnitude of the complex modulus, G^*, versus the phase angle, δ. The advantage with this method is that these graphs can be plotted without the use of temperature and frequency, which means that Black Diagrams allow all the rheological parameters to be presented in one graph and do not need to perform TTSP manipulations to shift the data. However, it has been found that there are strong relationships between Black Diagrams and TTSP. A smooth curve in a black diagram is a useful indicator of time-temperature equivalency, while a disjoined curve indicates the breakdown of TTSP. In addition to indicating the TTSP, a disjointed curve in a black diagram can also indicate the presence of either a high wax content bitumen, a highly asphaltene structured bitumen or a highly polymer modified bitumen (Airey, 2005).

3.4.5 Development of DSR modification

Ordinarily, measurements in DSRs are applied on bitumens placed between metal plates which are comprised of stainless steel and/or anodised aluminium. Such measurements are useful for comparing bitumens on a 'standard' material; however they do not quantify any effects imparted to the bitumens by mineral aggregates, with which they come into contact and therefore, such tests may lead to inappropriate characterisation of the bitumen in the context of its performance in a bitumen-aggregate mixture. Several attempts have been made by researchers so that the aggregate plates can be incorporated into the DSR tests.

Scholz and Brown (1996)

It was Scholz (1995) who first applied a novel way in which the rheological property of binders can be measured while in contact with mineral aggregate (Scholz, 1995; Scholz and Brown, 1996). In their study, a simple modification to the base plate of a Bohlin Model DSR50 dynamic shear rheometer was made to allow a small disc (either stainless steel plate or mineral aggregate plate) to be clamped and securely held in place directly below the parallel plate spindle. Although, as shown in Figure

3.6, only the lower plate is modified in this study (the upper plate is the standard 8 mm stainless steel spindle), it does provide an innovative way for conducting DSR tests on bitumens coated on aggregate discs.

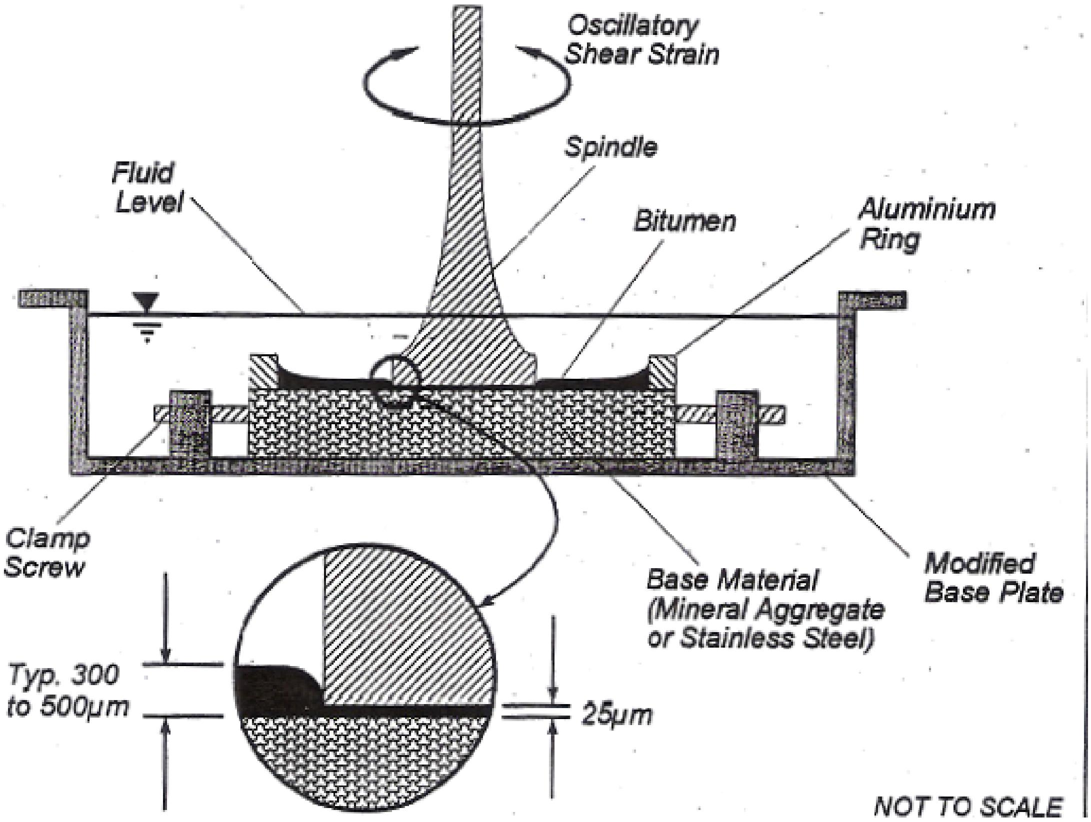
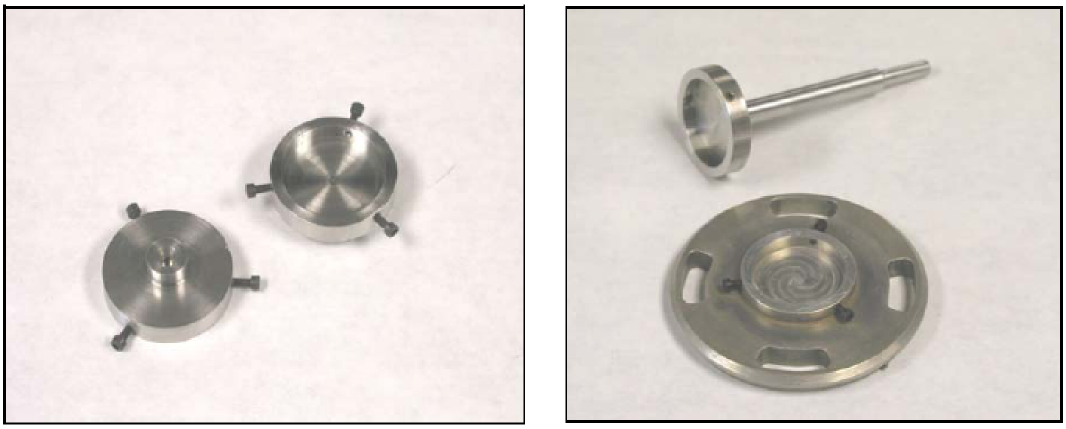


Figure 3.6 Experimental arrangement developed for use in DSR (Scholz and Brown, 1996)

Rottermond et al. (2004)

Rottermond et al. (2004) made some improvements based on Scholz's early work so that they can use ceramic discs on both upper and lower plates in their moisture susceptibility study. Figure 3.7 shows the new parts of the modified DSR for both air chamber and for water bath. In their modification, the new parts for the water bath were to be exactly the same as the conventional spindle and base plate, with the exception of an additional ring with the threaded holes for the set-screws. For the air chamber, because both the top and bottom plates are removable and identical, only the plates needed to be modified and machined.



a) New parts for air chamber b) New parts for water bath

Figure 3.7 New development for DSR plates (Rottermond et al., 2004)

Kvasnak (2006)

Rottermond et al. (2004) suggested some further changes for their modified water bath spindle, as they noticed that the top ceramic discs were not becoming saturated during testing. By examining the test procedure, it was found that when the spindle is placed in the DSR and lowered into the water bath, there is no way for the air under the spindle to escape and it is entrapped. Based on their suggestion, Kvasnak (2006) further developed the DSR modification by drilling three holes on the upper plate, which solved that problem properly, as shown in Figure 3.8.

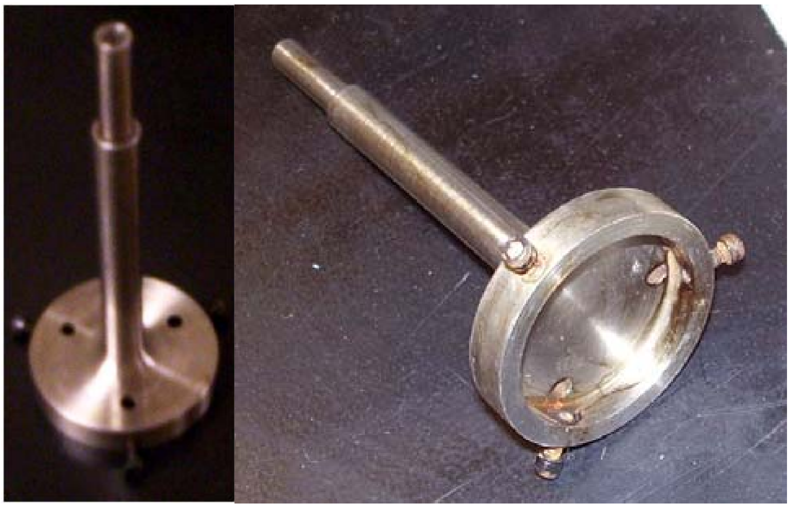


Figure 3.8 Kvasnak's modified DSR spindle

It is important to note that Kvasnak's DSR modification is very similar to the set developed by Rottermond et al., with the only difference that there are three holes on the spindle in Kvasnak's modification. However, with regard to the testing gap (the thickness of tested binder), they had different opinions. Rottermond et al. (2004) believed that a smaller gap size should more closely measure the effects at the interface. Therefore, a small gap size of 100 microns was chosen in their study, and they suggested that decreasing the gap to 50 or 25 microns would be more productive for the test. However, Kvasnak (2006) thought that smaller gap sizes are more sensitive to plates that are not parallel, which might result in unrepeatable results. These conclusions are highly dependant on the precision of disc fabrication. For instance, the discs used in Rottermond's study are ceramic discs that are produced with a high degree of precision, which will be suitable for small gap tests. However, studies carried out in this research have shown that it is difficult to achieve the same precision for discs produced by coring and cutting natural rocks.

Cho and Bahia (2007)

Cho and Bahia (2007) developed another way to fix cored rock disks on the standard DSR upper spindle and lower plate and used the modified plates in their study on the effects of aggregate surface and water on rheology of bitumen films. Instead of screws, Super Glue-Gel Epoxy was used to bond rock disks to the standard spindle, as shown in Figure 3.9. It was declared that the epoxy's temperature range is -36 to 149°C, and its strength is 10 MPa. However, it is felt that the way of using super glue to fix rock disks may cause some testing errors, especially when harder binders are used. For instance, an aged 15 pen binder used in this study has a stiffness at 25°C and 0.4 Hz of more than 12 MPa, which is even higher than super glue's strength.

Figure 3.9 Newly developed DSR test by Cho and Bahia (2007)

3.5 FTIR Test

Infrared absorption spectroscopy is one of the most powerful means of detecting and identifying chemical bonds (functional groups) in either organic or inorganic materials. Fourier transform infrared spectroscopy (FTIR) is therefore widely used to characterise the oxygen-containing functionalities found in bitumen, particularly those produced during oxidation.

3.5.1 Principle of FTIR

Molecular bonds can vibrate at different frequencies depending on the elements and the type of bonds. For any given bond, there are several specific frequencies at which it can vibrate, when activated by an external energy source (Williams and Fleming, 1980). In FTIR test, the energy from the IR light source, with wavenumbers of 400 to 4000 cm^{-1}, is transformed into vibrational energy in the molecules of bitumen. It is this vibrational energy that presents a series of absorption bonds which are recorded as transmittance (%) or absorbency against the wavelength (μm) or more often wavenumber (cm^{-1}). The positions of the peaks along the wavenumber axis are unique to certain chemical bonds and chemical functional groups present in the bitumen. Typical wave numbers for several bitumen ageing products are shown as follows:

- S=O, C-H in aromatic - 1020 cm^{-1}
- SO_2 from oxidation - 1108 cm^{-1}
- ester (R-COOR) - 1262 cm^{-1}
- C=C in aromatic - 1618 cm^{-1}
- C=O in carbonyl - 1702 cm^{-1}

3.5.2 Different ways for FTIR sample preparation

In general, the infrared spectra of substances are fairly easily determined if the sample is a gas, a liquid or a solid. However, the bitumen sample is a material that is soft and sticky at room temperature, which causes some problems in the course of sample preparation for infrared analysis. Various ways have been developed by researchers for preparing bitumen samples for FTIR test.

Most researchers (Smith, 1966; Petersen et al., 1975; and Curtis et al., 1987) have determined the spectra of bitumen samples in solution. This method uses solvent to dissolve bitumen; and then the obtained solution is analysed by FTIR. However, because all solvents absorb strongly in at least several regions of the infrared spectrum, it is necessary to use more than one solvent to be able to get a complete spectrum of the bitumen sample. The most commonly used solvents in the solution method are carbon tetrachloride (CCl_4) and carbon disulfide (CS_2).

Another common preparation technique is to utilise a compacted potassium bromide (KBr) or sodium chloride (NaCl) plate as a base to hold a thin bitumen film. Lamontagne et al. (2001) dissolved bitumen samples in dichloromethane (30 g/l) and then laid the solution on a potassium bromide (KBr) thin plate. The solvent was then evaporated under a nitrogen flow to avoid interference in the obtained spectra. A recording between 4000 and 400 cm^{-1} is realised with the KBr thin plate alone (reference acquisition) and then with the sample.

Glover et al. (1989) developed a KBr pellet technique for FTIR analysis. In their study, extremely dry (oven dried at 300^oC for 2 hours) KBr powder (0.975 g) and 0.025 g of frozen bitumen (freezer stored at -20^oC for at least 2 hours) were weighed to obtain a total mixture of 1.000g. Then the amount of this bitumen-KBr mixture needed for one pellet was accurately weighed and placed between two highly polished stainless steel discs inside a pellet press, where it was compressed at 25,000 Pa for 1 min to make a small pellet. A pellet of the same mass using pure KBr was similarly prepared for obtaining background comparisons. Analyses were made of both the blank and bitumen-KBr pellets.

3.5.3 Spectrometric index calculations in FTIR

Lamontagne et al. (2001) introduced a spectrometric index calculation method to avoid using spectrum normalisation in FTIR analysis. In their study, the FTIR spectrum for bitumens are obtained with a KBr plate test. Figure 3.10 shows the result for their original bitumen. The functional and structural indexes are then calculated from the band areas measured from valley to valley, based on which, several index types are calculated with band area ratio. They describe:

- aromatic structures (aromaticity index - $A_{1600}/\sum A$);

- aliphatic structures (aliphatic index - $A_{1460} + A_{1367}/\sum A$);
- oxygenated functions (carbonyl index - $A_{1700}/\Sigma A$, and sulphoxides - $A_{1030}/\Sigma A$).

The sum of the area represents:

$$\Sigma A = A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}.$$

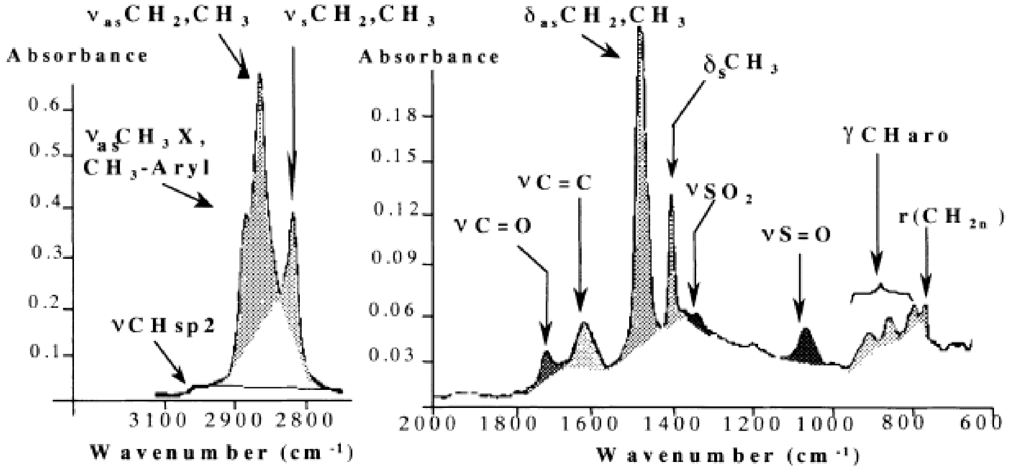


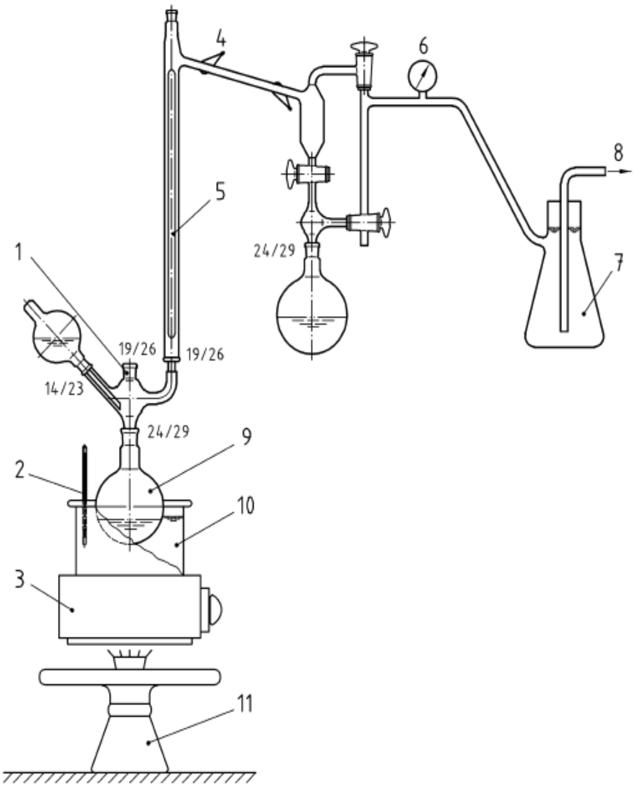
Figure 3.10 FTRI spectrum of a 4000-400 cm^{-1} original bitumen (Lamontagne et al., 2001)

3.6 Bitumen Recovery Technique

In order to check the ageing level of the binder in different stages, it is necessary to test the rheological properties of binders inside the asphalt. Therefore, researchers developed a very useful test that can recover binders from the asphalt mixtures. Figure 3.11 shows a schematic of one typical distillation apparatus used for the recovery of soluble bitumen (BS EN 12697-4:2005).

In this recovery test, a sample of the asphalt was soaked in dichloromethane (methylene chloride) to remove the bitumen from the aggregate into solution. In order to remove the aggregate, the bitumen solution was firstly decanted through a 63μm sieve to remove the larger sized aggregate. The other insoluble matter was then removed from the bitumen solution by centrifuging at an acceleration of at least 15000 m/s^2 for 20 ±5 minutes in a sample tube centrifuge. After removal of the aggregate, the bitumen solution was concentrated by atmospheric distillation in a fractionating column. The last traces of solvent were removed from the concentrate by distillation at a temperature of 100°C above the expected softening point or

175°C, whichever is the higher, with the pressure reduced from atmospheric pressure 100 kPa to 20 kPa with the aid of a stream of carbon dioxide gas.



KEY
1 fill stirrer or CO_2 tube here
2 thermometer with bulb opposite bottom of flask
3 enclosed electrical heater
4 condenser
5 fractionating column
6 vacuum gauge
7 water trap
8 pump
9 500 ml bottom flask
10 oil bath
11 jack

Figure 3.11 Distillation apparatus used for the recovery of soluble bitumen (BS EN 12697-4:2005)

4 EFFECTS OF BITUMEN AGEING METHOD AND BINDER VOLUMETRICS ON BITUMEN AGEING

4.1 Introduction

A pure bitumen ageing study and a study on the effects of bitumen film thickness on bitumen ageing have been conducted initially as preliminary tests. This is so that the bitumen oxidative ageing mechanism can be better understood and a proper film thickness could be selected for further asphalt mixture ageing studies.

Although the main purpose of this study is to investigate the influences of mineral aggregates on bitumen ageing while pure bitumen ageing does not take account of the aggregate influence, ageing bitumen in bulk is simpler to undertake than asphalt mixture ageing and can still be correlated to field performance (Airey, 2003). Therefore, bulk ageing on pure bitumen is still widely used by researchers and practitioners and provides an ideal reference standard to the study of the influences of aggregates on ageing.

As stated in Chapter Two, for a bituminous paving mixture where the bitumen coats on to the aggregate surface as a thin film, an adequate bitumen film thickness can effectively restrict the effects of both oxidative ageing and mineral aggregate, and thereby ensure reasonable durability of the mixture. However, with the aim of investigating the affecting mechanisms of mineral aggregate to bitumen ageing, a relatively thin film thickness would be more useful. Therefore, in order to choose a proper film thickness for further mixture ageing studies, and also to develop a general understanding of how the film thickness influences ageing, an ageing study on asphalt mixtures with different binder film thicknesses was undertaken.

4.2 Pure Bitumen Ageing Study

4.2.1 Ageing methods used in this study

In this study, two 'short-term' ageing simulation methods were used: the traditional RTFOT and a High-Shear mixing technique. The High-Shear ageing simulation is a non-standard method and its ageing needed to be correlated with RTFOT ageing. The standard 'long-term' Pressure Ageing Vessel (PAV) ageing simulation method was also applied on the aged residues from both the RTFOT and High-Shear tests. The HiPAT ageing protocol of 85°C, 2.1 MPa air pressure and 65 hours was used for the PAV ageing (Hayton et al. 1999).

Figure 4.1 shows a picture of the High-Shear mixer. In the ageing procedure, a desired volume (4 litres in this study) of hot bitumen between 160 and 180°C is placed in a clean tin on the hotplate below the mixer (entire system located in a fume cupboard). The shear mixing head is then lowered into the tin. The temperature of the hotplate is controlled and maintained at around 160°C which is similar to the temperature of the RTFOT (163°C). The mixer is operated at a speed of approximately 3500 rpm with the top surface of the binder being exposed to air.

Figure 4.1 Picture of High-Shear Mixer

During the High-Shear ageing test, binder samples were taken every 12 hours and their penetration and R&B softening point values were measured. Figure 4.2 shows the testing results at different ageing stages. By comparing these results with RTFOT values, an equivalent ageing period of 2.5 days was chosen. Therefore in this study, 'High-Shear aged binder' refers to binder aged in the High-Shear Mixer for 2.5 days.

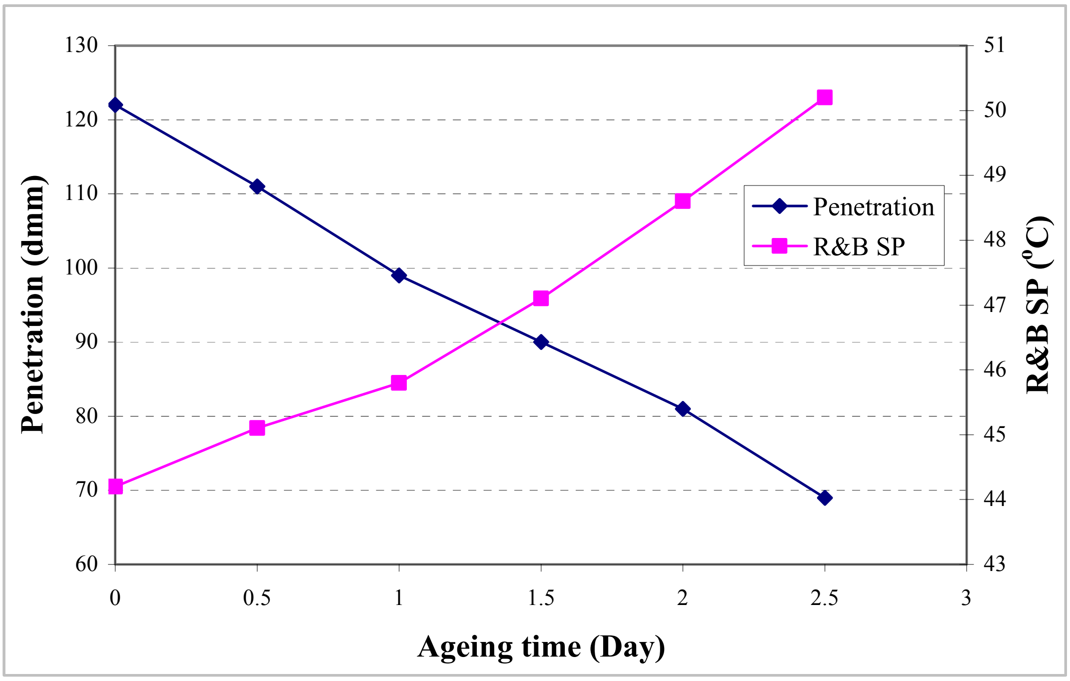


Figure 4.2 Penetration and R&B SP results for High-Shear aged bitumen at different ageing stages

4.2.2 Materials and experimental programme

The binder used in this study was a 100/150 penetration grade bitumen. Both the empirical and DSR rheological tests were performed on the binders at the following stages: virgin binder, RTFOT aged binder, High-Shear aged binder, RTFOT + PAV aged binder and High-Shear + PAV aged binder.

The empirical rheological tests included the penetration test (BS EN 1426: 2007) at 25^{o}C and ring and ball softening point (R&B SP) test (BS EN 1427: 2007).

The DSR rheological characteristics of the binder in this study were measured with a Bohlin Gemini 200 model DSR (as shown in Figure 4.3) under the following test conditions:

- Mode of loading: Controlled-strain,
- Temperatures: 0 to 80°C (5°C intervals),
- Frequencies: 0.1 to 10 Hz,
- Plate geometries: 8 mm diameter with a 2 mm gap (0 to 35°C) and 25 mm diameter with a 1 mm gap (25 to 80°C).

Figure 4.3 Picture of Bohlin Gemini 200 DSR

To ascertain the chemical changes induced by different ageing procedures, the unaged binder and the binders aged by RTFOT and High-Shear Mixer were subjected to a FTIR test with a Bruker Tensor 27 infrared machine (as shown in Figure 4.4). Binders were dissolved in toluene and laid on a sodium chloride (NaCl) plate. After the solvent is evaporated, binders in thin films were infrared scanned in wavenumbers ranging from 4000 to 600 cm^{-1}.

Figure 4.4 Picture of Bruker Tensor 27 FTIR machine

4.2.3 Testing results and discussions

Penetration and R&B SP results

Two penetration tests and two R&B SP tests were carried out on each sample and Table 4.1 shows the average results of these tests. The ageing indices calculated from R&B SP both after short-term and long-term ageing show that the High-Shear test is an ideal alternative method to the RTFOT being able to produce considerably larger quantities of aged binder compared to the RTFOT procedure. However, the penetration results in Table 4.1 reveal that although the penetration values are identical for the RTFOT and High-Shear test, a difference of 10 dmm in penetration appears between the two binders after PAV ageing. This indicates the possibility that the ageing mechanisms in the RTFOT and High-Shear test do differ.

Table 4.1 Summarized results of the empirical rheological tests

Binders	Pen (dmm)	SP (^{o}C)	Ageing index by SP
Virgin	122	44.2	-
RTFOT aged	69	49.6	1.12
High-Shear aged	69	50.2	1.14
RTFOT+PAV aged	46	59.2	1.34
High-Shear+PAV aged	56	60.2	1.36

DSR analysis

Frequency sweep DSR tests were applied to binders at different ageing stages and their results have been presented in complex modulus (*G**) master curves (with reference temperature of 25°C), phase angle (δ) master curves (with reference temperature of 25°C) and black diagrams, which are shown in Figures 4.5 to 4.7.

The complex modulus master curves show a consistent increase in stiffness for binders either aged in 'RTFOT+PAV' procedure or 'High-Shear+PAV' procedure, which has displayed the 'hardening' of bitumen during ageing simulation. The phase angle master curves for both ageing methods show a decrease with ageing, corresponding to an increased elastic behaviour after ageing.

Most empirical test results (Table 4.1) have shown the comparability of the two different ageing methods, and this is further supported by the data shown in DSR phase angle master curves and black diagrams, where the results for binders from the two different ageing methods are relatively identical both after short- and long-term ageing. However, significant differences are observed in complex modulus master curves between the two different ageing methods. In order to show this phenomenon more clearly, the phase angle (δ) and the complex modulus (G*) values at 25°C and 0.4 Hz for the 8 mm testing geometry are selected and presented in Table 4.2.

Table 4.2 Typical rheological data from DSR test (25°C, 0.4Hz)

Binders	δ (°)	G* (Pa)	Ageing index by G*
Virgin	74.9	83847	-
RTFOT aged	64.7	570100	6.8
High-Shear aged	67.1	225160	2.7
RTFOT+PAV aged	55.6	820030	9.8
High-Shear+PAV aged	53.3	1182300	14.1

From the data shown in Table 4.2, it can be seen that the phase angles are similar for RTFOT and the High-Shear aged binders, even after PAV ageing. However, their complex modulus results differ considerably especially after PAV ageing. An interesting phenomenon that should be noted is that the order of ageing index after long-term ageing is opposite to that after short-term ageing. After short-term ageing, the ageing index of the RTFOT aged binder is higher than that of the High-Shear aged binder, while after PAV long-term ageing, the index of the High-Shear aged binder is much larger than that of the RTFOT aged binder. Such order change response can also be observed in complex modulus master curves and phase angle master curves. This indicates that although most of the empirical rheological properties and part of the DSR rheological properties show a very close relationship between the binders aged with different methods, there may be some significant differences in the ageing mechanism between them.

The possible cause of this interesting phenomenon might be different degrees of oxidation and oxidative products occurring in the binders during the two ageing tests. In RTFOT ageing, binders are aged in eight glass containers that are fixed in a vertically rotating shelf. Hot air is blown into each sample bottle periodically (usually when at its lowest position). During the test, the bitumen flows continuously around the inner surface of each container in a relatively thin film. Therefore, the RTFOT ensures that all the bitumen is exposed to heat and air and the continuous bitumen flow ensures that all the bitumen is aged homogeneously (Read & Whiteoak 2003). All of these conditions are ideal for the oxidation of molecules in the binder. However, in the High-Shear ageing procedure, only the top surface of a large volume of binder is periodically exposed to air during the high shear mixing process. These conditions of course will limit the degree of contact of the binder to oxygen. As stated by Petersen (1984), oxidation of binder molecules is an extremely complex procedure (as seen in Figures 2.14 and 2.15) and, therefore, the periodic oxygen supply condition in the High-Shear method may result in smaller amount of oxidation products (sulphoxides and carbonyl functional groups) being formed in the High-Shear method compared to the RTFOT. These residual binders may have a different potential for further oxidation in the PAV compared to those from RTFOT ageing. This conclusion was shown to be correct by the FTIR test (see Table 4.3).

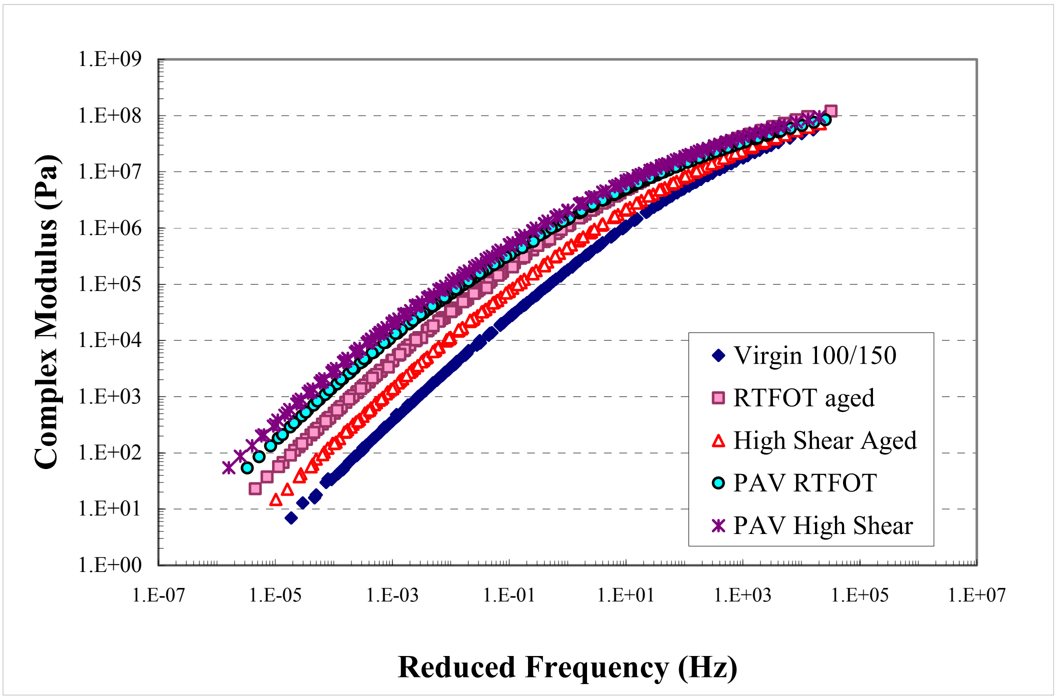


Figure 4.5 Complex modulus master curves for binders at different ageing stages

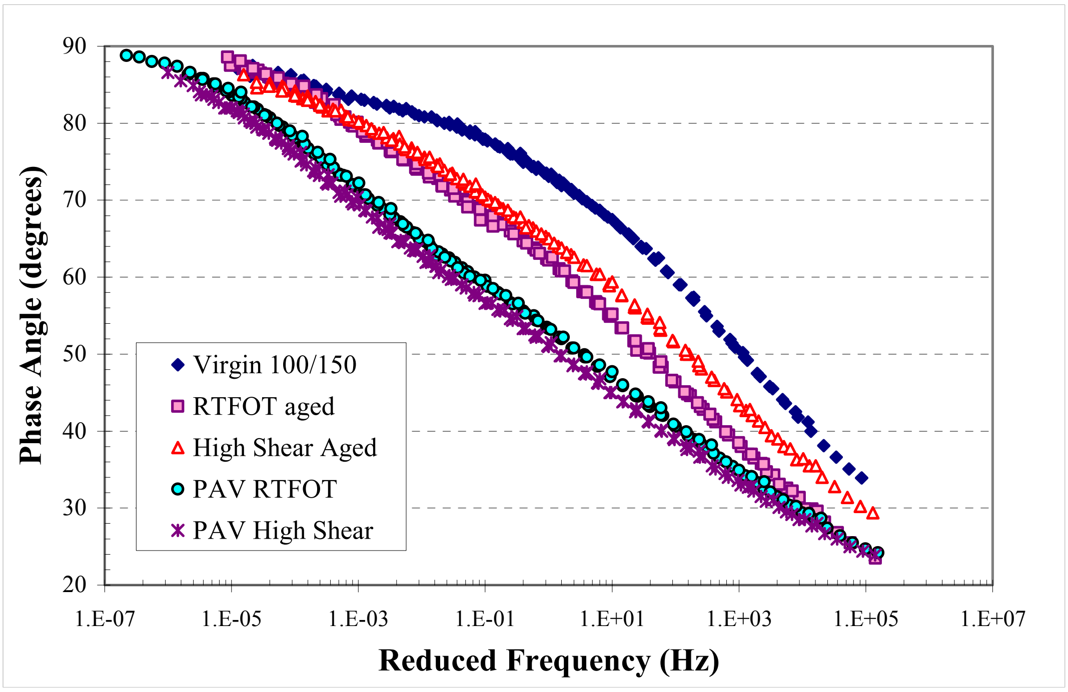


Figure 4.6 Phase angle master curves for binders at different ageing stages

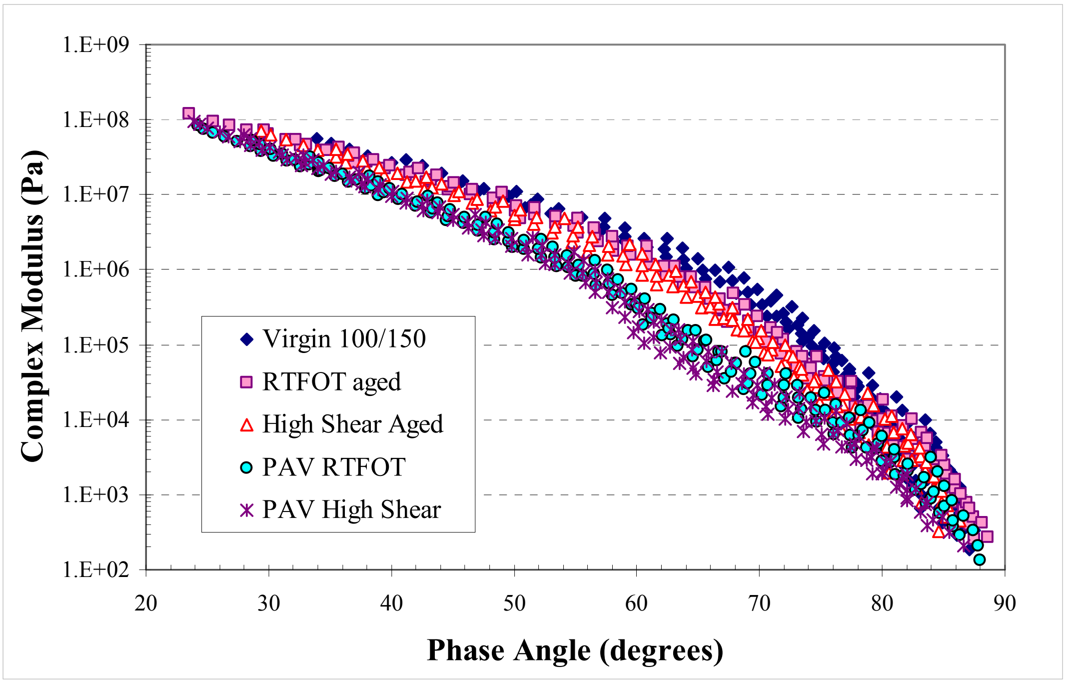


Figure 4.7 Black diagrams for binders at different ageing stages

FTIR analysis

As stated above, a FTIR spectrometer was used to determine the functional characteristics of the bitumen before and after ageing. Figure 4.8 presents the FTIR scan results for the unaged binder and the binders aged by different ageing simulation methods.

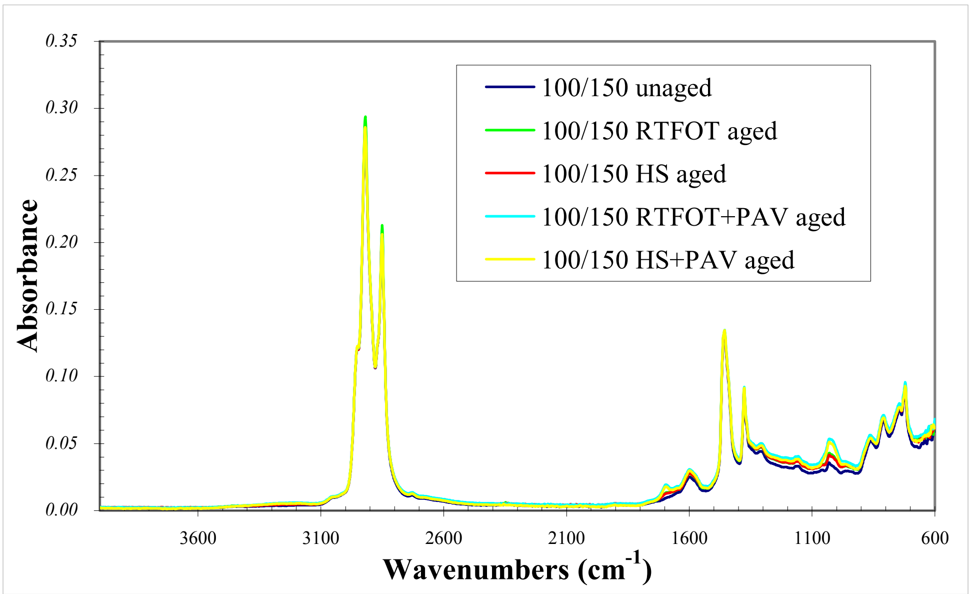


Figure 4.8 FTIR testing results for unaged and short-term aged binders

Special attention was paid to the results with wavenumbers ranging from 1800 to 600 cm $^{-1}$ (Figure 4.9 shows the expanded scan result in this region), which covers the regions for the main oxidative ageing products: carbonyls (1700 cm^{-1}) and sulphoxides (1030 cm^{-1}). From Figure 4.9, it can be seen that the absorbance values at wavenumbers representing carbonyl and sulphoxide both increase as the ageing simulation proceeds, which indicates that the amount of oxidation products in bitumen increased during the ageing simulation. However, quantitative comparison between the RTFOT and HS ageing based on the peak areas of these functional groups was felt impossible; the bitumen samples tested on the salt plate were found to have different thicknesses. Therefore, the spectrometric index method, which was firstly developed by Lamontagne et al. (2001) and introduced in Section 3.5.3, was adopted in this study for the comparison between different ageing simulation methods. The calculated indices for carbonyl and sulphoxide groups are presented in Table 4.3 and graphically compared in Figures 4.10 (for carbonyl index) and 4.11 (for sulphoxides index).

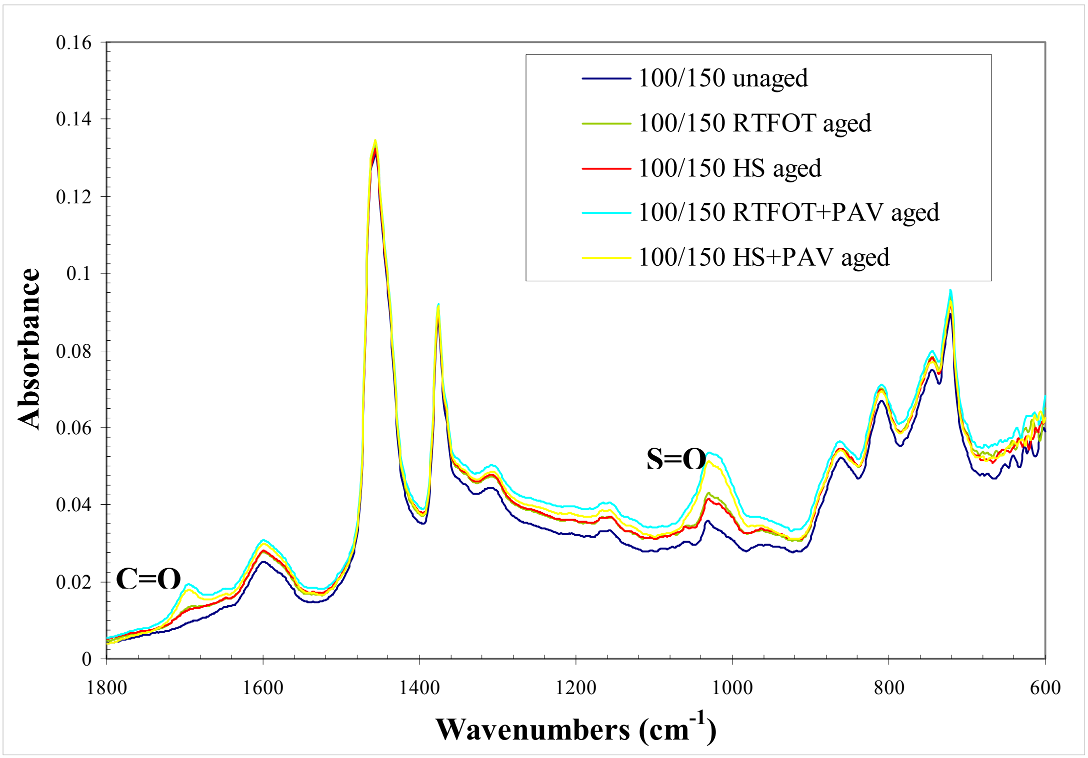


Figure 4.9 Expanded FTIR results of 1800 to 600 cm^{-1} for binders

Table 4.3 Spectrometric indices for the oxygenated functions in the bitumen at different ageing stages

Binders	$\sum A^{a}$	Carbonyl index – $A_{1700}/\sum A$	Sulphoxide index – $A_{1030}/\sum A$
Virgin	17.6528	0	0.0094
RTFOT aged	17.9204	0.0023	0.0157
High-Shear aged	17.4257	0.0004	0.0138
RTFOT+PAV aged	17.8837	0.0079	0.0261
High-Shear+PAV aged	18.0197	0.0075	0.0245

[a] $\sum A = A_{1700} + A_{1600} + A_{1460} + A_{1376} + A_{1030} + A_{864} + A_{814} + A_{743} + A_{724} + A_{(2953, 2923, 2862)}$.

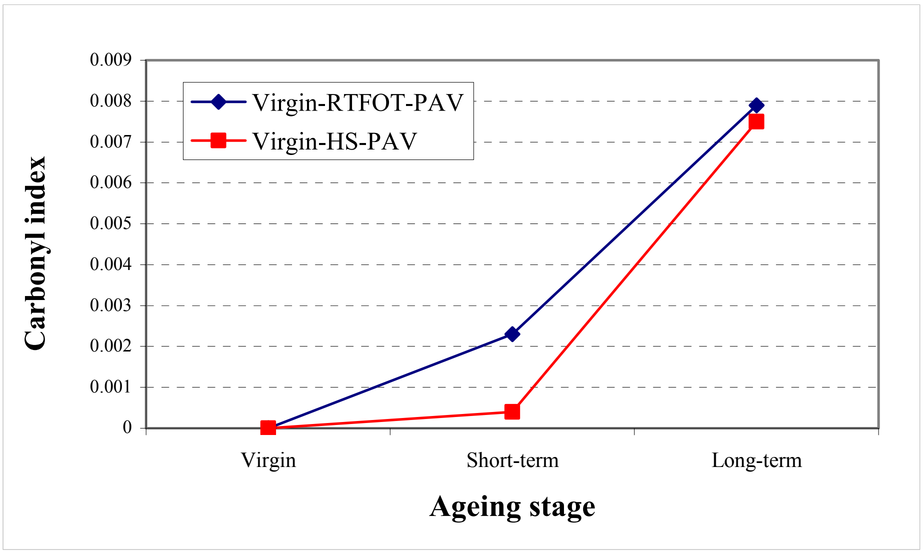


Figure 4.10 Comparison of carbonyl indices for the binders from different ageing methods

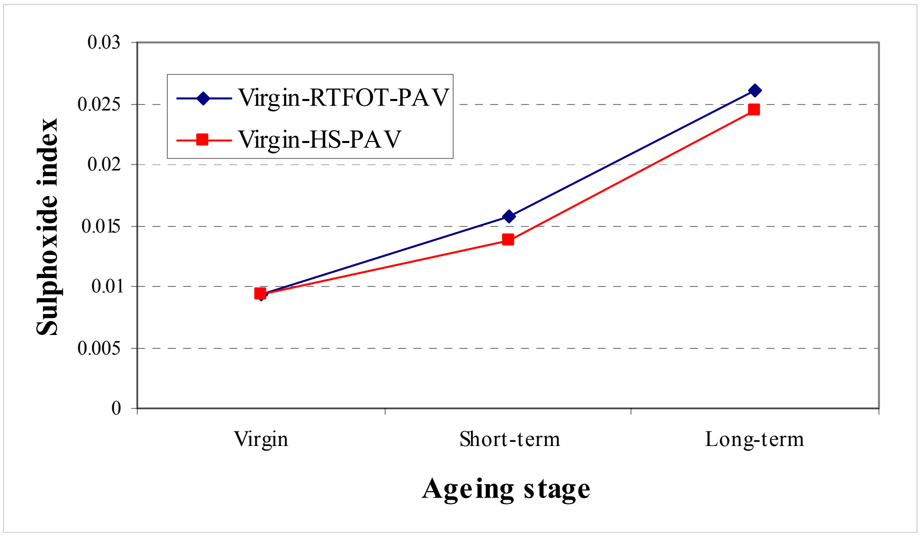


Figure 4.11 Comparison of sulphoxide indices for the binders from different ageing methods

From Figures 4.10 and 4.11, it can be seen that a much smaller amount of carbonyls and sulphoxides were detected by the FTIR test in the High-shear aged binder than the RTFOT aged binder, which indicates that these two binders hardened following different mechanisms during the short-term ageing simulation (although their penetration and SP values are almost the same, as shown in Table 4.1). It can be concluded that the oxidation of bitumen components played a more important role in the hardening of bitumen in the RTFOT ageing than it played in High-shear ageing. It is highly possible that the High-shear aged binder achieved similar penetration and SP values with RTFOT aged binder through evaporation of more oily components, since this is the most likely factor that may cause bitumen age hardening besides oxidation.

It is expected that, when the RTFOT aged binder and the High-shear aged binder were subjected to the PAV ageing where sufficient oxygen was applied, stronger oxidation has happened to the High-shear aged binder. This is because the High-shear aged binder contained more oxidisable molecules due to the poorer supply of oxygen during the short-term ageing simulation.

It should be noted that the complex modulus values (stiffness) of the HS+PAV aged binder are higher than those of the RTFOT+PAV aged binder (as seen in Table 4.2), whereas the carbonyl and sulphoxide indices of HS+PAV aged binder are still slightly lower than those of the RTFOT+PAV aged binder. This phenomenon further supports the above assumption that more volatiles evaporated from the binder aged in High-shear mixer than the RTFOT aged binder.

4.3 Effects of Bitumen Film Thickness on Ageing

4.3.1 Study methodology

The aim of this study is to quantify the relationship between hardening properties of asphalt mixtures and the binder contents (film thickness) by artificially ageing bitumen-aggregate mixtures with varying binder contents. In this project, asphalt slabs (305×305×100 mm), with five different binder contents: 3.5%, 4%, 4.5%, 5% and 5.5% (by mass), were compacted using a roller compactor. After compaction, five cylindrical specimens were cored from each slab and then cut to target height. The design details of the specimen are as follows:

- Height: 60 mm
- Diameter: 100 mm
- Target void content: 8%

It is not difficult to fabricate all the specimens with set binder content. However, because the void content within the slab, from which the specimens are cored, is not homogeneous, experience is needed to get the specimens with void contents as close to the target of 8% as possible. In order to fabricate specimens with void content of around 8%, the target void content of slabs should be set at 15% for this particular compactor.

After specimen coring, the bitumen from the off cuts was recovered and subjected to DSR testing. The stiffness of each specimen was tested using the ITSM test both before and after the specimen was aged in a forced draft oven for 5 days at 85^{o}C (SHRP long-term oven ageing condition). Finally, one representative specimen (which has an air void closest to 8%) from each slab was selected for bitumen recovery and DSR testing. The test sequence for this study is given in Figure 4.12.

With the results of the ITSM and DSR tests, as well as the binder contents and film thicknesses, several relationships were set up to show the effects of binder content (film thickness) on the properties of bitumen-aggregate mixtures undergoing age hardening.

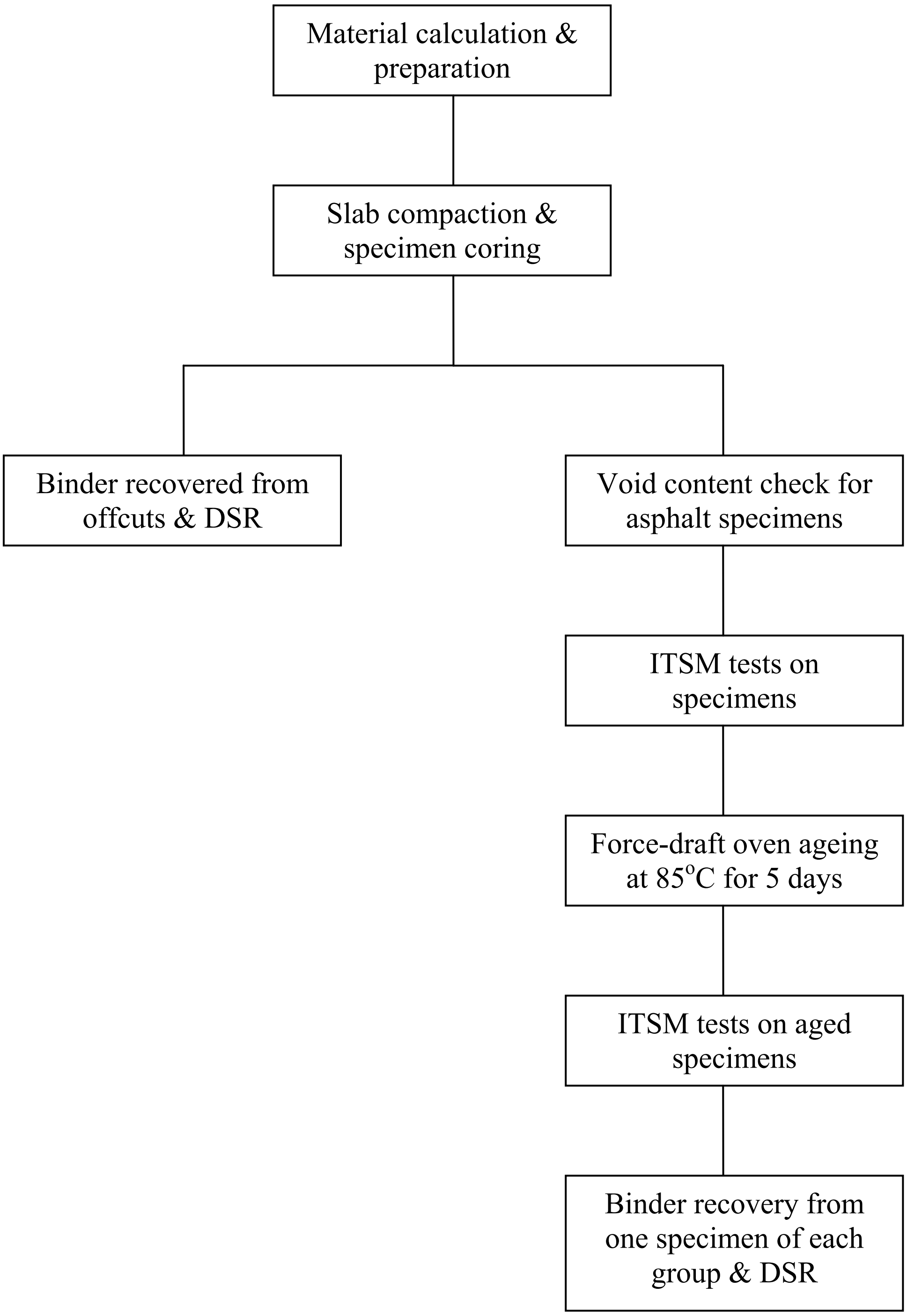


Figure 4.12 The testing sequence

4.3.2 Specimen preparation

Materials

The bitumen used in this study was a very hard bitumen with a penetration of 15 dmm. This grade of binder was selected to tie in with another ongoing research work. The aggregate used in this study was granite, and its batching details are given in Table 4.4 and compared against the 28mm DBM base specification (BS 4987-1, 2001) in Figure 4.13.

Table 4.4 Batching details for the granite

Material	Percentage	Sieve Size (mm)								
		37.5	28	20	14	10	6.3	3.35	0.3	0.075
28 mm	20	100	85.28	20.51	2.41	1.01	0.75	0.74	0.61	0.35
20 mm	11	100	100	87.5	8.96	1.4	1.1	0.93	0.6	0.3
14 mm	11	100	100	100	73.65	12.34	1.03	0.82	0.56	0.29
10 mm	10	100	100	100	100	95.39	20.02	6.03	2.66	2.12
6 mm	10	100	100	100	100	100	82.5	17.77	4.69	2.9
Dust	35	100	100	100	100	100	99.8	95.47	32.4	13.6
Filler	3	100	100	100	100	100	100	100	100	100
Total	100									

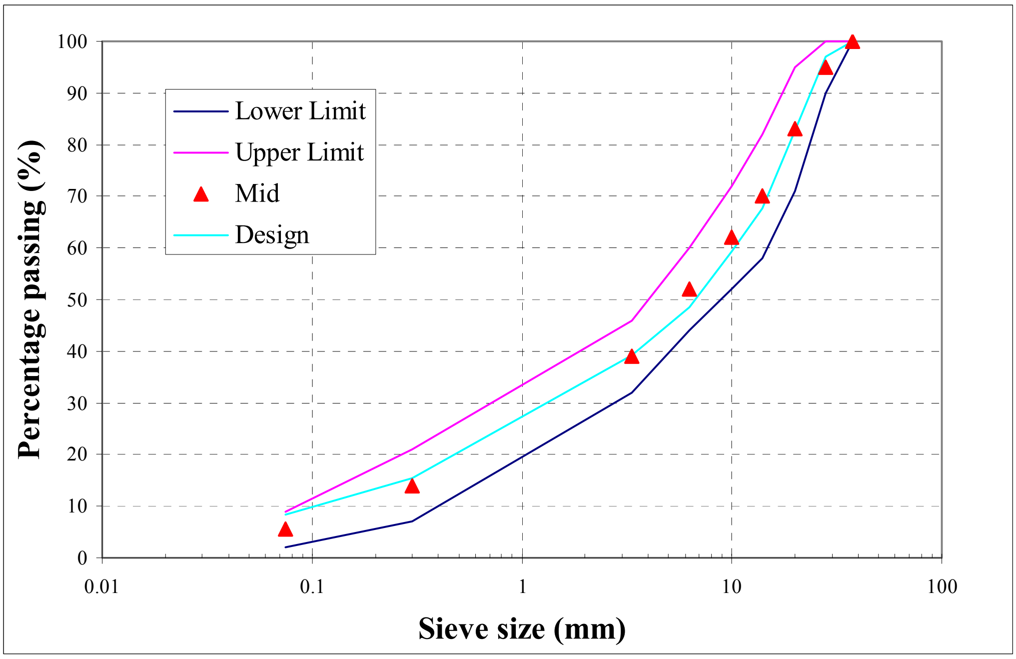


Figure 4.13 Gradation of granite aggregate

Maximum density test

The maximum density of asphalt with varying binder content is very important in the slab design to ensure the compacted slabs achieve the target void content. In this study, the maximum densities for asphalt mixtures with different binder contents were tested (BS EN 12697-5: 2002) and summarized in Table 4.5 and Figure 4.14. As shown in Figure 4.14, the tested result of the mixture with 3.5% binder content did not correlate well with the other four results. This is believed to be caused by the incomplete coating of aggregate by the bitumen (which was observed during the test). A softer binder would probably have coated more satisfactorily. As the density testing procedure includes a step of immersing mixtures into the water, the incomplete binder coating may enable water to penetrate into the aggregate, which can significantly affect the testing results. Accordingly, the theoretical maximum density for 3.5% binder content mixture was calculated using the following equation and the calculated result of 2510 kg/m^3 was used for the maximum density of the 3.5% binder content mixture in this study.

$$\gamma_{\max} = \frac{100 \times \gamma_w}{\dfrac{M_B}{G_b} + \dfrac{M_A}{G_a}} \tag{4-1}$$

where:

$\gamma_{\max}$ = theoretical maximum density (kg/m^3);

γ_w = density of water (kg/m^3);

M_B = binder content per cent by mass of total mix;

M_A = aggregate content per cent by mass of total mix;

G_b = specific gravity of binder, 1.02 in this study;

G_a = specific gravity of aggregate, 2.65 in this study.

Table 4.5 Maximum densities for asphalt with different binder contents

Binder content (%)	3.5	4	4.5	5	5.5
Tested maximum density (kg/m^3)	2522	2493	2486	2472	2466

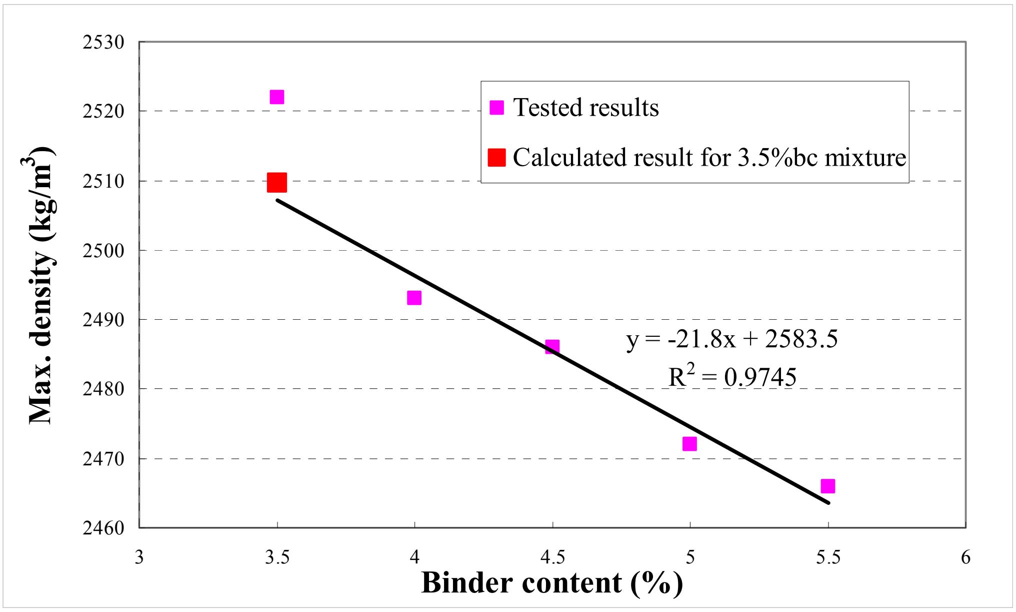


Figure 4.14 Plot of maximum density versus binder content

Air void content check

After the asphalt specimens were fabricated, their air void contents were tested using the sealed specimen method from the standard EN 12697-6:2003. Table 4.6 shows the void content for each asphalt specimen. From this table, it can be seen that the air void within the compacted slab is not uniform. In addition, by combining with the layout of specimens on each slab (as shown in Figure 4.15), it can be observed that samples cored from the centre of slabs (with yellow shading in the table) have the minimum air voids. It can also be observed that the average air void content for each group differs from each other.

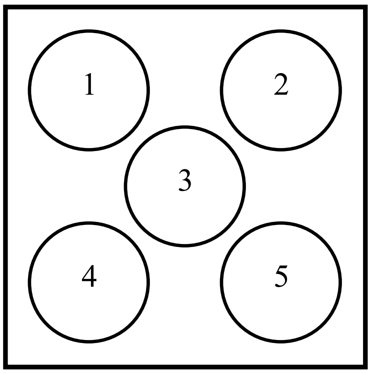


Figure 4.15 Layout of cores from fabricated slabs

Table 4.6 The void contents of asphalt specimens

Binder content	No.	Void content	Average
3.5%	A1	11.00%	10.55%
	A2	11.20%	
	A3	8.40%	
	A4	10.17%	
	A5	11.97%	
4%	B1	8.86%	8.82%
	B2	9.27%	
	B3	6.56%	
	B4	7.72%	
	B5	11.71%	
4.5%	C1	9.43%	8.94%
	C2	9.65%	
	C3	7.39%	
	C4	8.69%	
	C5	9.55%	
5%	D1	8.57%	7.73%
	D2	9.52%	
	D3	5.36%	
	D4	7.36%	
	D5	7.85%	
5.5%	E1	7.56%	8.15%
	E2	10.15%	
	E3	6.15%	
	E4	7.22%	
	E5	9.67%	

4.3.3 Theoretical film thickness calculation

Campen's method

Based on the batching and gradation details for the aggregate (as shown in Table 4.4 and Figure 4.13) the surface area factor for the aggregates used in this study was calculated and presented in Table 4.7.

With the calculated total surface area factor for the aggregate used in this study, the film thicknesses for the mixtures with different binder contents were calculated with Equation 3-1 (the density of bitumen used here was 1020 kg/m^3). The results of film thickness calculation are given in Table 4.8.

Table 4.7 The calculation of the surface area factor for Campen's method

Sieve size (mm)	Surface Area Factor (m^2/kg)	%	Calculated SAF (m^2/kg)
>4.75	0.41	55%	0.2255
2.36	0.82	9%	0.0738
1.18	1.64	6%	0.0984
0.6	2.87	8%	0.2296
0.3	6.14	6%	0.3684
0.15	12.29	4%	0.4916
0.075	32.77	12%	3.9324
			∑ = 5.4179

Table 4.8 Film thickness calculated with Campen's method

Binder content (%)	Film thickness (μm)
3.5	6.56
4.0	7.54
4.5	8.53
5.0	9.52
5.5	10.53

French method

According to the aggregate gradation data and its specific gravity, parameters needed in the French method were calculated and listed in Table 4.9. The binder film thicknesses of different mixtures calculated by this method are listed in Table 4.10.

Table 4.9 Parameters for French method of film thickness calculation

Parameters	Values
a	1
G	0.52
S	0.10
s	0.12
f	0.26
$\sum = 0.25G + 2.3S + 12s + 135f$	36.9

Table 4.10 Film thickness calculated with French method

Binder content (%)	Film thickness (μm)
3.5	17.00
4.0	19.43
4.5	21.87
5.0	24.30
5.5	26.73

Heitzman's method

The surface area factors for the Heitzman's method were calculated based on equation 3-7, and Table 4.11 shows the results. It should be noted that, as the aggregate in this study was from the same source, the parameter '*i*' had a fixed value of 1 in this calculation. In addition, to enable comparison between the three different methods of film thickness calculation, the shape of aggregate particles was assumed as uniform sphere and therefore, the shape factors (*VF* and *SAF*) were 1 as well. Based on the calculated $\sum SA_{(n)}$, binder film thicknesses for mixtures with different binder contents were calculated using equation 3-8, and Table 4.12 lists the results. It should be noted that the binder content used in equation 3-8 is 'effective binder content' which is the percent (by mix weight) of binder that is not absorbed into the aggregate. In this study, the water absorption property of aggregate was tested following BS EN 1097-6 (2000) and calculated by equation 4-2. The absorption of the granite in this study was 0.3%. Based on this, the effective binder contents for different asphalt mixtures in this study were calculated and presented in Table 4.12.

$$WA = \frac{M_s - M_d}{M_d} \times 100\% \tag{4-2}$$

where:

WA = water absorption (as a % of dry aggregate mass);

M_s = mass of saturated and surface-dry aggregate sample;

M_d = mass of dried aggregate sample (kept in oven at 110±5°C for 24 hours).

Table 4.11 The calculation of the surface area factor for Heitzman's method

n	Size (mm)	Calculated $SA_{(n)}$ (m^2/kg)
1	28	0.002035316
2	20	0.013517925
3	14	0.020188102
4	10	0.015691887
5	6.3	0.029687047
6	3.35	0.04425676
7	0.3	0.294948772
8	0.075	0.836950943
9	< 0.075	5.089750943
		$\sum SA_{(n)} = 6.3470$

Table 4.12 Film thickness calculated with Heitzman's method

Binder content (%)	Effective binder content (%)	Film thickness (μm)
3.5	3.2	5.05
4.0	3.7	5.87
4.5	4.2	6.70
5.0	4.7	7.54
5.5	5.2	8.38

By comparing the three calculated results above, it can be seen that although Campen's method and Heitzman's method used different standards for the calculation of surface area factors, similar results were worked out from these two methods. However, the thicknesses calculated using the French method differ considerably to those of the other two methods. This may be because the French method only roughly divides all the aggregates into four groups and each group contains aggregates with relatively large difference in their sizes. In this study, film thicknesses calculated by Campen's method were used in data analysis.

4.3.4 Results and discussions

ITSM result analysis

The indirect tensile stiffness modulus (ITSM) of each specimen was measured both before and after ageing with the testing temperature of 20°C. Table 4.13 shows the stiffness results for all the asphalt specimens.

Table 4.13 ITSM test results for all the specimens (at 20^{o}C)

Binder content (%)	No.	Stiffness before ageing (MPa)		Stiffness after ageing (MPa)	
		Sample	Group mean	Sample	Group mean
3.5	A1	7513	9008	10518	11472
	A2	9099		11572	
	A3	10765		14208	
	A4	9388		11478	
	A5	8276		9585	
4	B1	10135	9707	12848	12141
	B2	8287		11560	
	B3	11568		13825	
	B4	9758		11614	
	B5	8788		10862	
4.5	C1	7839	8227	8981	10239
	C2	7629		9495	
	C3	8941		11246	
	C4	8846		11012	
	C5	7878		10462	
5	D1	8220	7952[a]	9930	9368[a]
	D2	7622		9106	
	D3	10183		11692	
	D4	7856		8614	
	D5	8112		9823	
5.5	E1	7589	7719	8552	8673
	E2	6802		7802	
	E3	8028		9104	
	E4	8622		9629	
	E5	7554		8280	

[a] The stiffness of the specimens with 5% binder content were calculated as the mean result without the specimen D3, whose void content was too low.

It should be noted that, due to the variation of air void contents among the samples from different groups (as shown in Table 4.6), the average stiffness of each group may not be very reliable in the analysis of binder film thickness effects on the bitumen ageing, since the samples were not aged with the same level of void content. Therefore, in order to eliminate the influence of void content, plots of stiffness versus void content were made for each group; a trendline for the relationship between the stiffness and void content was added to each group before (BA) and after ageing (AA), as shown in Figures 4.16 to 4.20. Based on the stiffness versus air void content figures, a theoretical stiffness for each group was calculated at a void content of 8%. Comparison was made between the average and the theoretically predicted stiffness (at 8% air void content) of each group, and the ageing indices expressed by them also (seen in Table 4.14).

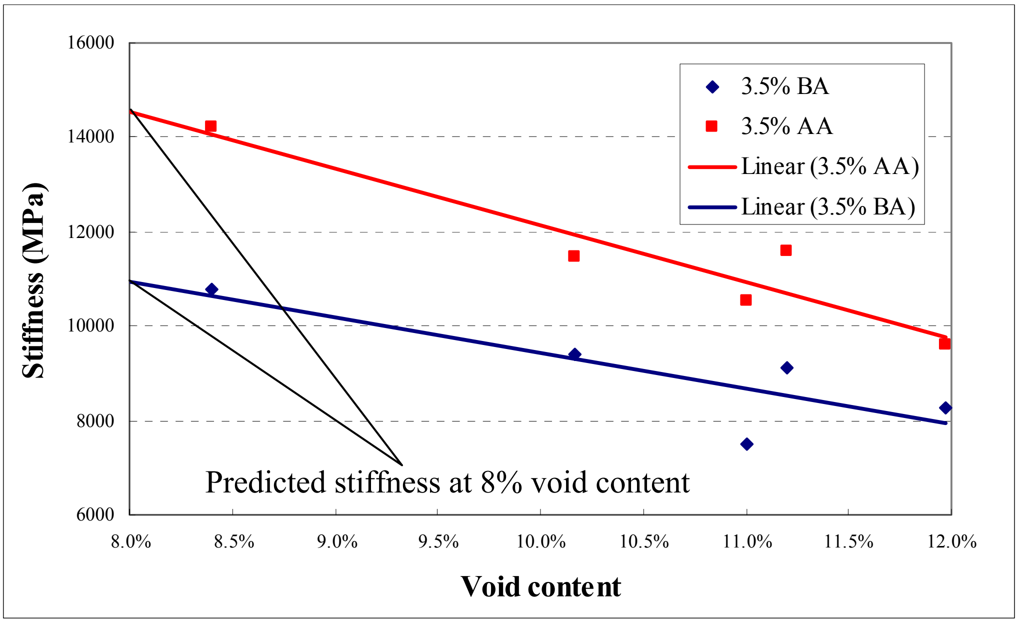


Figure 4.16 ITSM results for specimens with 3.5% binder content

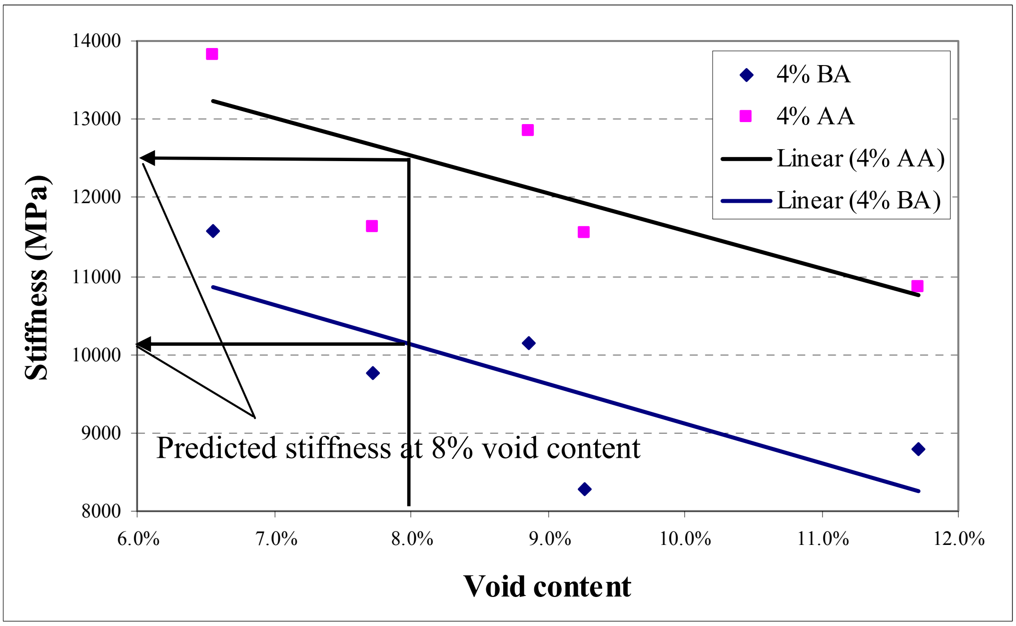


Figure 4.17 ITSM results for specimens with 4.0% binder content

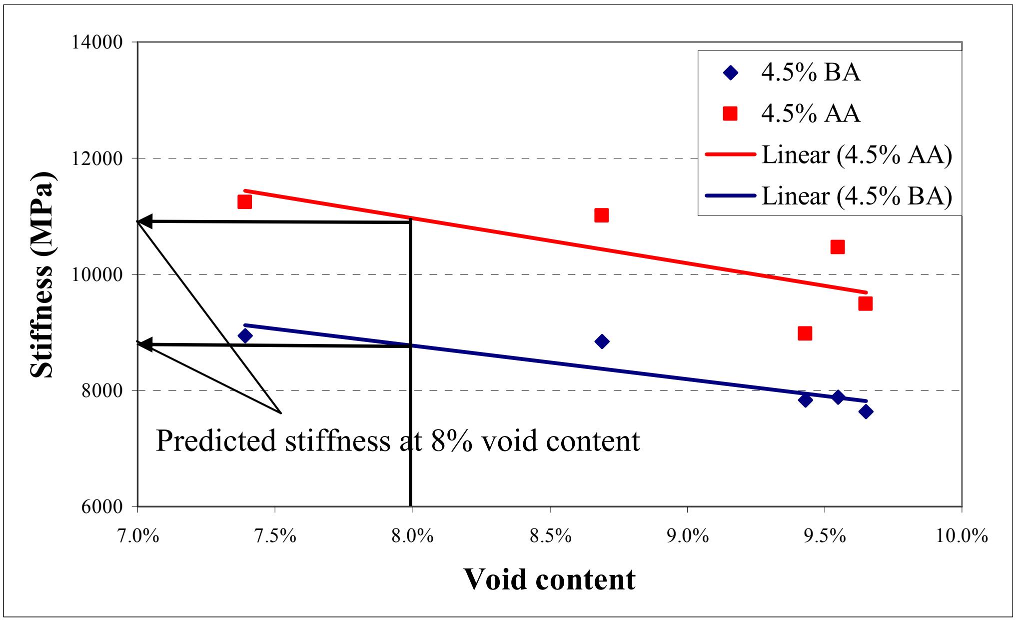


Figure 4.18 ITSM results for specimens with 4.5% binder content

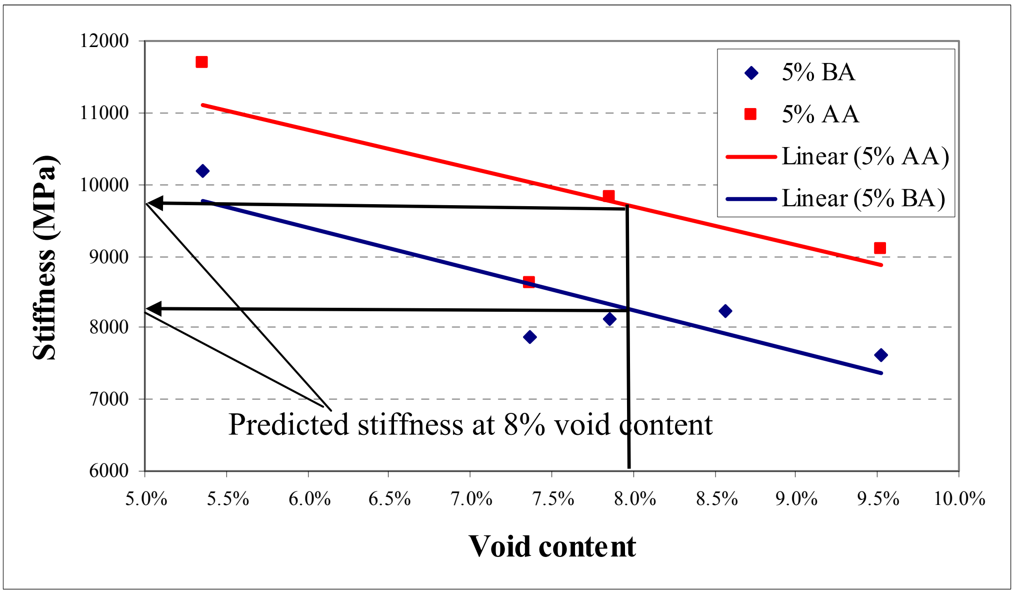


Figure 4.19 ITSM results for specimens with 5.0% binder content

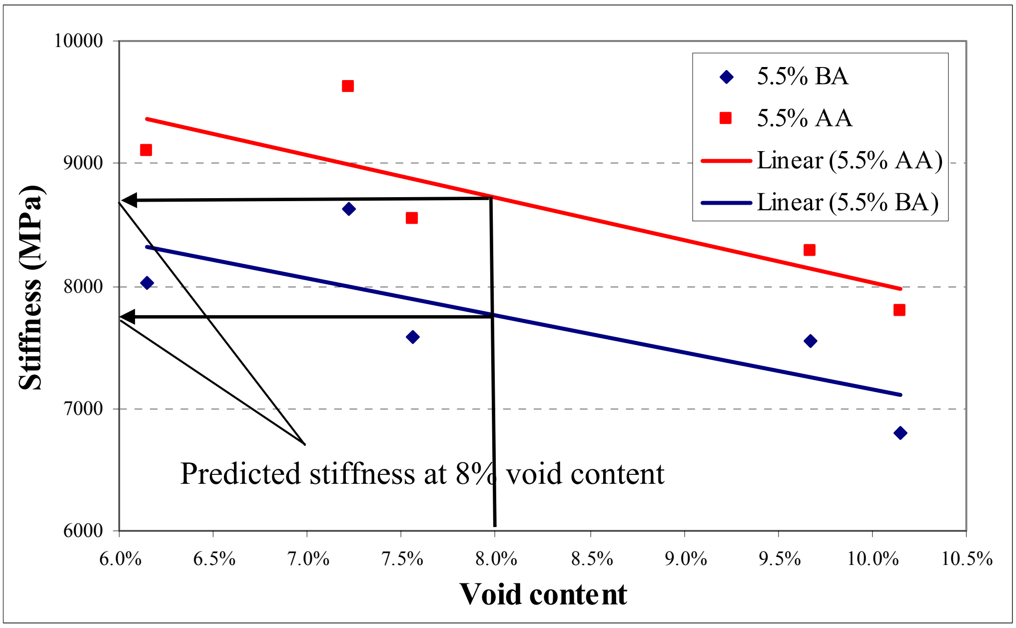


Figure 4.20 ITSM results for specimens with 5.5% binder content

Table 4.14 Average and predicted stiffness of each group before and after ageing

Film thickness (μm)	Average results			Predicted results		
	Stiffness BA (MPa)	Stiffness AA (MPa)	Ageing index	Stiffness BA (MPa)	Stiffness AA (MPa)	Ageing index
6.56	9008	11472	1.27	10926	14543	1.33
7.54	9707	12141	1.25	10125	12538	1.24
8.53	8227	10239	1.24	8776	10965	1.25
9.52	7952	9368	1.17	8243	9689	1.18
10.53	7719	8673	1.12	7763	8725	1.12

The relationship between the film thickness and stiffness values before and after oven ageing is presented in Figure 4.21. From this figure, a marked similarity between the curves obtained before and after ageing can be observed for both the average result and the predicted result. In addition, it can be seen that, because of the differences in the air void content among different groups, the relationship between the average stiffness result and binder film thickness is not as regular as that between the predicted stiffness and binder film thickness. Therefore, the following analysis and discussion are mainly based on the predicted data.

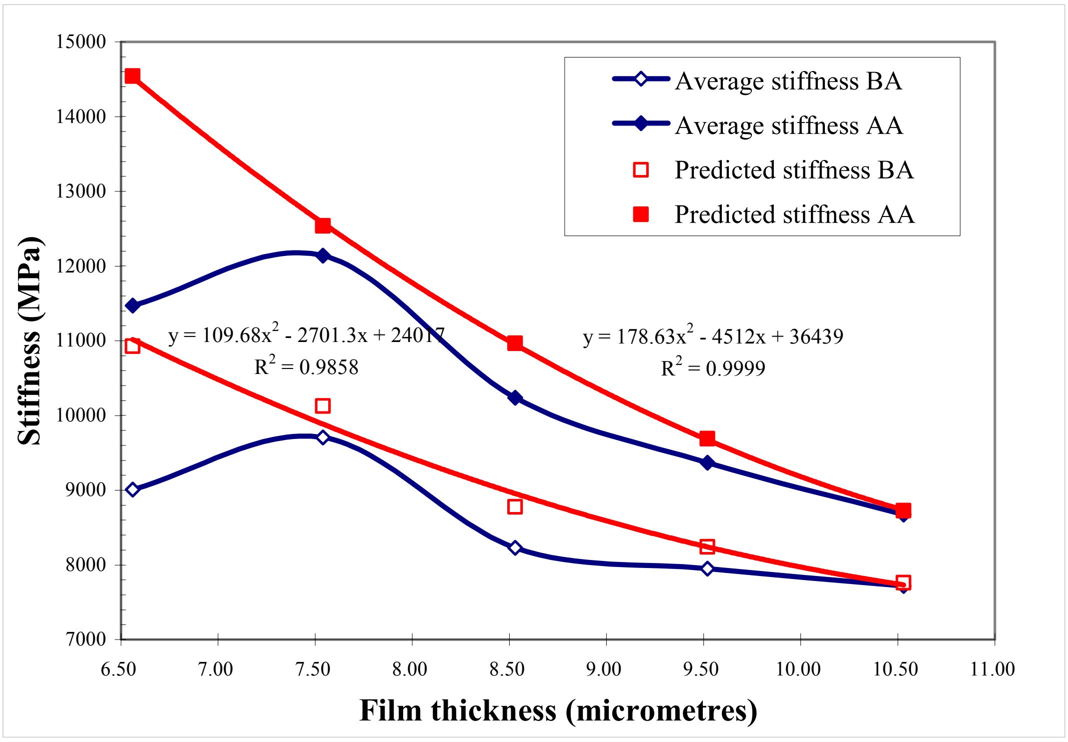


Figure 4.21 Plot of asphalt stiffness (at 20°C) versus film thickness

From the predicted results in Figure 4.21, it can be seen that the amount of stiffness increase due to the ageing reduces as the film thickness becomes thicker, which indicates that the influence of ageing on the mixture stiffness is reduced in the specimens with higher binder contents. In addition, a quadratic polynomial regression was used to quantify the relationship between the asphalt stiffness and its binder film thickness. The relationships for materials in this study are presented below:

Before long-term oven ageing:

$$S_{ba} = 109.68T^2 - 2701.3T + 24017$$

$$R^2 = 0.9858$$

where:

S_{ba} = asphalt stiffness at 20°C and 8% air void content before ageing (MPa);

T = film thickness (μm).

After long-term oven ageing:

$$S_{aa} = 178.63T^2 - 4512T + 36439$$

$$R^2 = 0.9999$$

where:

S_{aa} = asphalt stiffness at 20°C and 8% air void content before ageing (MPa).

In order to illustrate the influence of ageing on the mixture stiffness more clearly, the ageing index in terms of the asphalt stiffness (at 8% void content) was plotted against the film thickness in Figure 4.22. From this figure, it can be seen clearly that the ageing index decreases gradually as the binder film thickness increases, which indicated that asphalt mixtures with thicker binder films (higher binder content) are more resistant to age hardening. A linear regression gives an acceptable model for this relationship as follows:

$$I_s = -0.0484T + 1.6371$$

$$R^2 = 0.9248$$

where:

I_s = Ageing index expressed by asphalt stiffness at 20°C and 8% air void content.

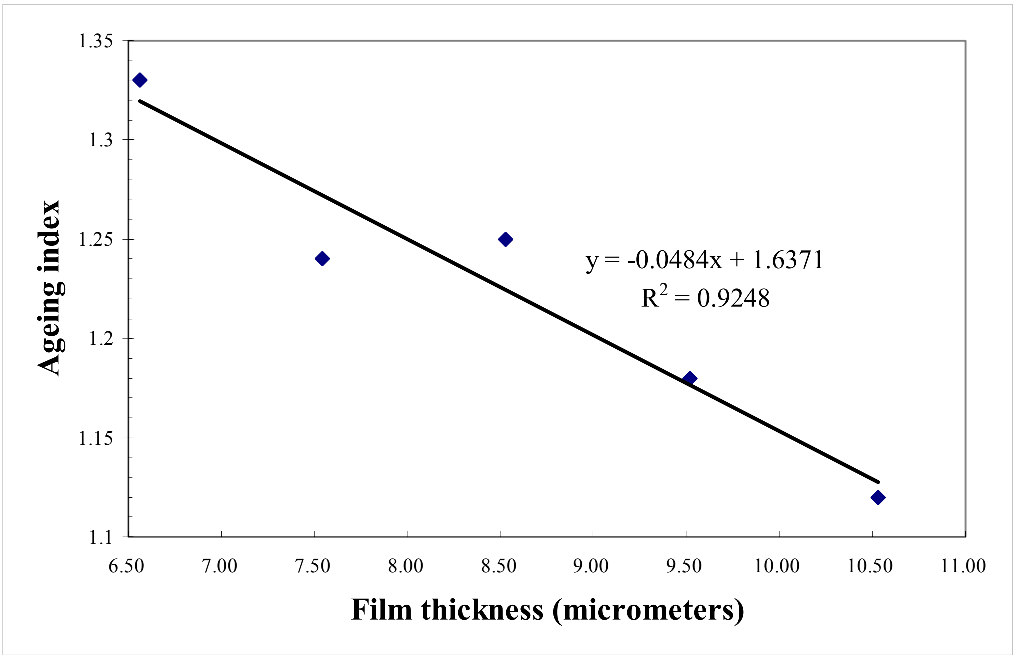


Figure 4.22 Plot of ageing index expressed by asphalt stiffness (at 20°C and 8% air void content) versus film thickness

DSR analysis

In order to study the influence of ageing on the binder properties, binder recovery and DSR testing were applied to the specimens with different binder contents both before and after ageing simulation. As stated above, bitumen recovered from the offcut part of the compacted slab was used as the binder before ageing; and bitumen recovered from representative specimen of each group (the one with an air void content closest to 8%) was used as the binder after ageing. The DSR tests were carried out with a Bohlin Gemini 200 DSR machine, using the following conditions:

- Mode of loading: Controlled-strain (strain limit: 0.15% for 8 mm geometry; 0.25% for 25 mm geometry),
- Temperatures: 0 to 70°C (5°C intervals),
- Frequencies: 0.1 to 10 Hz,
- Plate geometries: 8 mm diameter with a 2 mm gap (0 to 45°C) and 25 mm diameter with a 1 mm gap (25 to 70°C).

The DSR results for binders from different groups, both before and after ageing, have been presented as complex modulus (G^*) master curves (with a reference temperature of 25°C), as shown in Figures 4.23 and 4.24. As expected, the complex modulus decreases with increasing bitumen film thickness (binder content). This finding indicates that the presence of thicker films of bituminous binder in the asphalt paving mixtures minimizes ageing of bitumen. In addition, from Figure 4.23, it can be seen that, although the asphalt mixtures in this study have not been subjected to any short-term oven ageing simulation, the binders recovered from slab offcuts show significant difference in their stiffness (G*); this means that age hardening has already occurred in the bitumen during the material preparation and slab compaction. Further, the amount of bitumen stiffness increase is highly dependant on the binder content (film thickness) of the asphalt mixture.

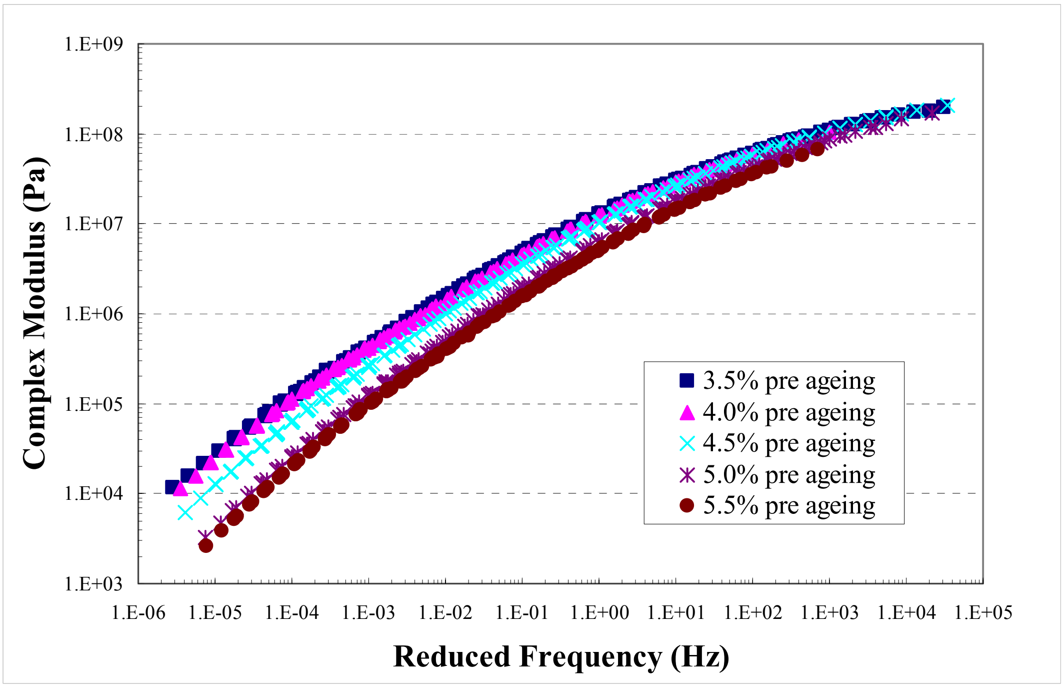


Figure 4.23 Complex modulus master curves for binders before ageing (with a reference temperature of 25°C)

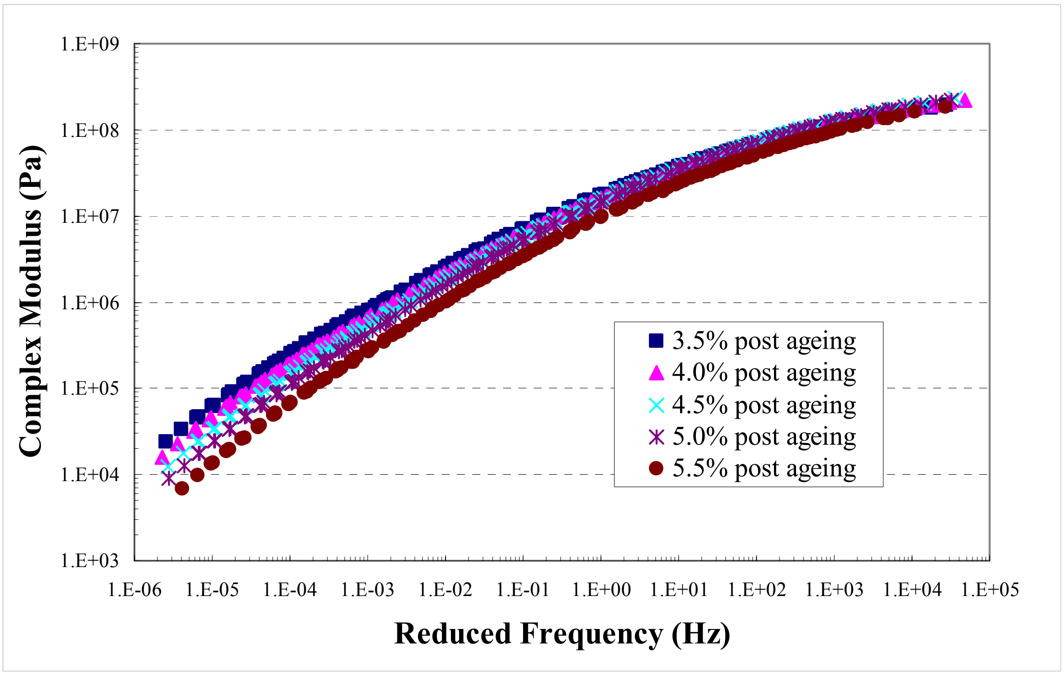


Figure 4.24 Complex modulus master curves for binders after ageing (with a reference temperature of 25°C)

In order to show the influence of bitumen film thickness on the bitumen ageing more quantitatively, the complex moduli at 60°C and 0.4 Hz for binders at different ageing stages were selected and used in ageing index calculations, as shown in Table 4.15. Accordingly, the ageing indices in terms of bitumen complex modulus are graphically summarized in Figure 4.25. From this figure, it can be seen that the ageing index increases consistently as the bitumen film thickness decreases, which indicates that a thinner binder film in asphalt mixtures can result in stronger age hardening to the bitumen. It can also be observed that the fitted curves for the data both before and after ageing become flatten at thicker binder film thickness, which indicates that the film thickness has a decreasing effect on the ageing properties of the bitumen when the asphalt mixtures have a relatively high binder content (thicker binder film). Two quadratic polynomial models were obtained from regression analysis for the relationship between ageing index (in terms of complex modulus) and binder film thickness both before and after ageing:

Before long term oven ageing:

$$I_{ba} = 0.7867T^2 - 16.389T + 87.859$$

$$R^2 = 0.9995$$

where:

I_{ba} = ageing index in terms of complex modulus (60°C, 0.4 Hz) before ageing.

After long term oven ageing:

$$I_{aa} = 0.4715T^2 - 11.085T + 70.211$$

$$R^2 = 0.9999$$

where:

I_{aa} = ageing index in terms of complex modulus (60°C, 0.4 Hz) after ageing.

Table 4.15 Ageing index calculation for binders at different ageing stages

Film thickness (μm)	Complex modulus at 60°C and 0.4 Hz (Pa)			Ageing index	
	Virgin binder	BA[a]	AA[b]	BA	AA
6.56	11480	98150	204350	8.55	17.80
7.54		103100	153990	8.98	13.41
8.53		61731	113720	5.38	9.91
9.52		35023	86117	3.05	7.50
10.53		29089	65750	2.53	5.73

[a] Before artificial ageing, but after compaction.

[b] After artificial ageing.

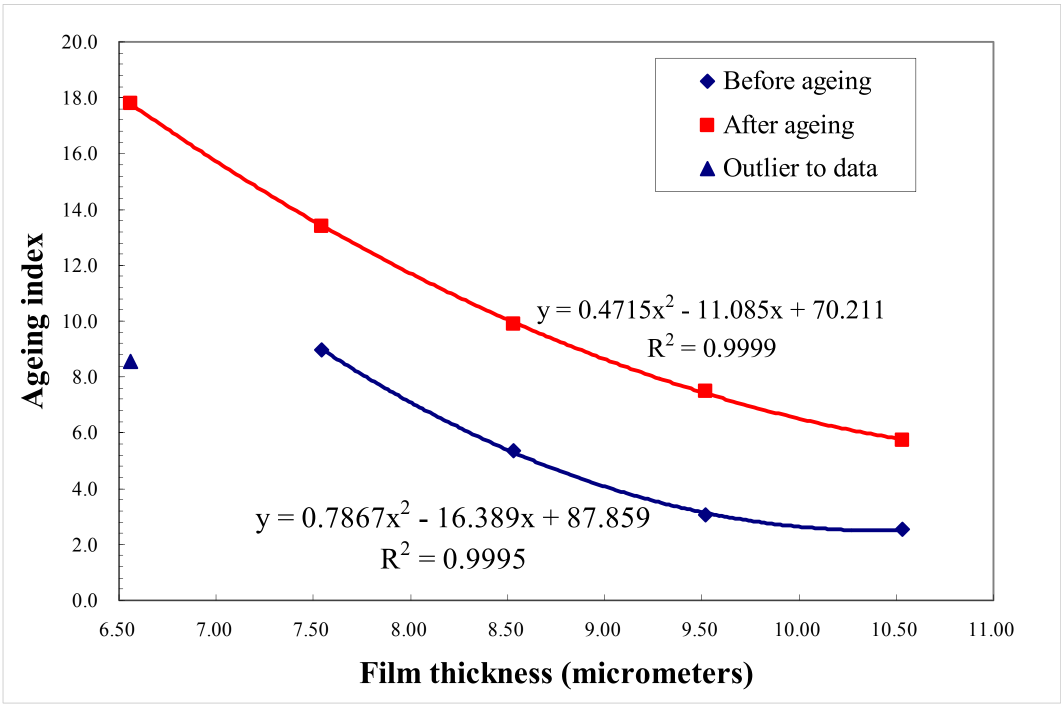


Figure 4.25 Plot of ageing index expressed by complex modulus (at 60°C and 0.4 Hz) versus film thickness

4.4 Conclusions

Based on the two studies reported above, several conclusions can be drawn as follows:

- Although both the penetration and R&B softening point values of the binder aged in High-Shear mixer for 2.5 days are similar to those found for the RTFOT aged binder, their ageing mechanisms are not the same;
- The FTIR tests have shown that more oxidation has happened to the binder aged in RTFOT, and the amount of oxidation products in RTFOT aged binder is higher than that in High-Shear aged binder;
- Compared with conventional empirical tests (penetration test and R&B SP test), the DSR test is more sensitive to the component changes within bitumen;
- Ageing procedures can significantly affect the bitumen ageing mechanism. A study combining rheological simulation of the bitumen behaviour in different ageing procedures, chemical tests for bitumen component changes and DSR rheological tests is strongly recommended;

- The binder content (film thickness) in asphalt mixture can also significantly influence the ageing of bituminous material. With the same ageing time, asphalt mixtures with thinner binder film can be affected by age hardening more strongly, and binders recovered from these mixtures have much higher stiffness;

- As the binder film thickness increases, its influence on the ageing properties of both the asphalt mixtures and bitumen binders becomes smaller and stabilised, which means that with thicker binder films, the ageing of bituminous materials will be less sensitive to the changes in film thickness;

- Although these conclusions are based on a study using a very hard binder, it is expected the effect of the binder film thickness would be proportionally similar for all binder grades.

5 INFLUENCE OF AGGREGATE TYPE ON BITUMEN AGEING

5.1 Introduction

Findings from the Literature Review (Chapter 2) indicated that the age hardening of the binder in bituminous mixtures is influenced by both the bitumen and the mineral aggregate. In terms of the influence of aggregate, findings also indicated that, besides absorbing oily components from bitumen, the petrographic nature of different aggregates may have some added effects on the age hardening of bitumen (Barbour et al., 1974; Petersen et al., 1974 (a); Plancher et al., 1976; and Huang et al., 2002). In addition, results from the previous chapter have shown that the ageing procedure and binder film thickness of the mixture also significantly affect the age hardening of bitumen.

In order to investigate the influence of aggregate type on bitumen ageing, a typical acidic aggregate (granite) and a typical basic aggregate (limestone) were used for producing different 28mm DBM specimens. The specimens were artificially aged using the SHRP short-term ageing (STA) and the SHRP long-term ageing (LTA). Ageing properties of both the mixture specimens and the recovered binders were tested at different ageing stages using ITSM and DSR tests. In addition, two different binders, a 100/150 penetration and its 2.5 days High-shear aged binder which were the same as those used in the previous pure bitumen ageing study, were adopted in this study so that the effect of binder type on ageing could be investigated and the ageing properties of bitumen when it was aged in bulk and in asphalt mixture could be compared. Evidence is provided to show that both the varying binder type and mineral aggregate can significantly affect the ageing properties of bituminous materials. However, in terms of the applicability of the binder recovery technique in the ageing study, there are reservations as the stiffness of asphalt mixtures and that of their recovered binders were found to be inconsistent.

5.2 Material Description and Specimen Design

5.2.1 Material description

In this study, four different 28mm DBM specimens were fabricated with the material combinations of:

- virgin binder + limestone,
- virgin binder + granite,
- High-Shear aged binder + limestone and,
- High-Shear aged binder + granite.

The virgin binder and High-Shear aged binder were taken from the preliminary study on pure bitumen ageing. As stated previously, the virgin binder is 100/150 pen bitumen, and the High-Shear aged binder is the 100/150 pen binder being aged in the High-Shear mixer at 165^{o}C for 2.5 days.

In terms of aggregates, a typical ‘basic’ aggregate of limestone and a typical ‘acidic’ aggregate of granite were used in this study so that the effect of aggregate on bitumen ageing could be clearly shown. The limestone in this project is Dene limestone and its batching details are shown in Table 5.1 and Figure 5.1. There were two sources of granite. The granite dust was from Torr Works, whereas the rest of the granite was from Mount Sorrel. Batching details for the Granite are shown in Table 5.2 and Figure 5.2.

Table 5.1 Batching details for the limestone

Material	Percentage	Sieve Size (mm)								
		37.5	28	20	14	10	6.3	3.35	0.3	0.075
28 mm	20	100	89	14	6	5	4.2	2.5	0	0
20 mm	10	100	100	86.8	4.6	2	2	2	1.2	1
14 mm	10	100	100	100	87.2	15.2	2.95	2.5	1.9	1.4
10 mm	10	100	100	100	100	81.05	6.99	2.2	1.3	1.15
6 mm	8	100	100	100	100	100	93	18	8	8
Dust	42	100	100	100	100	100	100	81.5	25	13.5
Total	100									

Table 5.2 Batching details for the granite

Material	Percentage	Sieve Size (mm)								
		37.5	28	20	14	10	6.3	3.35	0.3	0.075
28 mm	20	100	85.28	20.5	2.41	1.01	0.76	0.74	0.61	0.35
20 mm	10	100	100	87.5	8.97	1.41	1.11	0.93	0.6	0.29
14 mm	10	100	100	100	73.65	12.34	1.02	0.82	0.56	0.29
10 mm	10	100	100	100	100	95.39	22	6.03	2.66	2.12
6 mm	8	100	100	100	100	100	82.5	17.76	4.69	2.9
Dust	42	100	100	100	100	100	100	98.25	25.48	11.5
Total	100									

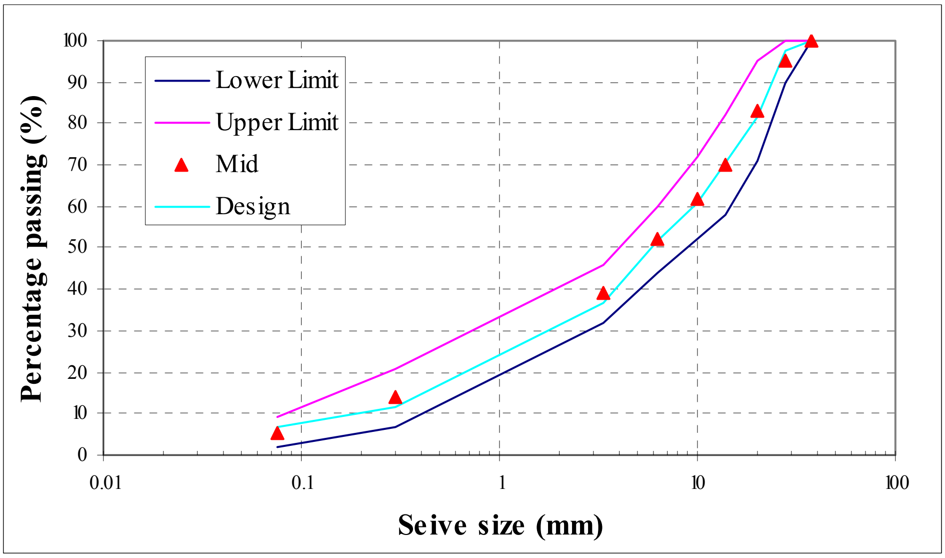


Figure 5.1 Gradation of limestone aggregate

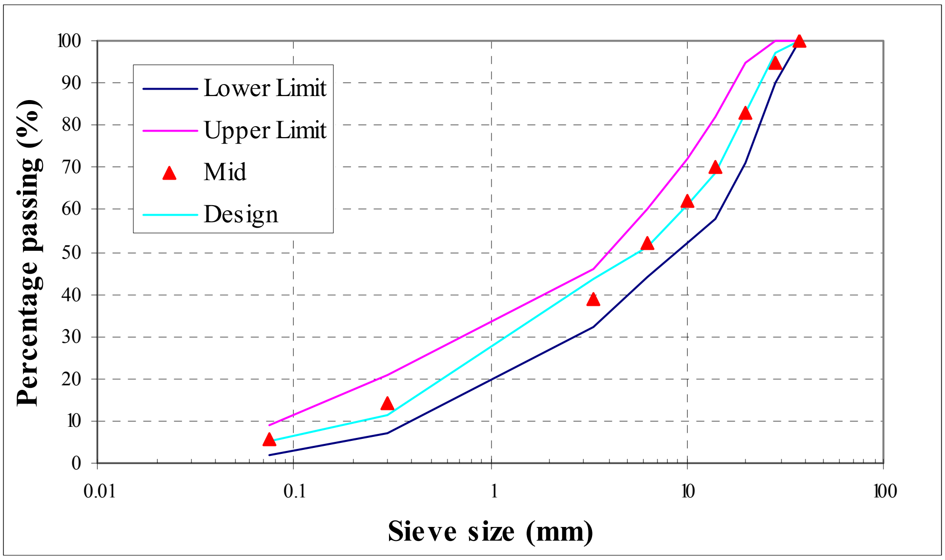


Figure 5.2 Gradation of granite aggregate

5.2.2 Target binder content and air void content

Findings from Chapter 4 have indicated that binder content (binder film thickness) can significantly affect the ageing of bituminous mixtures. A high binder content (thick binder film) can effectively limit the effects of age hardening to the asphalt (as seen in Figure 4.22). Therefore, to investigate the influence of aggregate type on ageing, a relatively low binder content (thin binder film) was preferred in this study. However, because it was observed that the aggregate in asphalt mixture with 3.5% binder was not well coated by the bitumen, the binder content adopted in this study was 4%.

As the ageing of bitumen requires presence of sufficient oxygen, a relatively high target air void content of 8% was designed for asphalt specimens in this study. Again, because the specimens were cored from compacted slabs and their actual void content values were not perfectly consistent with the design value, the same treatments as those shown in Figures 4.16 to 4.20 were carried out during data analysis to eliminate the effects of void content differences.

5.2.3 Theoretical binder film thickness calculation

Although both the target binder content and the batching details are exactly the same for granite and limestone specimens, the differences in the detailed gradation of each size of the aggregates may still lead to different binder film thicknesses. Therefore, it is necessary to check the binder film thicknesses for the two asphalt mixtures. In this study, Campen’s traditional method and Heitzman’s method were adopted to estimate the binder film thickness.

Campen’s method

Based on the total gradations for the aggregates as shown in Figures 5.1 and 5.2, the surface area factors for the limestone and the granite in this study were calculated and shown in Tables 5.3 and 5.4.

Table 5.3 Calculation of the surface area factor for the limestone (Campen's method)

Sieve size: mm	Surface Area Factor (m^2/kg)	%	Calculated SFA (m^2/kg)
>4.75	0.41	52%	0.2132
2.36	0.82	9%	0.0738
1.18	1.64	9%	0.1476
0.6	2.87	8%	0.2296
0.3	6.14	9%	0.5526
0.15	12.29	2%	0.2458
0.075	32.77	11%	3.6047
			∑ = 5.0673

Table 5.4 Calculation of the surface area factor for the granite (Campen's method)

Sieve size: mm	Surface Area Factor (m^2/kg)	%	Calculated SFA (m^2/kg)
>4.75	0.41	52%	0.2132
2.36	0.82	7%	0.0574
1.18	1.64	11%	0.1804
0.6	2.87	8%	0.2296
0.3	6.14	8%	0.4912
0.15	12.29	4%	0.4916
0.075	32.77	10%	3.277
			∑ = 4.9404

With the calculated total surface area factors for the two aggregates, the film thicknesses for these two asphalt mixtures were calculated with Equation 3-1 (the density of binder is 1020 kg/m^3). The results of the calculations are given as follows:

- Binder film thickness in the asphalt with limestone: 8.1 μm;
- Binder film thickness in the asphalt with granite: 8.3 μm.

The above results have shown that binder film thicknesses for the two asphalt mixtures with different aggregates are very close. However, because these two results were theoretically calculated using Campen's method, which assumes that the specific gravity of both aggregates is 2.65, the relatively advanced Heitzman's method, which takes aggregate specific gravity into account, was also employed in this study for film thickness comparison. The specific gravities for limestone and granite in this study were 2.75 and 2.68 respectively.

Heitzman's method

Tables 5.5 and 5.6 present the calculation of surface area factors for limestone and granite using Heitzman's method. It should be noted that, although there are two sources for granite in this study, as the specific gravities and shape factors for these two aggregates are very similar, the calculation for the granite was conducted by treating the granites as from the same source. In addition, shape factors for sphere particles (i.e. $VF = 1$ and $SAF = 1$) were adopted for both aggregates.

Table 5.5 The calculation of the surface area factors for limestone (Heitzman's method)

n	Size (mm)	Calculated $SA_{(n)}$ (m^2/kg)
1	28	0.001466
2	20	0.014836
3	14	0.014246
4	10	0.017373
5	6.3	0.025033
6	3.35	0.066174
7	0.3	0.301988
8	0.075	0.571927
9	< 0.075	3.877818
		$\sum SA_{(n)} = 4.8909$

Table 5.6 The calculation of the surface area factors for granite (Heitzman's method)

n	Size (mm)	Calculated $SA_{(n)}$ (m^2/kg)
1	28	0.002013
2	20	0.01325
3	14	0.018579
4	10	0.014231
5	6.3	0.02733
6	3.35	0.035056
7	0.3	0.392938
8	0.075	0.736263
9	< 0.075	3.232597
		$\sum SA_{(n)} = 4.4723$

With the calculated total surface area factors ($\sum SA_{(n)}$) for the two aggregates, the film thicknesses of mixtures with different aggregates were calculated with Equation 3-8. The absorption values of these two aggregates were 0.7% for limestone and 0.3% for granite; therefore, the effective binder contents for limestone and granite mixtures were 3.3% and 3.7% respectively. Based on these, the results of the film thickness calculations using Heitzman's method are given as follows:

- Binder film thickness in the asphalt with limestone: 6.9 μm;
- Binder film thickness in the asphalt with granite: 8.4 μm.

Discussion

The results from both calculation methods have shown that, although with the same binder content (4% by mass), asphalt mixtures containing granite aggregate have a thicker binder film than the mixtures with limestone. In addition, it can be seen that binder film thicknesses calculated using Heitzman's method show a bigger difference between the mixtures containing different aggregates than those calculated with Campen's method. In this study, the results from Heitzman's method are believed to be more reliable as this method has advantages of considering specific gravities and absorption values of different aggregates.

Results of the previous study, i.e. Chapter 4, have proved that binder film thickness can significantly affect the ageing properties of both the asphalt mixtures and the binders they contain. It can be seen from Figures 4.22 and 4.25 that, for the same ageing time, the ageing index of both the asphalt mixtures and the recovered binders increased constantly with a decrease in binder film thickness, which means that a larger amount of age hardening has happened to the mixtures with thinner binder film. In addition, Figure 4.25 also shows that, as the film thickness becomes relatively low, the ageing index becomes more sensitive to the changes in binder film thickness and, therefore, it is recognized that a difference of 1.5 μm in the binder film thickness between the two asphalt mixtures in this study cannot be neglected and special attention should be paid to this factor during the data analysis.

5.3 Ageing Regimes and Specimen Preparation

5.3.1 Ageing regimes

As stated above, there were four material combinations in this study: virgin binder + limestone, virgin binder + granite, High-Shear aged binder + limestone and High-Shear aged binder + granite. These four material combinations were tested in two stages. In the first stage, the mixtures were compacted into slabs of size:

305×305×100 mm immediately after mixing. Two slabs were fabricated for each material combination. After that, five specimens were cored from each slab and were trimmed into cylinders with a diameter of 100 mm and a height of 60 mm. Binders from the remaining parts of the cored slabs were recovered and their rheological properties were tested. The stiffness of the cored specimens was tested using the ITSM test. The specimens were then subjected to the SHRP long-term oven ageing protocol (at 85°C for 5 days), followed by a further ITSM test. Finally, two representative specimens for each material combination were selected and used for the binder recovery and rheological testing.

The second stage was similar to the first, with the only difference between them being that the loose materials after mixing were subjected to the SHRP short-term oven ageing protocol (4 hours at 135°C) before compaction.

Figure 5.3 shows a schematic of the testing methodology:

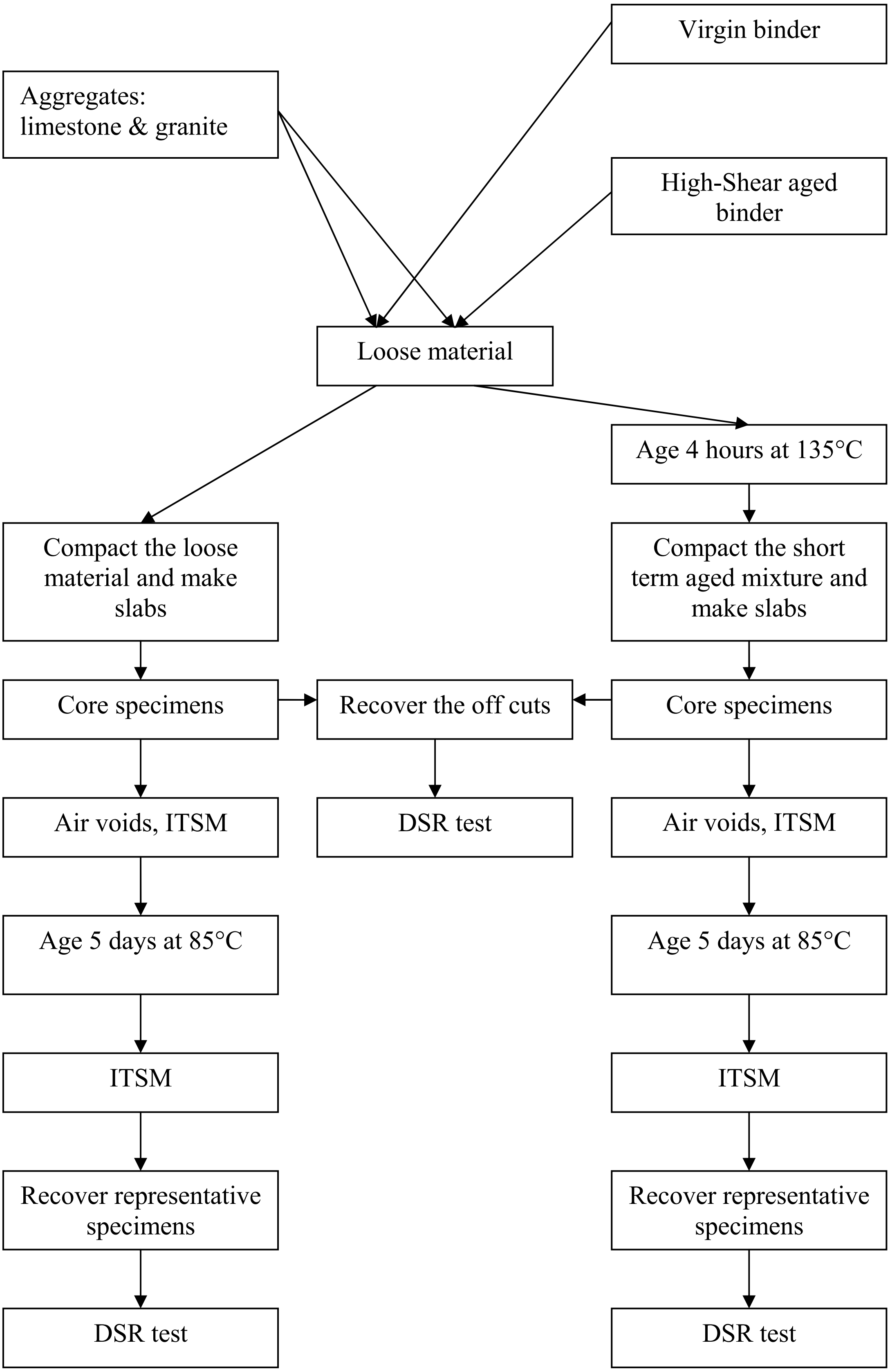


Figure 5.3 The testing sequence

5.3.2 Specimen description

Eighty specimens with different combinations of binders, aggregates and ageing procedures were fabricated in this study. Table 5.7 gives a general description for all of these specimens.

Table 5.7 Specimen description

Asphalt Mixture ID	Aggregate Type	Binder Condition	Pre-Compaction Conditioning	Amount
LV_U	Limestone	Virgin	None	10
GV_U	Granite	Virgin	None	10
LHS_U	Limestone	High Shear Aged	None	10
GHS_U	Granite	High Shear Aged	None	10
LV_STA	Limestone	Virgin	Short-term Aged	10
GV_STA	Granite	Virgin	Short-term Aged	10
LHS_STA	Limestone	High Shear Aged	Short-term Aged	10
GHS_STA	Granite	High Shear Aged	Short-term Aged	10

Note:
L: Limestone
G: Granite
V: Virgin bitumen
HS: High Shear aged bitumen
U: Unaged mixture
STA: Short term aged mixture

5.3.3 Void content check for specimens

The air void content for each specimen was determined using the sealed specimen method from the standard EN 12697-6:2003. As the maximum density of asphalt mixture is required in the final calculation of air void, Table 5.8 gives the maximum densities for the mixtures with different material combinations. It should be noted that, with the same aggregate, the maximum densities of asphalt mixtures with High-Shear aged binder are both smaller than those with Virgin binder. It was concluded in Chapter 4 that a large amount of oily components had evaporated during the High-Shear ageing; therefore, when these two different binders were mixed with aggregates, there were more oily components in the virgin binder that were available for absorption, which would leave less free bitumen within the mixture and therefore lead to a smaller volume and a larger maximum density.

Table 5.8 Maximum density results for different asphalt mixtures (kg/m^3)

Binders / Aggregates	Virgin binder	High-Shear aged binder
Limestone	2508	2502
Granite	2500	2494

With the maximum densities shown above, the air voids for all the specimens were determined and summarized in Table 5.9. The layout of specimens on each slab was the same as that shown in Figure 4.15.

From Table 5.9, several interesting phenomena can be observed:

- Most of the specimens from the middle of slabs (with yellow shading in the table) had a void content smaller than the average void content of the specimens from the same slab. This can indicate that mixtures in the middle of each slab are subjected to better compaction and normally denser than the mixtures from the side of slab;
- At the same ageing stage, the granite mixtures have a higher void content than the limestone mixtures. This might be a result of differences in the individual gradings of these two aggregates, although they have the same batching details, which can be seen in Figures 5.1 and 5.2;
- With the same material combinations, the mixtures that were short-term aged (STA) have a larger void content than the ones without short-term ageing (U). The absorption and/or adsorption of binder fractions by the aggregate surface might be the cause of this;
- The designed void content in this study was 8%; however, as stated above, the void content within the slab is not homogeneous and is difficult to control during compaction. Therefore, the final average void content of the specimens in this study was approximately 10%.

Table 5.9 Air void content results

Methods	Materials	Slabs	Code	Void contents (%)	average (slab)	Average (group)
U	L&V	A	A1	8.65	8.50	8.64
			A2	8		
			A3	7.8		
			A4	8.44		
			A5	9.59		
		B	B1	9.2	8.78	
			B2	10.12		
			B3	8.18		
			B4	8.08		
			B5	8.34		
	G&V	C	C1	10.46	10.78	10.91
			C2	11.66		
			C3	9.9		
			C4	10.26		
			C5	11.6		
		D	D1	12.12	11.04	
			D2	11.71		
			D3	10.82		
			D4	10.09		
			D5	10.46		
	L&HS	E	E1	8.14	8.94	9.23
			E2	9.42		
			E3	8.12		
			E4	9.74		
			E5	9.29		
		F	F1	10.22	9.51	
			F2	10.62		
			F3	7.78		
			F4	9.29		
			F5	9.66		
	G&HS	G	G1	12.41	11.10	10.90
			G2	9.94		
			G3	10.39		
			G4	12.11		
			G5	10.65		
		H	H1	10.33	10.71	
			H2	11.59		
			H3	10.48		
			H4	10.08		
			H5	11.06		

Table 5.9 Air void content results (Cont.)

Methods	Materials	Slabs	Code	Void contents (%)	Average (slab)	Average (group)
STA	L&V	I	I1	10.31	9.19	9.75
			I2	8.73		
			I3	8.96		
			I4	9.7		
			I5	8.24		
		J	J1	9.79	10.31	
			J2	11.76		
			J3	10.57		
			J4	9.44		
			J5	9.99		
	G&V	K	K1	10.33	11.17	11.31
			K2	10.87		
			K3	11.57		
			K4	11.25		
			K5	11.81		
		L	L1	12.11	11.45	
			L2	11.55		
			L3	11.47		
			L4	10.78		
			L5	11.35		
	L&HS	M	M1	11.41	9.28	9.40
			M2	9.24		
			M3	8.24		
			M4	9.11		
			M5	8.42		
		N	N1	10.86	9.53	
			N2	9.51		
			N3	8.46		
			N4	9.19		
			N5	9.61		
	G&HS	O	O1	11.03	10.65	10.83
			O2	11.6		
			O3	10.25		
			O4	10.61		
			O5	9.74		
		P	P1	11.76	11.01	
			P2	11.32		
			P3	10.38		
			P4	10.82		
			P5	10.77		

5.4 Test Results

5.4.1 DSR results

As stated above, binders were recovered from the asphalt mixtures at different ageing stages. After recovery, the recovered binders were subjected to DSR frequency sweep tests using the Bohlin Gemini 200 model DSR. The testing conditions were as follows:

- Mode of loading: Controlled-strain,
- Temperatures: 0 to 80°C (5°C intervals),
- Frequencies: 0.1 to 10 Hz,
- Plate geometries: 8 mm diameter with a 2 mm gap (0 to 35°C) and 25 mm diameter with a 1 mm gap (25 to 80°C).

In order to quantitatively illustrate the effects of different ageing conditions and aggregates on the age hardening of bitumen binder within the asphalt mixture, the complex modulus (G*) at 25°C and 0.4 Hz was selected from the DSR data of each group, and used to calculate ageing indices. Table 5.10 shows the summarized results.

Table 5.10 Complex moduli at 25°C and 0.4Hz from the DSR tests

Groups	G* before mixing (Pa)	After compaction		After LTOA	
		G* (Pa)	Ageing Indices	G* (Pa)	Ageing Indices
LV_U	83847	129005	1.54	371490	4.43
GV_U	83847	228570	2.73	634500	7.57
LHS_U	225160	307695	1.37	790400	3.51
GHS_U	225160	627865	2.79	987120	4.38
LV_STA	83847	221305	2.64	466240	5.56
GV_STA	83847	475320	5.67	878050	10.47
LHS_STA	225160	382880	1.70	818930	3.64
GHS_STA	225160	706330	3.14	1257100	5.58

5.4.2 ITSM results

The stiffness of each specimen was tested both before and after they were aged, using the ITSM tests at 20°C. Table 5.11 shows the results of the ITSM tests. It should be noted that the specimens with the code number of C5, L3 and P5 were found to be cracked after ageing, and their stiffness results were lower than other specimens. The results of these specimens will, therefore, not be included in the data analysis.

From the results of the void content tests in Table 5.9, it can be seen that the differences in air void value between the different groups are large. Accordingly, the average stiffness of each group may not reliably reflect the aggregate influence, because they are not all at the same level of void content. In order to eliminate the influence of void content difference, the same procedure as that used in Chapter 4 (as shown in Figures 4.16 to 4.20) was carried out for different groups so that the theoretically predicted stiffness at 8% void content could be used in the data analysis. The plot of stiffness versus air void content for each group has been attached in Appendix A, and Table 5.12 gives both the average stiffness and theoretical stiffness of each group, and the ageing indices expressed by them also.

Table 5.11 ITSM stiffness results for asphalt specimens (20°C)

Methods	Materials	Slabs	Code	Stiffness BA (MPa)	Stiffness AA (MPa)
U	L&V	A	A1	1773	3445
			A2	2003	4026
			A3	1671	3854
			A4	1454	2790
			A5	1532	3230
		B	B1	1644	3772
			B2	1921	3170
			B3	1736	3101
			B4	2057	3934
			B5	1674	3676
	G&V	C	C1	1156	1588
			C2	775	1145
			C3	1286	1566
			C4	1339	1473
			C5	1016	989(cracked)
		D	D1	1050	1235
			D2	1001	1410
			D3	1204	1694
			D4	1135	1443
			D5	925	1540
	L&HS	E	E1	2381	4327
			E2	2239	3810
			E3	2661	4579
			E4	2209	3661
			E5	2605	4571
		F	F1	2411	3781
			F2	1940	3570
			F3	2745	4482
			F4	2247	3898
			F5	2292	4281
	G&HS	G	G1	1052	1956
			G2	1385	1902
			G3	1237	2171
			G4	1345	2240
			G5	1506	2446
		H	H1	1361	2429
			H2	1361	2090
			H3	1451	2314
			H4	1278	2214
			H5	1588	2179

Table 5.11 ITSM stiffness results for asphalt specimens (20^{o}C) (Cont.)

Methods	Materials	Slabs	Code	Stiffness BA (MPa)	Stiffness AA (MPa)
STA	L&V	I	I1	1826	3238
			I2	2009	3275
			I3	2140	3176
			I4	2036	3482
			I5	1872	3403
		J	J1	1870	3515
			J2	1476	2354
			J3	1580	2520
			J4	2057	3158
			J5	1878	4226
	G&V	K	K1	1643	1905
			K2	1388	1643
			K3	1430	1774
			K4	1189	1598
			K5	1338	1725
		L	L1	1418	1915
			L2	1340	1611
			L3	1347	1324(cracked)
			L4	1559	2016
			L5	1398	1743
	L&HS	M	M1	2319	2976
			M2	2153	3750
			M3	2672	4440
			M4	2464	3812
			M5	2502	3847
		N	N1	2042	3473
			N2	2328	3762
			N3	2944	4537
			N4	2431	4319
			N5	2606	3452
	G&HS	O	O1	1604	2086
			O2	1533	1933
			O3	1655	2134
			O4	1571	2104
			O5	1833	2159
		P	P1	1393	1874
			P2	1668	1936
			P3	1932	1948
			P4	1918	1948
			P5	1701	1674(cracked)

Table 5.12 Stiffness and ageing indices

Groups	Average			Theoretical (8%)		
	Stiffness BA (MPa)	Stiffness AA (MPa)	Ageing Indices	Stiffness BA (MPa)	Stiffness AA (MPa)	Ageing Indices
LV_U	1747	3500	2.00	1770	3648	2.06
GV_U	1097	1455	1.33	1490	1878	1.26
LHS_U	2373	4096	1.73	2616	4494	1.72
GHS_U	1356	2194	1.62	1537	2346	1.53
LV_STA	1874	3235	1.73	2157	3684	1.71
GV_STA	1411	1770	1.25	1849	1960	1.06
LHS_STA	2446	3837	1.57	2676	4395	1.64
GHS_STA	1679	2014	1.20	2199	2363	1.07

5.4.3 General observation

From Tables 5.10 and 5.12, an interesting phenomenon can be observed. When undergoing the same ageing period, asphalt mixtures with limestone aggregates had higher ITSM values than granite mixtures that contained the same type of binder as limestone mixtures. However, binders recovered from limestone mixtures were softer than those from granite mixtures. Several factors were considered as possible causes of this phenomenon.

Firstly, it can be seen from Figures 5.1 and 5.2 that the gradation of granite aggregate in this study was not as continuous as that of limestone aggregate. This could lead to a poorer aggregate contact and a larger air void content (as seen in Table 5.9) in granite mixture and therefore a lower ITSM stiffness. Secondly, as stated above, the ability for absorbing oily components of the limestone aggregate (with a WA value of 0.7%) was higher than that of the granite aggregate (with a WA value of 0.3%). Because the limestone absorbed more oily components, the binders coating the limestone aggregates were harder than those coating the granite, which would result in higher ITSM values from limestone mixtures. In addition, as the absorbed binder was inside the aggregate, it was protected from oxidation; therefore, when the absorbed components were recovered back to the bitumen, it led to a softer recovered binder for the limestone mixture. Finally, the calculated binder film thicknesses showed that the binder films in granite mixtures were thicker than those in limestone mixtures. According to the findings from Chapter 4, the thicker binder films in granite mixtures could also lead to lower ITSM values.

5.5 Analysis of Results

5.5.1 The effects of binder type on ageing

The main aim of this test programme was to investigate the influences of mineral aggregate types on bitumen ageing. However, it was also proposed that the effect of binder type on bitumen ageing could be studied as well. As stated above, two different binders were used in this study: the virgin 100/150 pen binder (V) and the 100/150 pen binder that was High-shear aged (at 165°C for 2.5 days) (HS). Because the HS binder is much harder than the V binder, it is expected that, with the same aggregate type and ageing time, asphalt mixtures containing the HS binders have a higher stiffness and their recovered binders are harder than those recovered from asphalt mixtures containing V binders (as seen in Tables 5.10 and 5.12). However, in terms of the study on ageing properties of different binders, it is suggested that more attention be paid to the ageing indices.

The effects of binder types on the ageing indices in terms of complex moduli (at 25°C and 0.4 Hz) are shown in Figures 5.4 (for limestone mixtures) and 5.5 (for granite mixtures). From these figures, it can be seen that the ageing properties of bitumen can be significantly affected by binder types. When mixed with a particular aggregate (either limestone or granite in this study) and undergoing the same ageing procedure, the ageing indices for V binders are generally higher than those for the HS binders. It is a reasonable result as the HS binder had already been aged in High-shear mixer at 165°C for 2.5 days and, therefore, the amount of oxidizable molecules (potential for ageing) it contains should be smaller than that in the V binder, which can result in a smaller amount of oxidative age hardening to the HS binder during the testing programme.

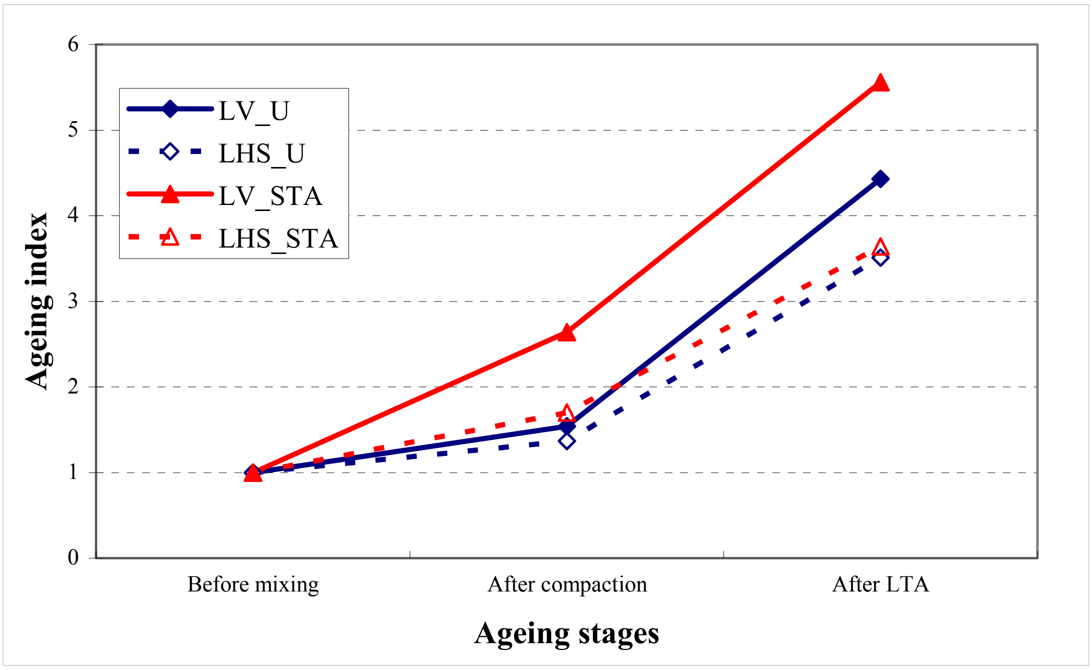


Figure 5.4 Comparison of ageing indices in terms of complex moduli for binders recovered from limestone mixtures

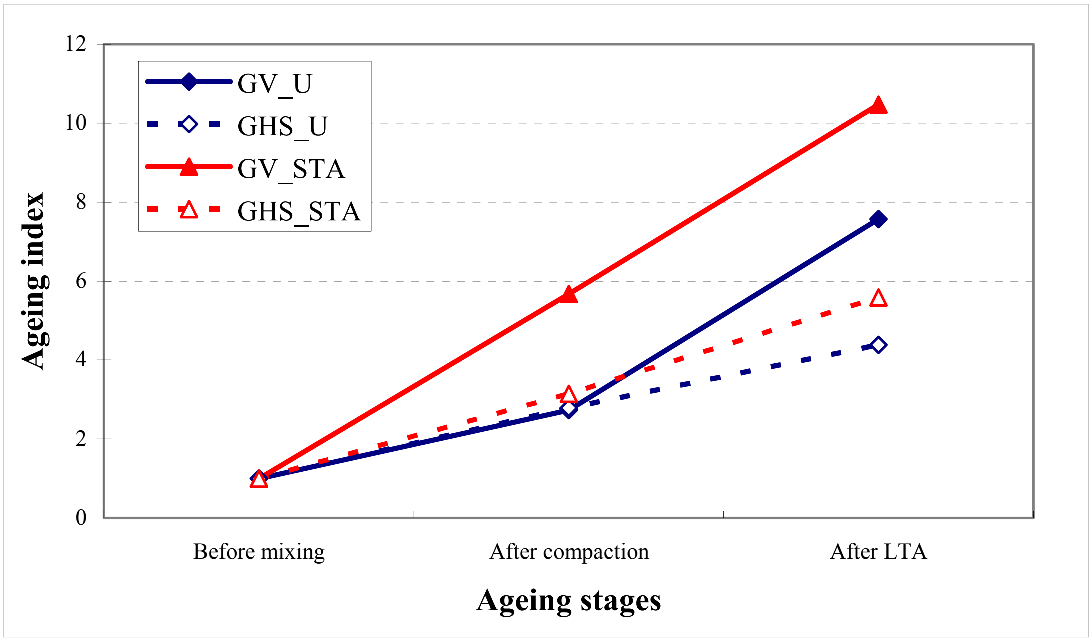


Figure 5.5 Comparison of ageing indices in terms of complex moduli for binders recovered from granite mixtures

The effect of binder types on the ageing indices in terms of the stiffness (at 8% air void content) of asphalt specimens is shown in Figure 5.6. It can be seen that, for the limestone group, the ageing indices for asphalt mixtures containing V binder are higher than those for asphalt mixtures containing HS binder, which is the same as the results shown in Figures 5.4 and 5.5. However, a completely opposite result is observed from the granite group. In this group, the ageing indices for asphalt mixtures containing V binder are lower than those for HS binder mixtures, which implies that stronger age hardening has happened to the mixtures containing HS binder. It should be noted that several granite mixtures were found to be cracked during the sample preparation (as shown in Table 5.11) and, therefore, there are reservations about the reliability of the ITSM results for the granite mixtures after long-term ageing. In addition, as the ITSM tests were applied to the fabricated asphalt specimens, Figure 5.6 only presents the binder effects on the ageing during the SHRP long-term ageing, which is different from Figures 5.4 and 5.5. Detailed comparison of the differences between the DSR results and ITSM results will be presented later.

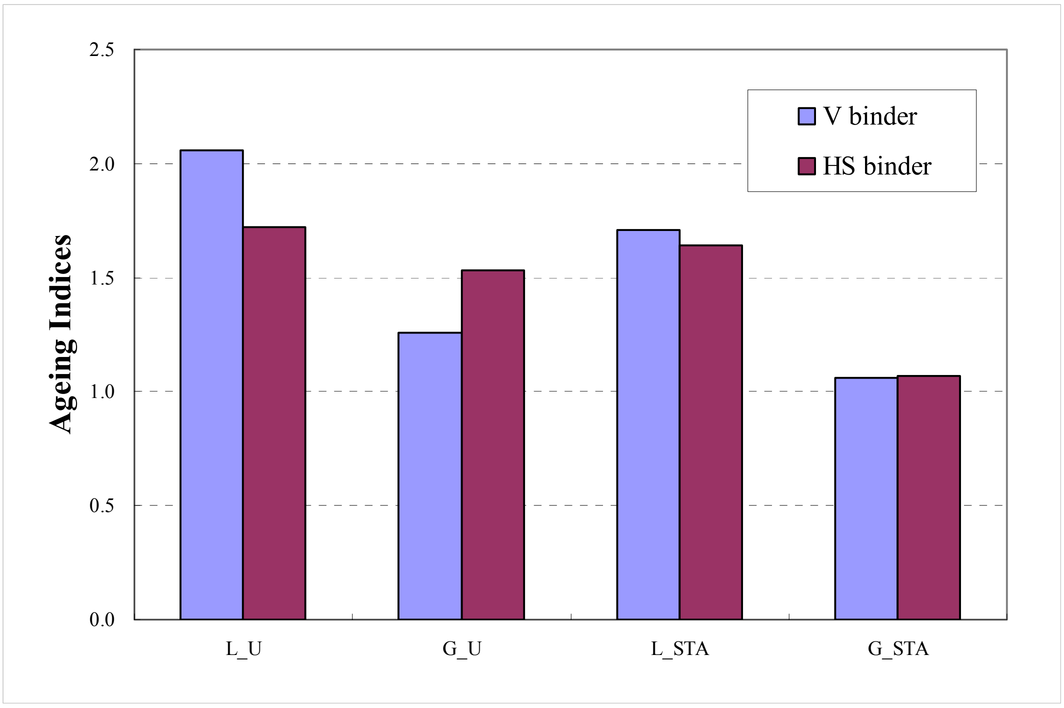


Figure 5.6 Effect of binder types on the ageing indices in terms of theoretical asphalt stiffness at 8% air void content

5.5.2 The effect of aggregate type on ageing

When the effect of aggregate type on ageing is considered, it should be firstly noted that, for a particular bitumen, the ageing properties of asphalt mixtures and their recovered binders are affected not only by the type of aggregate they contained, but also by the varying binder film thickness and air void content due to the differences in the total gradation and shape factors amongst the various aggregates. Therefore, special attention should also be paid to the other two factors, i.e. binder film thickness and the air void content, when the effect of aggregate type on ageing is analysed.

DSR results analysis

The ageing indices in terms of binder complex moduli (at 25^{o}C and 0.4 Hz) at different ageing stages are summarized and presented in Figures 5.7 for V binder mixtures and 5.8 for HS binder mixtures. It can be seen that, for a particular binder type, the ageing indices for the binders mixed with granite are much higher than those for the binders mixed with limestone, which means stronger age hardening has happened to the binders in granite mixtures.

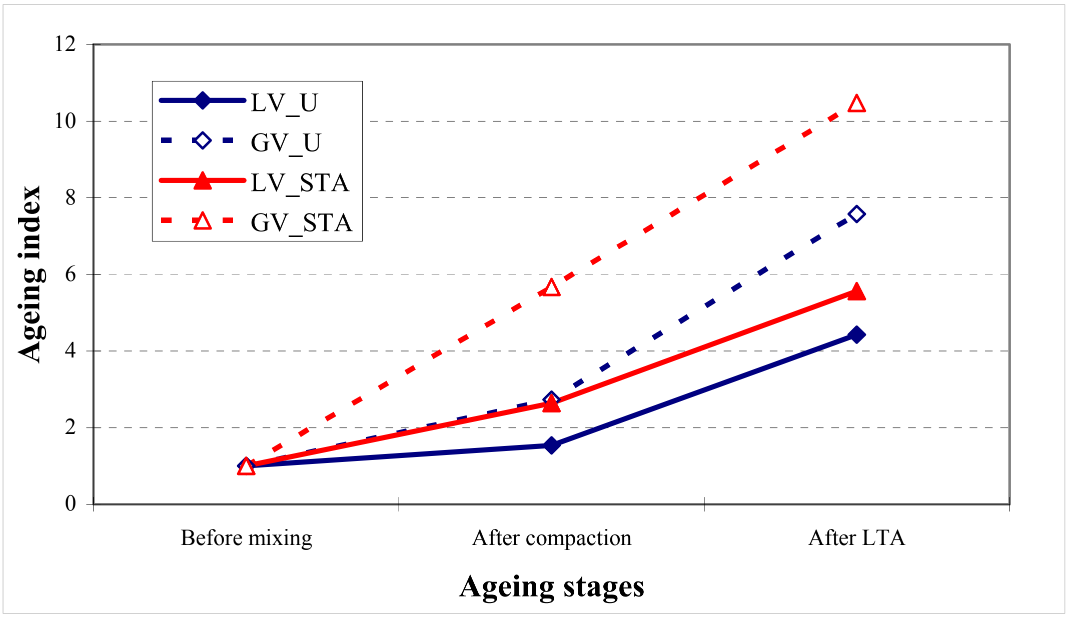


Figure 5.7 Comparison of ageing indices in terms of complex moduli for recovered V binders at different ageing stages

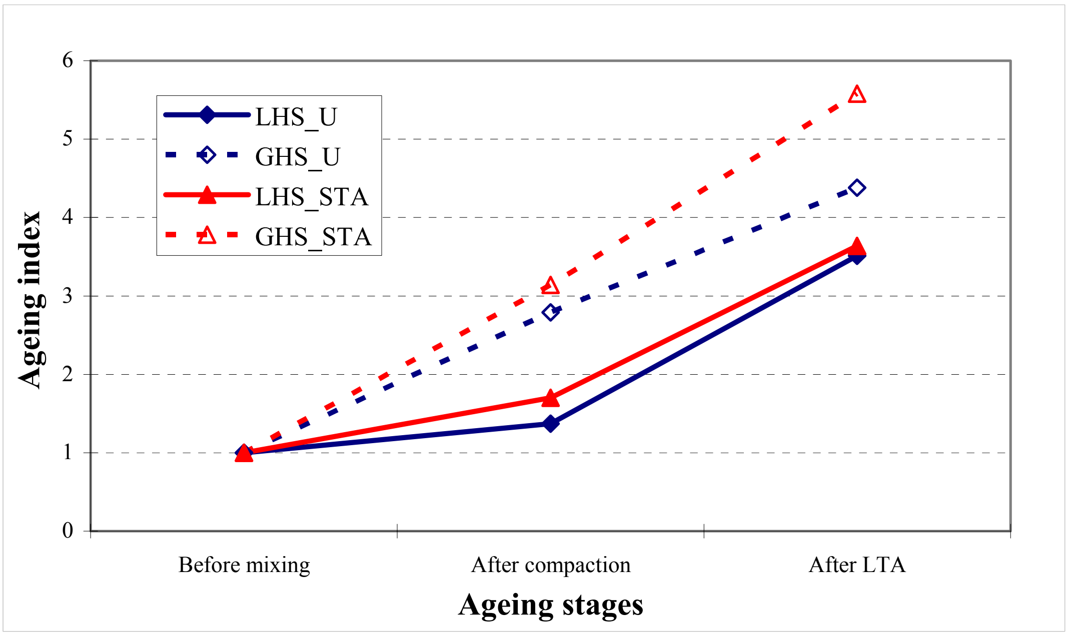


Figure 5.8 Comparison of ageing indices in terms of complex moduli for recovered HS binders at different ageing stages

As stated above, three possible factors that are related to the aggregate may cause the results shown in Figures 5.7 and 5.8: 1) difference in air void content, 2) difference in binder film thickness and, 3) the aggregate type. It has been found from the results shown in Table 5.9 that, at the same testing stage, the granite mixtures had a higher void content than the limestone mixtures with the same binder. This higher void content might also lead to higher ageing indices for the binders recovered from the granite mixtures due to the easier penetration for oxygen to the bitumen. As it can be seen from Figures 5.7 and 5.8, the ageing indices for the binders recovered from granite mixtures after slab compaction is already much higher than those for the binders recovered from limestone mixtures. During the time before slab compaction, there is no difference in ‘air void content’ among the loose mixtures with different aggregates. Therefore, the difference in air void content is not considered as the major factor that led to the results in Figures 5.7 and 5.8.

With regard to the binder film thickness, the calculations carried out in the previous subsection have shown that the binder film thickness of the granite mixtures (8.4 μm) is thicker than that of the limestone mixtures (6.9 μm). According to the findings from Chapter 4, the binder film thickness can significantly affect the ageing of binders in asphalt mixtures (as shown in Figure 4.25). However, based on the conclusions drawn in Chapter 4, the ageing indices of the binders recovered from the limestone mixtures should be higher than those of the binders recovered from the granite mixtures, because the binder film in limestone mixtures is thinner than that in granite mixtures.

According to the above analysis, it is, therefore, believed that the differences in ageing indices shown in Figures 5.7 and 5.8 are mainly caused by the varying aggregate types. As stated in Chapter 2, besides absorbing oily components from bitumen, mineral aggregates have some added effects on the age hardening of bitumen (Barbour et al., 1974; Petersen et al., 1974 (a); Petersen, et al., 1974 (b); Plancher et al., 1976; and Huang et al., 2002). Firstly, the charged and polarised aggregate surface can adsorb polar groups (either naturally occurring ones or the oxidation products) within bitumen, which may decelerate the bitumen hardening process. In addition, some mineral components on the surface of aggregates can catalyze bitumen oxidation. However, the catalytic activity of the aggregate surface can be limited by the adsorption of polar components from bitumen to aggregates.

Anderson et al. (1994) stated that aggregates with the least adsorption of highly polar fractions (e.g. quartzite and granite) exhibit the greatest catalytic effect in bitumen oxidation, whereas those showing the largest adsorption (e.g. limestone) exhibited the smallest catalytic effect. This statement is proved to be correct by the data shown in Figures 5.7 and 5.8. Firstly, the stronger catalytic ability of the granite led to more oxidative ageing of the binders in the granite mixtures, which can result in an increased ageing index. Secondly, the limestone adsorbed a greater amount of polar components from the bitumen which, as stated by Petersen et al. (1974 (a)), could protect the adsorbed components from oxidation. This would result in a decrease in ageing indices for the binders recovered from limestone mixtures. Thirdly, Petersen et al. (1974 (a)) declared that some of the polar component adsorption might be irreversible and most of these are not recoverable through normal bitumen recovery techniques. Therefore, it is possible that some polar components were still kept on the limestone surface after bitumen recovery, which can also lead to a lower ageing index for the binders recovered from limestone mixtures. Finally, as analyzed in Section 5.4.3, the different abilities of these two aggregates in absorbing oily fractions might also be one of the main causes for this phenomenon.

ITSM results analysis

The effect of aggregate type on the ageing indices in terms of the stiffness (at 8% air void content) of asphalt specimens is shown in Figure 5.9. It can be seen that the ageing indices of limestone mixtures in terms of ITSM stiffness are higher than those of granite mixtures, which implies that, during the long-term ageing simulation, stronger age hardening has happened to limestone mixtures. For comparison, the binder stiffness ratios (BSRs) in terms of bitumen complex moduli (at 25^{o}C and 0.4 Hz) at the same stages of ITSM tests are calculated using the following equation:

$$BSR = \frac{Complex \quad Modulus \quad after \quad LTA}{Complex \quad Modulus \quad after \quad Compaction}$$

The results of the calculation using the above equation are summarized in Figure 5.10. It can be seen that the BSRs for the binders recovered from limestone mixtures are also higher than those for the binders recovered from granite mixtures. This result is coincident with the situation shown in Figure 5.9. However, by comparing these two figures with the Figures 5.7 and 5.8, an interesting phenomenon can be observed. The ageing indices in terms of bitumen complex moduli (shown in Figures 5.7 and 5.8) illustrate that, during either the period before LTA or the whole ageing programme, stronger age hardening has happened to the granite mixtures; whereas the ageing indices in terms of asphalt stiffness (shown in Figure 5.9) and the BSRs in terms of bitumen complex moduli (shown in Figure 5.10) show that, during the long-term ageing simulation, stronger age hardening has happened to the limestone mixtures.

Therefore, it is evident that, for a particular bitumen, the aggregate type can significantly affect the ageing of bituminous materials. In addition, the type of aggregate also appears to influence the proportion of total age hardening in different ageing periods. As stated above, it is the difference in the abilities of adsorbing bitumen polar components and/or catalyzing bitumen oxidation amongst various aggregates that causes the different ageing properties of bitumen in contact with them. In this study, the limestone is stronger in adsorbing highly polar fractions from bitumen and it delays the increase of the bitumen stiffness upon ageing. The granite is better in catalyzing the oxidation of bitumen and it caused a larger amount of bitumen stiffness increase upon ageing. These are the two main factors that caused the differences in ageing indices shown in Figures 5.7 and 5.8.

With regard to the effect of aggregate type on the proportion of ageing that happened in different ageing periods, it is believed to be caused by the degradation of adsorbing and catalyzing abilities of aggregates. As stated in Chapter 2, only the charged sites on the aggregate surface are able to interact with (adsorb) the polar components of bitumen. For the limestone (basic) mixtures where adsorption dominates, as the ageing proceeds, the constant adsorption would lead to reduced charged active sites on the aggregate surface and, therefore, its ability of decreasing the amount of ageing will be weakened. In addition, Petersen et al. (1974 (a)) stated that the interactions of bitumen components with the aggregate surface (adsorption) reduce the surface catalytic activity of bitumen oxidation. For the granite (acidic) mixtures, although the catalytic effect is dominant in the bitumen ageing, adsorption of polar components from bitumen to aggregate surface still happens during ageing; and this will deactivate the granite surface in accelerating the bitumen ageing. It is believed that the results shown in Figures 5.9 and 5.10 are caused by the above mechanisms.

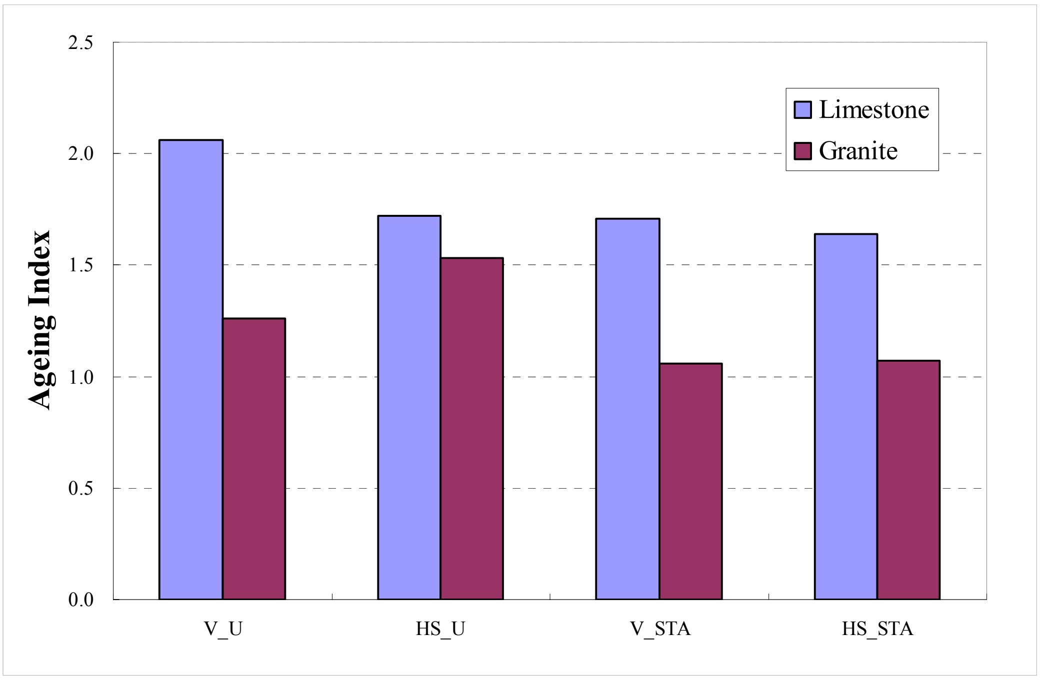


Figure 5.9 Effect of aggregate types on the ageing index in terms of theoretical asphalt stiffness at 8% void content

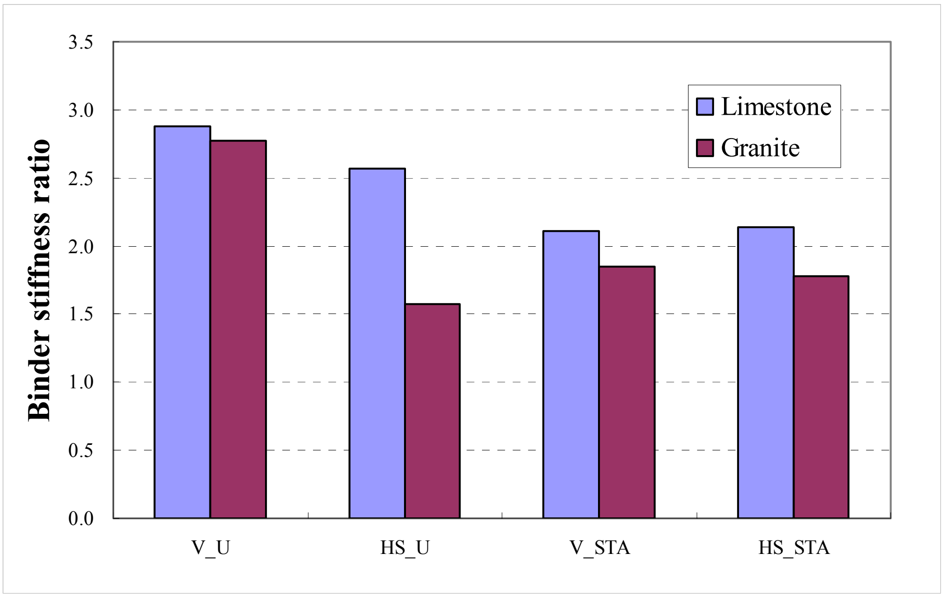


Figure 5.10 Effect of aggregate types on the binder stiffness ratio in terms of complex modulus (LTA/comp.)

5.5.3 Correlations between Binder and Asphalt Mixture Ageing

As stated in Chapter 4, the High-Shear ageing method is not a standard one, and it is therefore worth comparing its ageing results with those of the standard methods (e.g. RTFOT, PAV, SHRP short-term oven ageing and SHRP long-term oven ageing). The G* and phase angle at 25^{o}C and 0.4 Hz were chosen from the DSR results for the different ageing combinations (pure bitumen and recovered bitumen) and compared in Figure 5.11.

From this figure, it can be seen that the short-term ageing simulation results for the High-Shear and SHRP short-term oven ageing for the binder in the limestone mixture are similar. However, the SHRP short-term oven ageing result for the binder from the granite mixture is almost the same as the SHRP long-term oven ageing result of the binder from the limestone mixture, which means that a large amount of ageing has already happened to the binder in the granite mixture during the short-term ageing procedure. This increased ageing of the binder in the granite mixture may be due to increased exudation ageing or the granite aggregate acting as a catalyst for increased oxidation of the binder. In terms of the SHRP long-term ageing result of the binder from the granite mixture, this is similar to the result of binder after RTFOT+PAV ageing but significantly different from the rheological properties of the High-Shear + PAV aged binder.

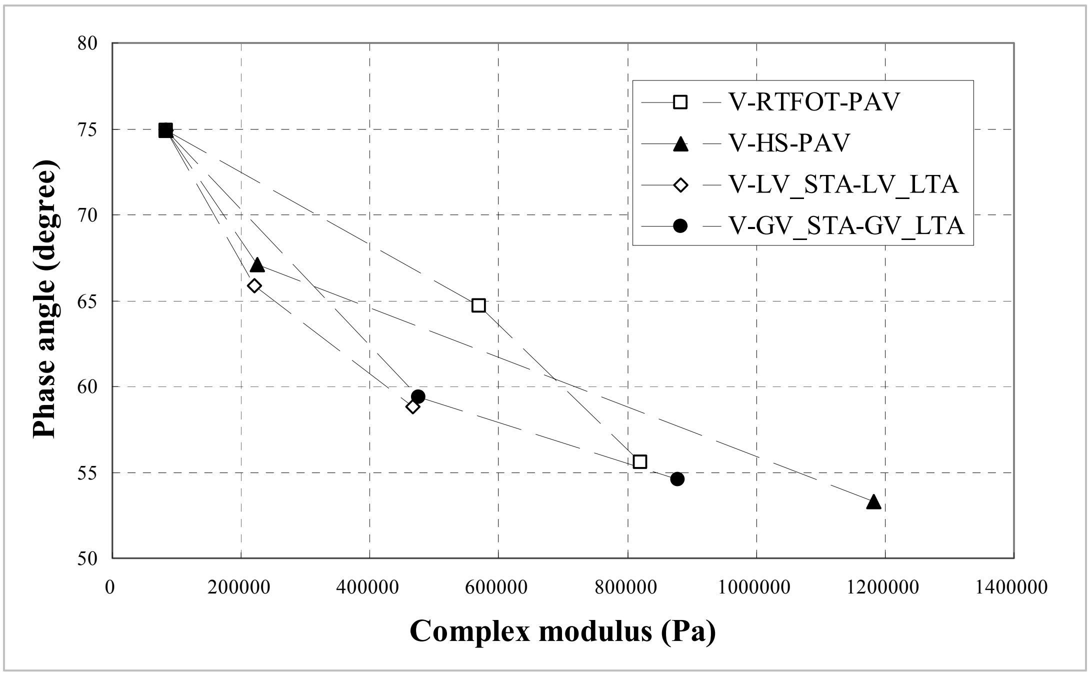


Figure 5.11 Correlations between binder and asphalt mixture ageing methods

5.6 Summary and Discussion

In this study, an ageing test programme involving two different bitumen types and two aggregate types was conducted by testing the stiffness of asphalt mixture specimens and the complex modulus of recovered binders at different ageing stages. The testing results showed that both the bitumen and aggregate types can significantly affect the ageing properties of the bituminous materials, which strongly supported some of the findings from the literature review. In addition, it was also found from this study that, for a particular bitumen, the aggregate type appears to influence whether the majority of the total age hardening occurs in the initial ageing period or in the subsequent period.

A comparison among the different pure bitumen ageing simulation methods and the standard SHRP asphalt mixture ageing tests with different aggregates (limestone and granite) was carried out based on the DSR testing data at different ageing stages. It was found difficult to get any strong correlations among these ageing simulation programmes. As stated in Chapter 2, bitumen is an extremely complex organic mixture whose ageing properties can be significantly affected by various factors. Any small change in the ageing test conditions, the materials or the testing procedures may cause considerable differences in the properties of aged binder. Therefore, this comparison imparted that, when the effect of a particular factor on bitumen ageing is studied, it is extremely important that most of the other factors that affect the bitumen ageing should be retained at a similar level.

In this study, the ageing properties of bituminous materials were studied by analyzing the mechanical and/or rheological properties of the asphalt mixtures and their recovered binders at different ageing stages. It showed a general tendency about the change of ageing between the beginning ageing period and subsequent periods. However, it was felt that these mechanical tests should be conducted more frequently and the ageing period should be extended, so that the effect of aggregate type on the age hardening ‘rate’ at different ageing stages could be presented.

6 AGEING OF BITUMEN-FILLER MASTICS

6.1 Introduction

The study of asphalt mixture ageing has shown that both bitumen type and mineral aggregate can significantly influence the ageing properties of bituminous materials. However, in terms of the effects of mineral aggregate on ageing, it is important to recognise that the more intimate contact between bitumen and aggregate in a paving mixture involves the fine aggregate and filler. Anderson et al. (1992) stated that, in terms of physical-chemical interactions between the bitumen and mineral surface, the properties of the fine fraction should dominate because the fines are embedded in the bitumen and, therefore, the majority of the surface area generated by the aggregate is within the fines.

Therefore, in order to develop a better understanding of the manner by which mineral aggregates affect bitumen ageing, an ageing study on the bitumen-filler mastics involving DSR and FTIR tests at different ageing stages was carried out. Compared with asphalt ageing, mastic ageing has its advantages. Firstly, as stated above, the surface area of fillers is much greater than that of the coarse aggregate with the same volume, which will make the adsorbing and catalyzing phenomenon more obvious. In addition, as the fillers in mastics can be viewed as being embedded in the binder, the effects of ‘void content’ and ‘binder film thickness’, which were concerns during the data analysis in the mixture ageing studies, could be eliminated in the mastic ageing.

6.2 Materials and Experimental Programme

6.2.1 Materials

In this study, three mastics were produced from one type of bitumen and three different fillers. Neither the bitumen nor the filler sources were the same as those used in earlier chapters; however, the purpose was not to make direct comparison but to generate independent data on ageing of mastics.

The binder used in this study was a 70/100 pen bitumen; the specification parameters of this bitumen are presented in Table 6.1.

Table 6.1 Basic bitumen parameters

Bitumen type	Specific gravity	Penetration (dmm)	R&B SP (^{o}C)
70/100 pen	1.02	89	47.6

The mineral fillers used in this study are satisfactory to the requirement of 90 percent of particles passing a 63 μm sieve. The three fillers used in this study were limestone (LS), gritstone (GS) and ordinary Portland cement (OPC). Among these three fillers, the limestone and OPC are basic fillers, whereas the gritstone is acidic. It was initially proposed that granite filler should be used to make this study more systematic; however, the size distribution of granite filler was found to be significantly different from the other fillers and therefore, was not used in this study. The physical properties of fillers are given in Table 6.2.

Table 6.2 Physical properties of mineral fillers

Filler types	Source	Specific gravity	Rigden Voids (%)
Limestone	Longcliffe	2.74	24.9
Gritstone	Bayston Hill	2.65	32.9
OPC	Blue Circle	3.18	35.7

6.2.2 Experimental programme

This bitumen-filler mastic ageing study was generally carried out in two stages, as shown in Figure 6.1. In the first stage, three mastics containing different fillers were mixed using the same filler content (40% filler by volume) and were aged in the TFOT oven (at 165^{o}C for 5 hours) at a thickness of 3 mm in the TFOT plate. A DSR frequency sweep test was undertaken on the three mastics both before and after ageing. It was observed that the fillers had settled to the bottom of the TFOT plates after ageing and, therefore, before the aged mastics were subjected to DSR tests, they were simply re-mixed by hand in a small tin after conditioning in an oven at180°C for 30 minutes. Binders were recovered from aged mastics and then DSR tested.

In the second stage, in order to show the effects of different fillers on the ageing rate of bituminous materials, samples of limestone mastics and gritstone mastics (with the same mixing proportion as the first stage) were aged in the TFOT oven (165°C, 3 mm thickness) for different ageing times, namely 1 hour, 3 hours, 10 hours and 20 hours, presented in shading in Figure 6.1. The DSR tests were applied to the unaged and aged mastics, and their recovered binders, using the same testing conditions as in the first stage. In addition, in order to provide a reference for the mastic ageing, the pure 70/100 pen bitumen was aged and tested in the same ageing procedure.

The chemical changes during the ageing were evaluated using a FTIR test.

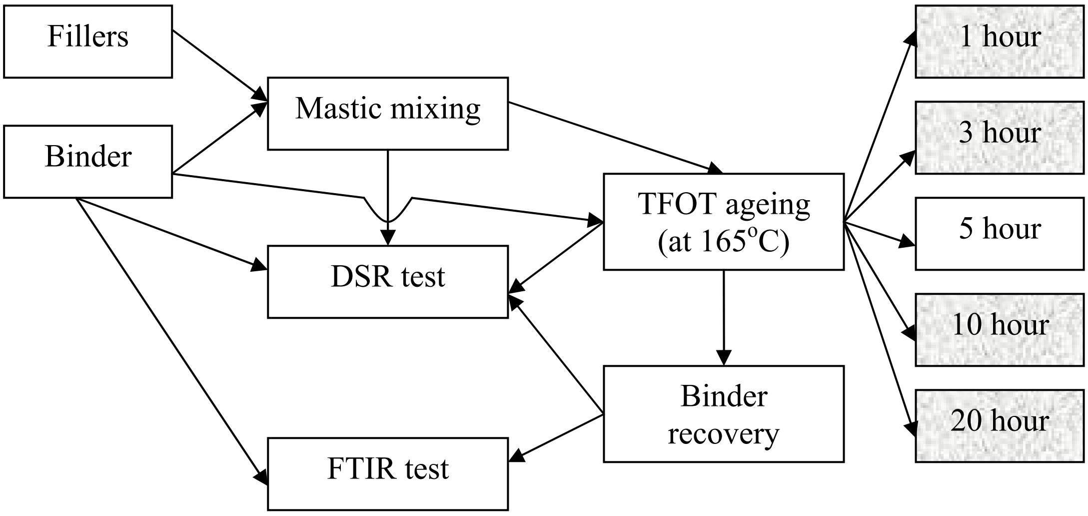


Figure 6.1 Testing programme of bitumen-filler mastic ageing study

6.3 Mastic Preparation and Linear Visco-elastic Limit Check

6.3.1 Methods for mastic mixing

In this study, a series of ageing and rheological tests were applied to different types of mastics which contain the same filler content but different filler types. Therefore, it is extremely important to guarantee that the fillers are homogeneously distributed within the mastics. Otherwise, it will be difficult to judge whether the differences in the testing results are caused by the varying mineral types of fillers or by the inhomogeneous filler distribution.

In order to check the reliability of mastic mixing methods, a mastic consisting of 40/60 pen binder (note: different to the binder in the main study) and OPC filler (65% by mass) was mixed by the following two methods: 1) mixing by paddle stirrer, as shown in Figure 6.2 and, 2) mixing by hand, as shown in Figure 6.3. Both methods were conducted at 160^{o}C, and the mixing time was restricted to a maximum of 5 minutes. The mixing procedures for these two different methods are similar and details are introduced as follows:

- Mineral filler was put into a 160^{o}C oven for 24 hours to ensure moisture-free particle surface.
- The 40/60 pen bitumen stored in a 5 litre tin was preheated in a 160^{o}C oven for 5 hours to make bitumen liquid and ready for mixing.
- The accurate quantity of bitumen was poured into a 2.5 litre tin. The tin containing the bitumen was then placed on a hot plate maintained at 160^{o}C.
- The bitumen was stirred for 30 seconds, either by the paddle stirrer or by hand. After that, the accurate mass of filler was added slowly while the stirring was continued for 4.5 minutes.
- The mastic was continuously stirred as it was cooling down until the temperature became low enough (approximately 75^{o}C) for preventing the filler from settling.
- Three samples were taken from different parts of the mastic and were kept in silicone moulds (25 mm diameter) so that their rheological properties could be tested and compared.

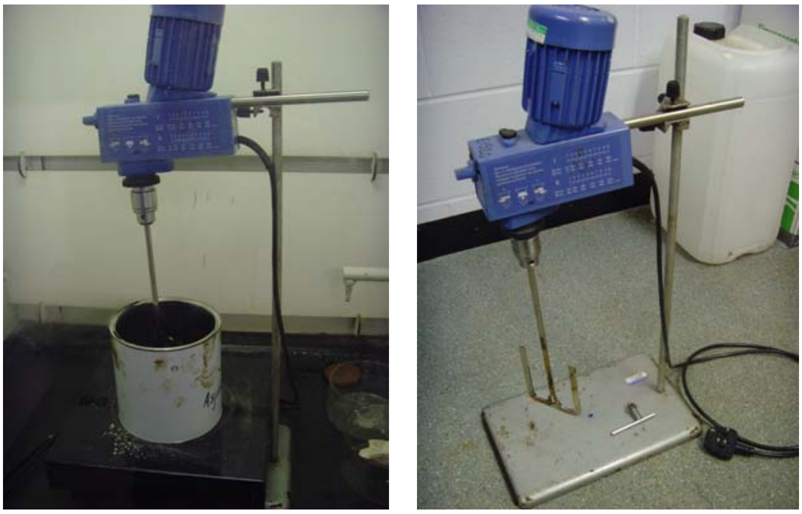


Figure 6.2 Picture of paddle stirrer mixer

Figure 6.3 Picture of hand mixing of mastic

In this study, samples taken from different mastic mixing methods were tested in a single temperature DSR frequency sweep test (at 45^{o}C). Figures 6.4 and 6.5 present the complex modulus and phase angle results for these different samples. With regard to the hand mixing, the homogeneity may also be affected by a different operator due to different mixing speed and force and, therefore, Figure 6.5 also includes a set of testing results for a mastic sample mixed by a different operator with different mixing speed. In order to compare these two mixing methods more quantitatively, the average, standard deviation and coefficient of variation, which is the ratio of standard deviation to average value expressed as a percentage, of the testing results for the different samples from each mixing method have been calculated and the coefficient of variation values are presented in Table 6.3. It should be noted that these are affected not only by the homogeneity of filler distribution, but also by the repeatability of the DSR test. Therefore, the relatively low variation coefficient values in Table 6.3 illustrates that both mixing methods are suitable for mastic mixing. In this study, mastic-mixing by hand was adopted.

Table 6.3 Percentage variation of complex modulus (G*) and phase angle (δ) with regard to different mastic mixing methods

	Mixing methods	Coefficient of variation (%)										
		0.1Hz	0.2Hz	0.3Hz	0.4Hz	0.6Hz	1Hz	1.6Hz	2.5Hz	4Hz	6.3Hz	10Hz
G*	Paddle stirrer	4.4	5.2	4.9	3.4	3.9	3.6	2.2	3.7	2.7	2.5	2.1
	Hand	1.8	3.6	4.0	2.1	2.1	2.2	0.9	1.9	1.8	1.9	1.6
δ	Paddle stirrer	0.3	0.6	0.5	0.4	1.2	0.5	0.9	1.5	1.0	1.5	2.1
	Hand	0.7	0.9	1.4	0.4	0.5	0.4	1.7	0.4	0.6	0.8	1.1

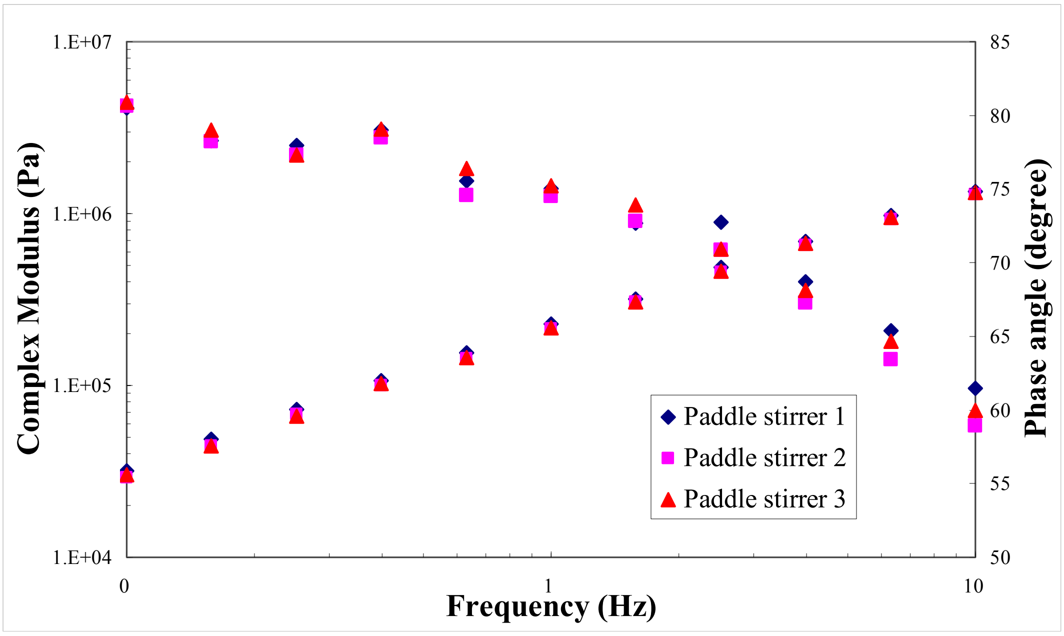


Figure 6.4 Homogeneity check for paddle stirrer mixing

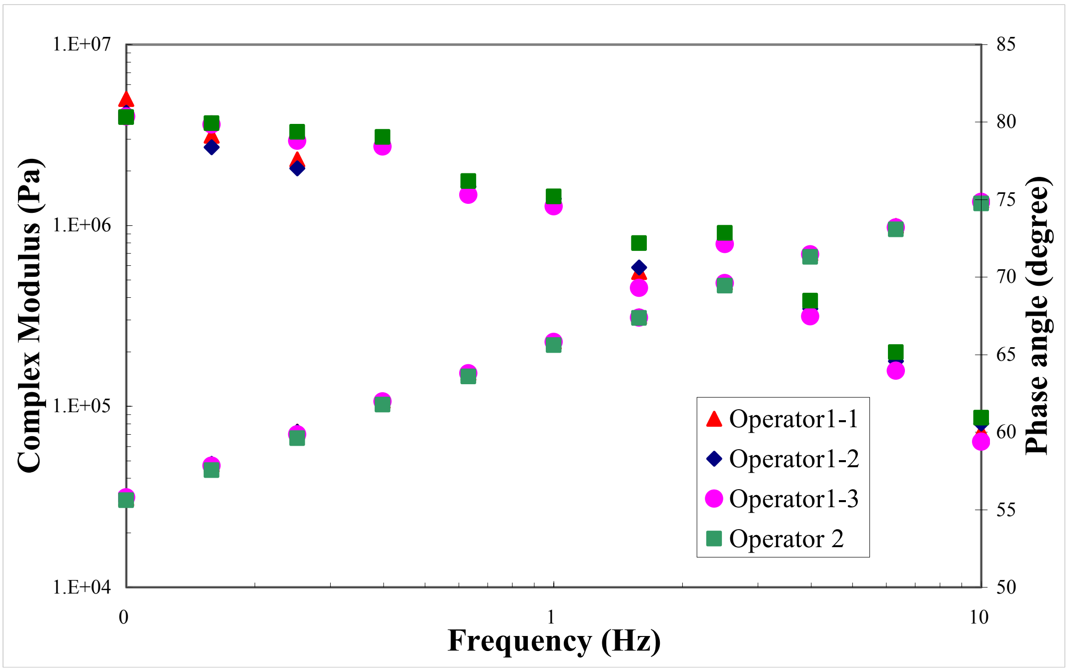


Figure 6.5 Homogeneity check for hand mixing

6.3.2 Stress sweep tests for mastics

Materials such as bitumen, which exhibit aspects of both elastic and viscous behaviour, are called viscoelastic materials, and must be characterised with test methods and analytical techniques that account for the time of loading and loading temperature (Anderson et al., 1994). It is usually advisable to confine the characterisation of a bituminous binder to its linear viscoelastic response to simplify the mathematical modelling of the material, as nonlinear response, particularly for viscoelastic materials, is difficult to characterise in the laboratory and model in practical problems (Airey et al., 2002). Generally, bituminous materials display nonlinear stress-strain behaviour with nonlinearity only becoming negligible at small strains. As the viscoelastic parameters of shear complex modulus, phase angle, storage modulus and loss modulus are all defined under linear viscoelastic conditions, the relationship between stress and strain is influenced only by temperature and loading time (frequency) and not by the magnitude of the stress and strain (Ferry, 1980). Therefore, it is important that the DSR tests are conducted within the linear viscoelastic (LVE) range of the tested materials. Strain/stress sweeps are usually conducted at selected temperatures and frequencies, and the strain/stress linearity limits determined as the point beyond which the measured shear modulus reduces to 95% of its zero strain/stress value (Petersen et al., 1994), as shown in Figure 6.6.

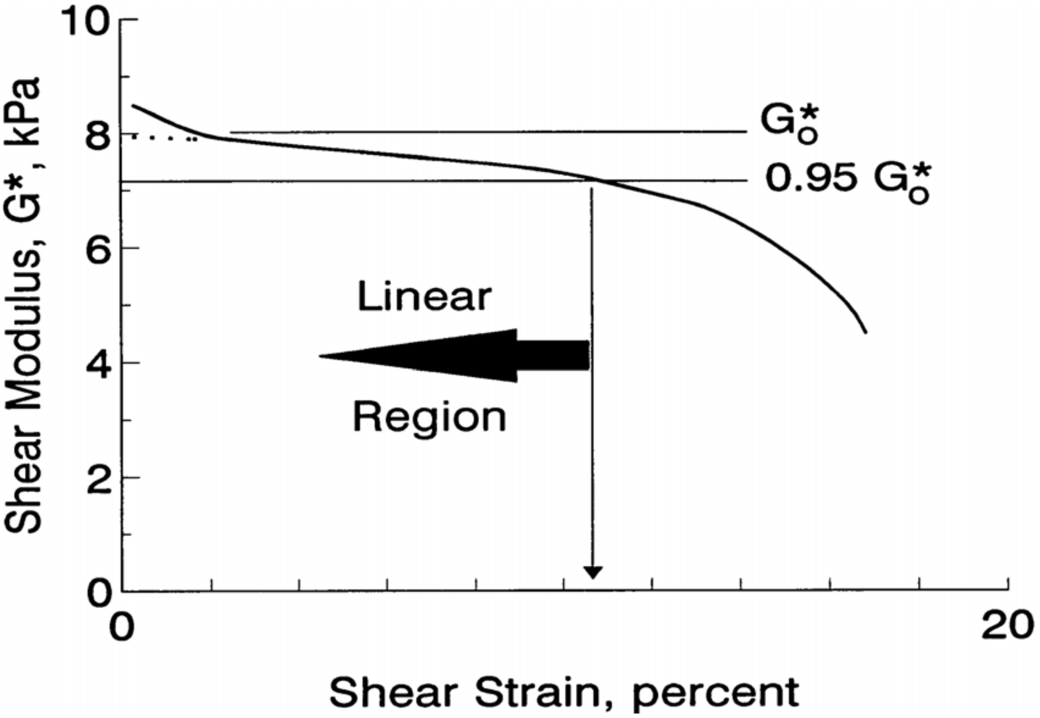


Figure 6.6 Strain sweep used to determine linear region (Petersen et al., 1994)

In this study, in order to determine the mastic linear viscoelastic strain level that was needed in the frequency sweep tests, stress sweep tests were carried out on both the unaged and aged mastics, using the following testing conditions:

- Mode of loading: Controlled-stress (stress value: from the lowest limit of the machine to 80,000 Pa),
- Testing points: 2000,
- Temperature: 30°C,
- Frequency: 1 Hz,
- Plate geometries: 8 mm diameter with a 2 mm gap.

The results for gritstone mastics are presented in Figure 6.7. The results for the other mastics are similar. According to the stress sweep test results, a controlled strain of 0.2% for 8 mm geometry and 0.3% for 25 mm geometry was adopted in the DSR frequency sweep tests for the mastics.

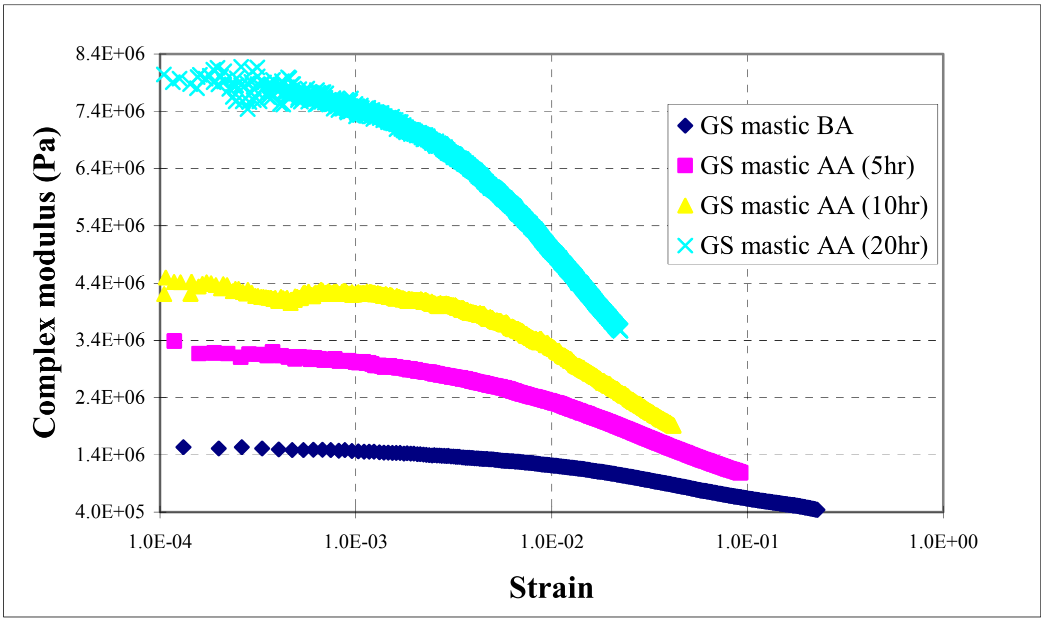


Figure 6.7 Stress sweep test results for gritstone mastics (30°C, 1 Hz)

Accordingly, the DSR frequency sweep testing conditions for the mastics were set as follows in this study:

- Mode of loading: Controlled-strain (0.2% for 8 mm geometry and 0.3% for 25 mm),
- Temperatures: 10 to 80°C (5°C intervals),
- Frequencies: 0.1 to 10 Hz,
- Plate geometries: 8 mm diameter with a 2 mm gap (10 to 50°C) and 25 mm diameter with a 1 mm gap (35 to 80°C).

6.4 Results and Discussion

6.4.1 The effect of mineral fillers on mastic ageing

A comparison between the TFOT ageing on bitumen-filler mastic and pure bitumen was carried out. Figure 6.8 shows the complex modulus (G*) master curves for different mastics both before and after 5 hour TFOT ageing. No obvious differences can be seen among mastics containing different fillers, both before and after ageing. In order to make the comparison more quantitatively, the Complex modulus at 35°C and 0.4 Hz for each test was selected for the ageing index calculation (as shown in Figure 6.9).

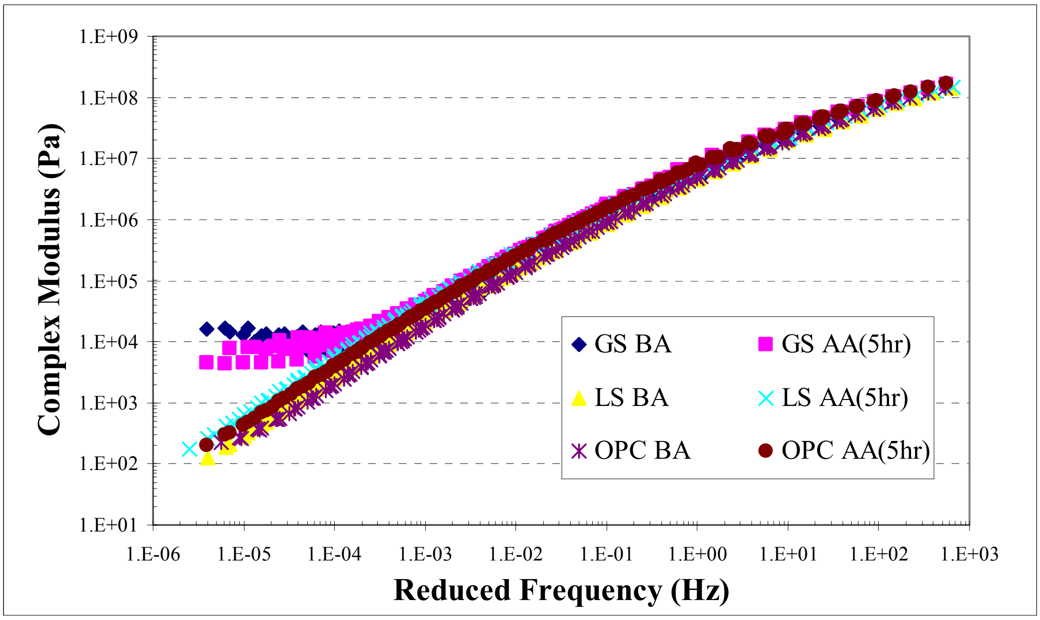


Figure 6.8 Complex modulus master curves for different mastics both before and after 5 hour TFOT ageing

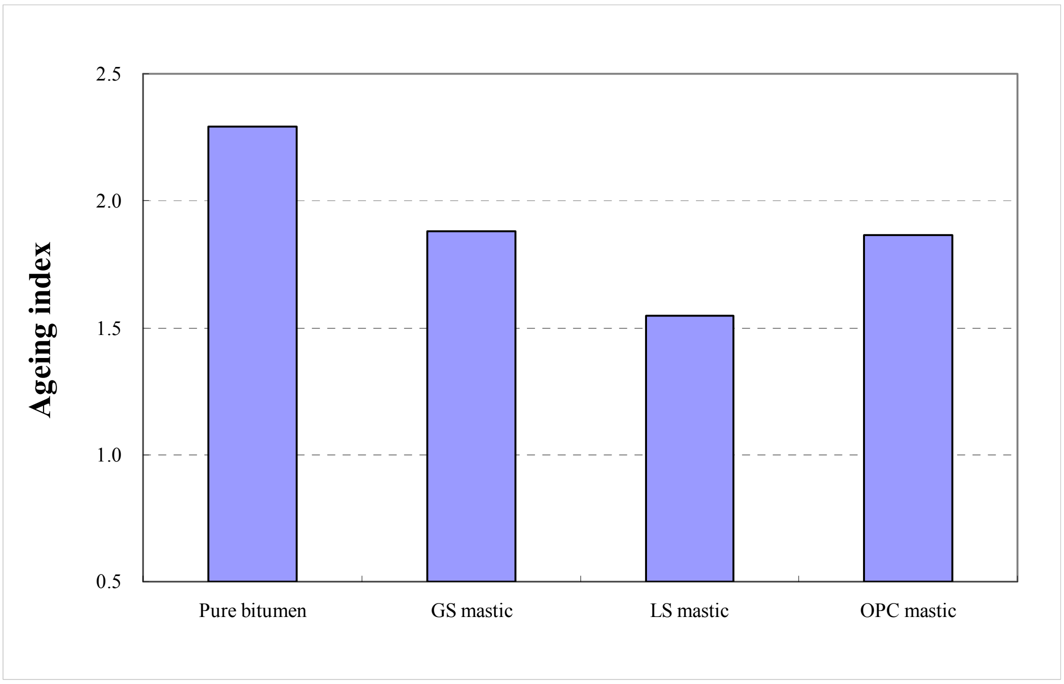


Figure 6.9 Ageing indices for mastics and pure bitumen after 5 hour TFOT ageing

From Figure 6.9, it can be seen that the ageing indices for the 5 hour TFOT aged mastics containing different mineral fillers are all lower than the ageing index for the pure bitumen undergoing the same ageing procedure. This result strongly supports the claim of a SHRP report (Curtis et al., 1993) that the presence of mineral matter (filler, sand and aggregates) delays the increase in the viscosity of binders upon ageing compared to bulk bitumen ageing for equivalent ageing times. Curtis et al. (1993) believed that the difference in viscosity is caused by the mineral particles holding some of the polar functional groups that prevent formation of viscosity build-up. In addition, the result in Figure 6.9 also supports the conclusion in Chapter 5 that the basic limestone has stronger ability in adsorbing the polar components from bitumen than the acidic minerals (e.g. granite and gritstone).

Figure 6.9 has shown the different effects of different fillers on the mastic ageing. However, as stated in Chapter 5, the intensity of the influence of the mineral on ageing keeps changing as the ageing simulation continues due to the changes in its adsorbing and catalyzing abilities. It was felt that an ageing study with only one ageing time is not enough to describe the whole situation about the way mineral filler affects the bitumen ageing. Therefore, mastics containing the acidic gritstone (GS) and the basic limestone (LS) were further studied at different ageing times (1 hour, 3 hours, 5 hours, 10 hours and 20 hours). Figures 6.10 and 6.11 show the complex modulus master curves for gritstone and limestone mastics, which were aged in TFOT oven at 165°C for different ageing times.

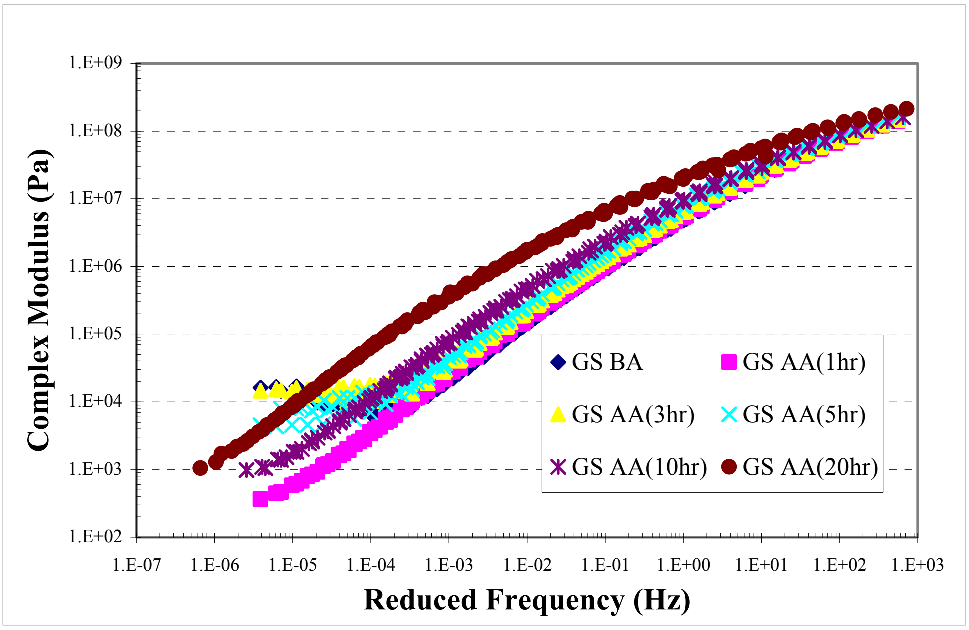


Figure 6.10 Complex modulus master curves for gritstone mastics with different ageing times

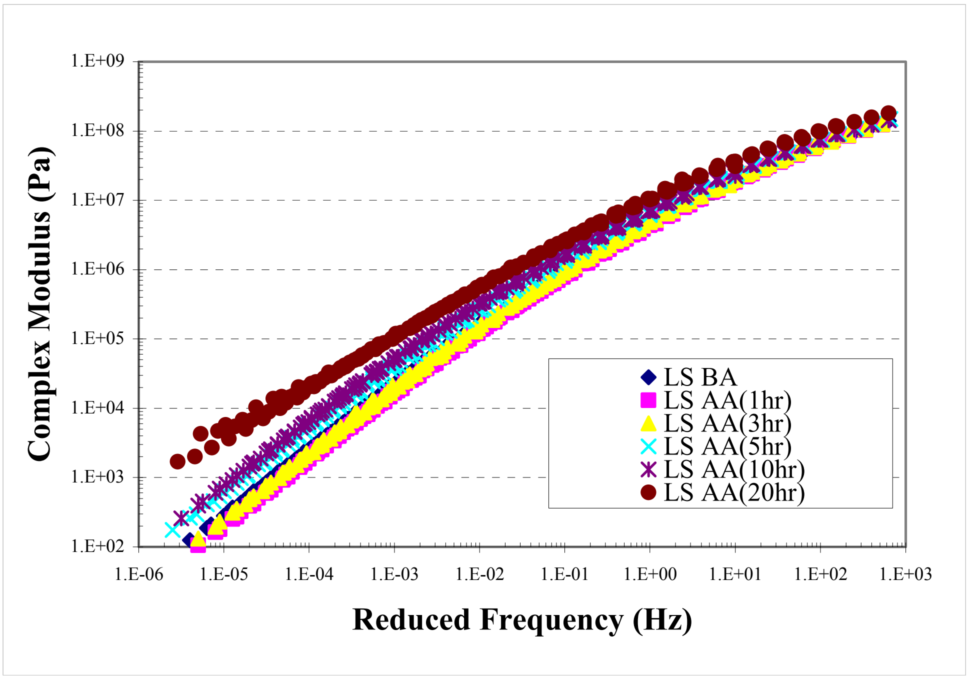


Figure 6.11 Complex modulus master curves for limestone mastics with different ageing times

From these two figures, it can be observed that the gritstone mastic and the limestone mastic hardened in different ways. As expected, the complex modulus of the gritstone mastics increased as the ageing time increased. However, an initial reduction is observed for the limestone mastic modulus, with the lowest value at 1 hour ageing. It is believed that this phenomenon is caused by the adsorption of heavier fractions from bitumen to the mineral surface of the limestone filler.

A composition-related bitumen ageing model depicts ageing happening on two interfaces: the air-bitumen interface and the bitumen-aggregate interface, as shown in Figure 2.11. Analysis based on that figure suggests that several ageing conditions in this study may lead to softer aged mastics than unaged. Firstly, as the materials were not agitated or rotated during the TFOT test, ageing through oxidation and volatile loss might be limited to the 'skin' of the testing samples (Read and Whiteoak, 2003). Secondly, the total surface area of the filler is believed much larger than that of the coarse aggregate with the same volume, which will result in a significantly expanded amount of adsorption of heavier polar fractions from the binder to filler. Finally, although findings from the literature review suggest that the mineral surface of aggregate can catalyse the oxidation of bitumen, in this study, because the fillers were found to settle under gravity to the bottom of TFOT plates due to the relatively high testing temperature, the catalytic action of mineral fillers was considered to be displayed to a limited extent.

Based on the analysis above, it can be seen that most of the factors that can harden the material were limited in this study, while the polar fraction adsorption, which can decelerate the age hardening, was enhanced due to the considerably large surface area. These factors are considered as the main causes for the softer aged limestone mastics than the unaged.

In order to show the effects of different fillers on the mastic ageing more clearly, ageing indices for the pure bitumen and mastics containing different fillers at different ageing stages were calculated using the complex modulus at 35^{o}C and 0.4 Hz. The calculated results are summarized in Table 6.4 and compared in Figure 6.12. It can be seen that, during the whole ageing simulation programme, the ageing indices of limestone mastics are lower than those of the pure bitumen and gritstone mastics, which supports the findings from both the literature review (Anderson et al., 1994) and the study in Chapter 5 that the limestone minerals usually show great adsorption of polar components from bitumen. In addition, it can also be seen from Figure 6.12 that the increase of the ageing index of limestone mastics is not as steep as the other two, which indicates that the function of delaying age hardening by adsorption of polar components from bitumen to limestone is relatively stable and continuous during the whole ageing programme.

With regard to the gritstone mastics, an ageing index slightly higher than that of the pure bitumen after 1 hour TFOT ageing implies that the acidic gritstone surface might have catalyzed the bitumen oxidation at the beginning of the ageing programme. However, as stated above, it was observed that the fillers settled to the bottom of the TFOT plates during the ageing due to the relatively high temperature and, therefore, it is considered that the catalytic effects of the gritstone fillers were limited after the fillers had settled. It can be seen that, after 1 hour ageing, the ageing indices of the gritstone mastics at different ageing stages (3 hours, 5 hours, 10 hours and 20 hours) are all lower than those of the pure bitumen, which indicates that the adsorption action dominated during these ageing stages. However, Figure 6.12 also shows that the increase in ageing index of the gritstone mastic becomes steeper after 10 hour ageing and the slope is generally similar to that of the pure bitumen. This indicates that the adsorption action of the acidic gritstone did not last as long as that of the basic limestone.

Table 6.4 Ageing index calculation for the pure bitumen and mastics at different ageing stages

Ageing times	Pure binder		GS mastic		LS mastic	
	G* (Pa)	AI	G* (Pa)	AI	G*(Pa)	AI
0	3.96E+04	1.00	3.62E+05	1.00	3.40E+05	1.00
1	4.16E+04	1.05	4.13E+05	1.14	2.89E+05	0.85
3	6.23E+04	1.57	5.38E+05	1.49	2.93E+05	0.86
5	9.09E+04	2.29	6.81E+05	1.88	5.27E+05	1.55
10	1.60E+05	4.04	8.90E+05	2.46	6.68E+05	1.96
20	3.65E+05	9.21	2.71E+06	7.49	1.09E+06	3.22

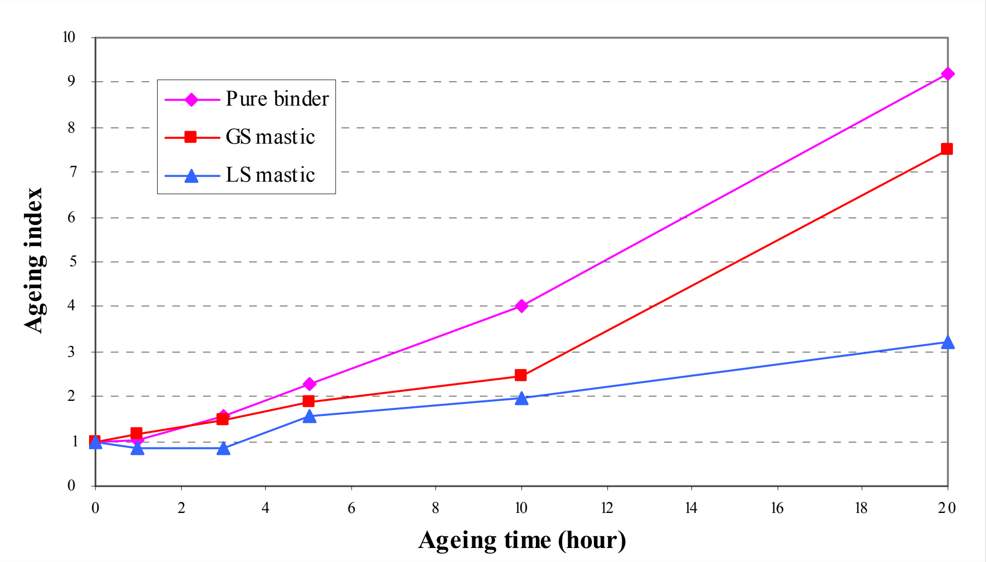


Figure 6.12 Ageing indices of the pure bitumen and mastics at different ageing stages

6.4.2 The effect of mineral fillers on the binders recovered from mastics

In order to assess the influences of different fillers on the ageing of bitumen that is in contact with fillers, binders were recovered from all the aged mastics and were subjected to the DSR frequency sweep test with almost the same testing conditions as above but a strain control of 0.5%.

Figure 6.13 gives the complex modulus master curves of binders recovered from the 5 hour aged mastics. The three completely different curves for the recovered binders indicate that fillers can significantly influence the ageing properties of binder in contact with them. In addition, from this figure, it can be observed that most binders recovered from 5 hour aged mastics are softer than the 5 hour aged pure bitumen; and the binder recovered from 5hr aged LS mastic is even softer than the unaged pure binder. These results have further proved the claim of Curtis et al. (1993) that the presence of mineral matter can delay the age hardening of bitumen by holding the polar functional groups of bitumen on the mineral surface; these adsorbed components, as stated by Petersen et al. (1974 (a)), could not be completely recovered by the normal bitumen recovery techniques.

By comparing the results in Figures 6.8 (for mastics) and 6.13 (for recovered binders), more obvious differences among the complex moduli of recovered binders are observed than those of the mastics at the same ageing stage (5 hours). This is considered to result from the different abilities of the various fillers in absorbing and adsorbing fractions from bitumen and the resistance of the interactions (adsorption) on binder recovery. Such phenomena will be discussed more quantitatively based on the test results of the binders recovered from gritstone and limestone mastics at different ageing stages.

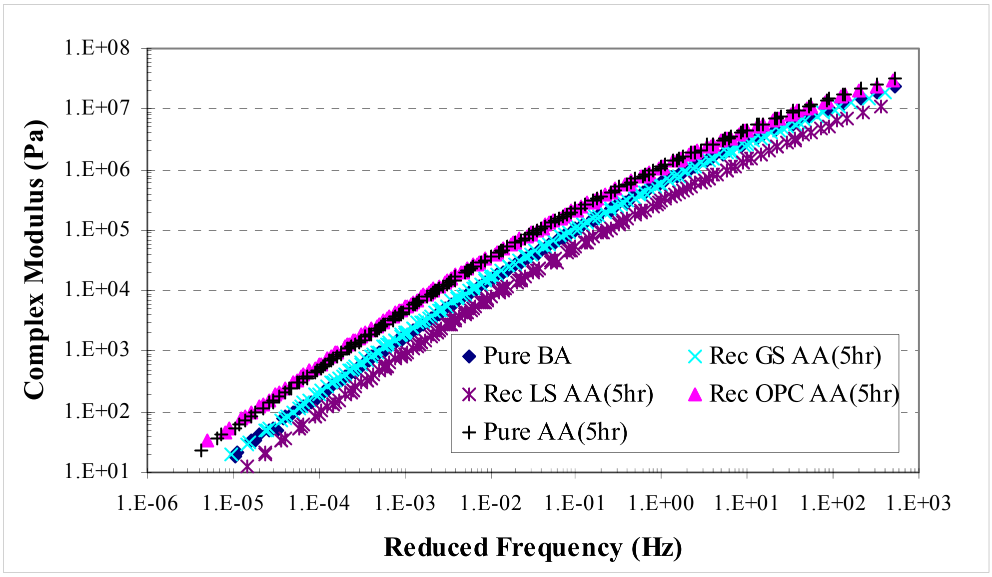


Figure 6.13 Complex modulus master curves for binders recovered from different mastics (5 hour aged)

The complex modulus master curves for binders recovered from GS mastics and LS mastics at different ageing stages are presented in Figures 6.14 and 6.15. Based on these results, the ageing indices in terms of complex moduli at 35^{o}C and 0.4 Hz were calculated in Table 6.5 and graphically presented in Figure 6.16.

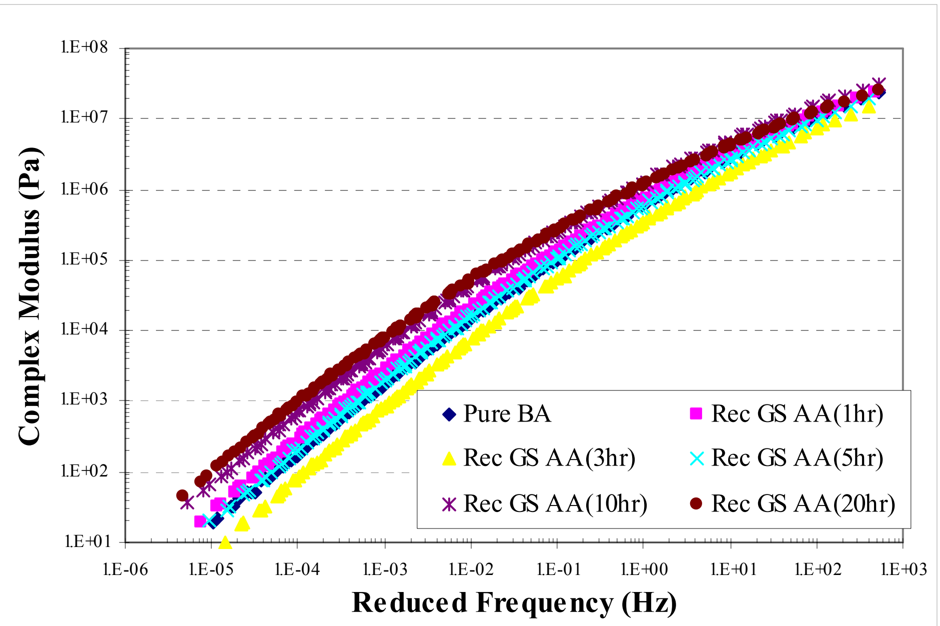


Figure 6.14 Complex modulus master curves for binders recovered from GS mastics with different ageing times

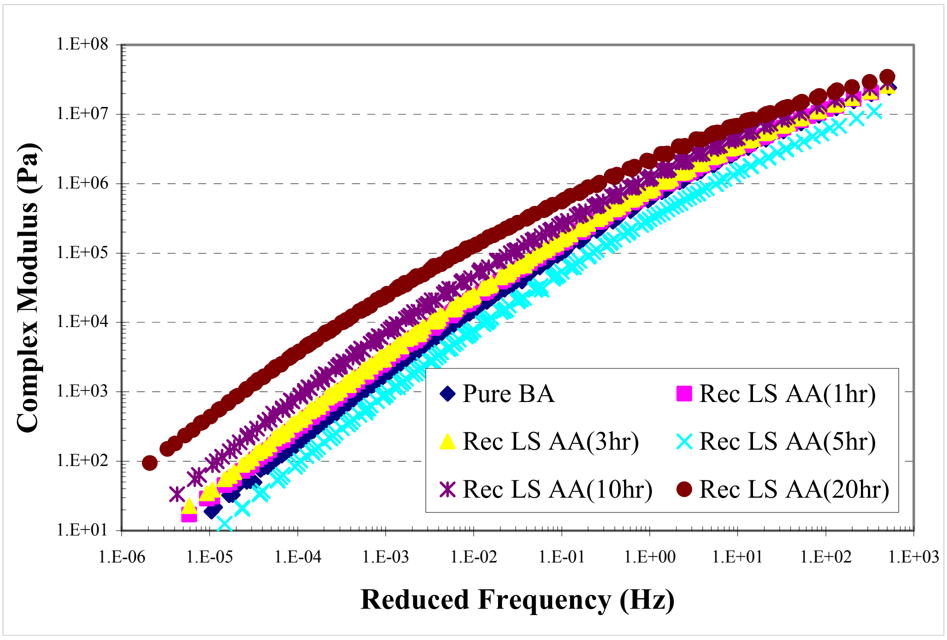


Figure 6.15 Complex modulus master curves for binders recovered from LS mastics with different ageing times

Table 6.5 Ageing index calculation for the pure bitumen and binders recovered from mastics at different ageing stages

Ageing times	Pure binder		Binder from GS mastic		Binder from LS mastic	
	G* (Pa)	AI	G* (Pa)	AI	G*(Pa)	AI
0	3.96E+04	1.00	3.96E+04	1.00	3.96E+04	1.00
1	4.16E+04	1.05	5.08E+04	1.28	5.66E+04	1.43
3	6.23E+04	1.57	2.21E+04	0.56	6.45E+04	1.63
5	9.09E+04	2.29	4.54E+04	1.15	2.31E+04	0.58
10	1.60E+05	4.04	1.07E+05	2.69	1.11E+05	2.79
20	3.65E+05	9.21	1.20E+05	3.03	2.43E+05	6.14

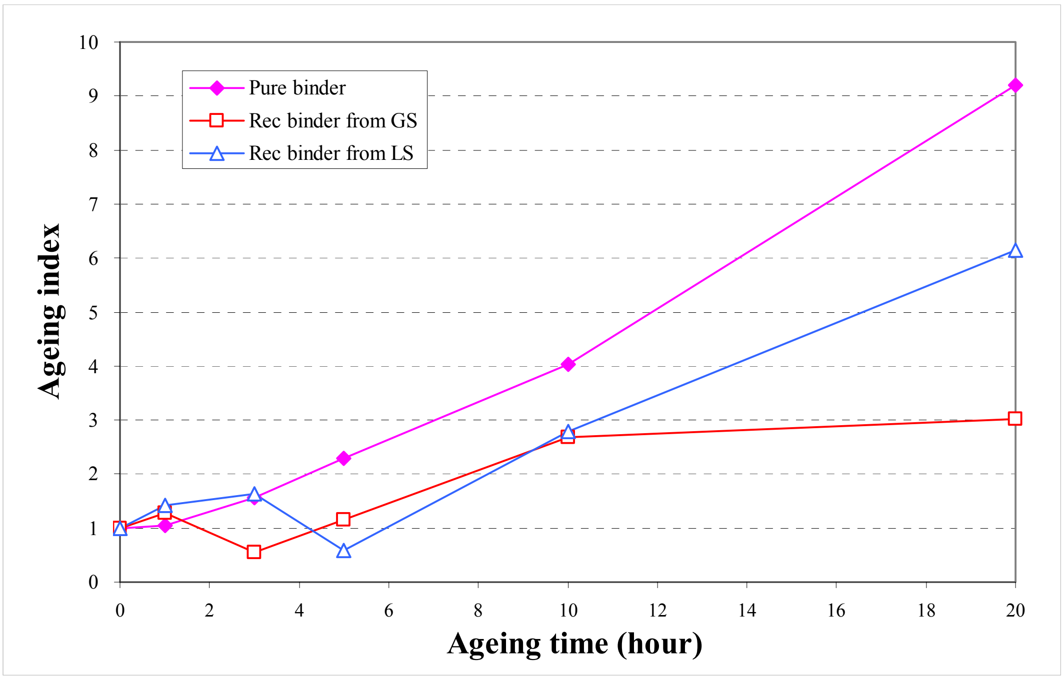


Figure 6.16 Ageing indices of the pure bitumen and binders recovered from mastics at different ageing stages

From Table 6.5 and Figure 6.16, it can be seen that most of the ageing indices in terms of complex moduli for binders recovered from limestone mastics are higher than those for the binders recovered from gritstone mastics. This indicates that more age hardening has been experienced by the binders recovered from limestone mastics. However, this result is completely opposite to the result for the mastic mixtures, as shown in Figure 6.12. In order to establish the causes for the higher stiffness for the binders recovered from limestone mastics than those recovered from gritstone mastics, the chemical changes of bitumen during ageing were tested using FTIR. Figure 6.17 shows the scan results for the binders recovered from 3 hour aged mastics. In addition, according to this scan result, the spectrometric indices of the main oxygenated products due to age hardening, carbonyl and sulphoxide, were calculated and presented in Table 6.6. From Table 6.6, it can be seen that the binder recovered from limestone mastic contains more oxygenated products, which explains the reason for its higher stiffness than the binder recovered from gritstone mastic. With regard to the lower ageing indices of limestone mastics than those of gritstone mastics, a reasonable explanation for this is that, although there are more oxygenated products within the binders recovered from limestone mastics, a large proportion of them did not contribute to the mastic stiffness build-up due to the greater ability of the limestone filler to adsorb and hold these polar components on its surface.

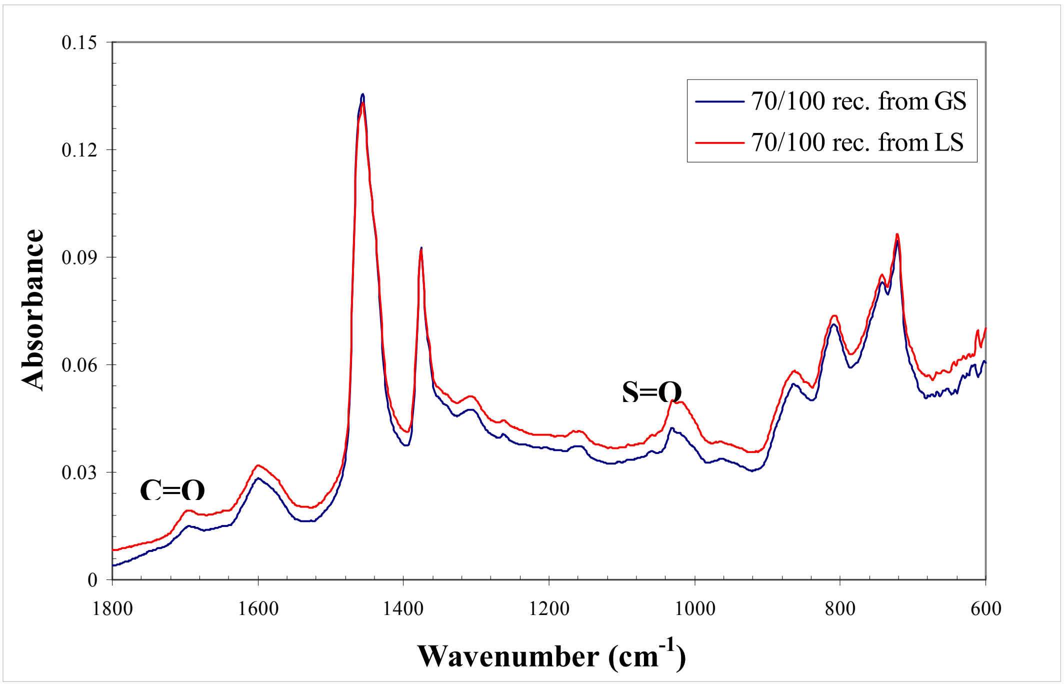


Figure 6.17 Expanded FTIR results of 1800 to 600 cm^{-1} for binders recovered from 3 hour aged mastics

Table 6.6 Spectrometric indices for the oxygenated functions in the binders recovered from 3 hour aged mastics

Binders	Carbonyl index – $A_{1700}/\sum A$	Sulphoxide index – $A_{1030}/\sum A$	$A_{1700}/\sum A+ A_{1030}/\sum A$
Recovered from GS mastic	0.0036	0.0121	0.0157
Recovered from LS mastic	0.0053	0.0195	0.0245

It has been stated by Anderson et al. (1994) that the mineral aggregates showing the largest adsorption (e.g. limestone) exhibit the smallest catalytic effect on bitumen ageing. This point has been proved to be correct in Chapter 5 and the analysis above has also proved the greater ability of limestone in adsorbing polar components from bitumen. However, with regard to the catalytic effect, the results in Figure 6.16 show that the ageing indices of the binders recovered from limestone mastics after 1 hour and 3 hours ageing are higher than those of the pure binder and the binders recovered from gritstone mastics. This appears to indicate that the limestone can also significantly catalyze the bitumen oxidation. It is felt that more limestone fillers from different sources should be tried in future studies so that the catalytic abilities of limestone may be more rigorously assessed. This is because the mineral materials (aggregate, sand or filler) from different sources may contain varying kinds of metal salts which, as stated by Knotnerus (1971), can significantly catalyse bitumen oxidation.

Another interesting phenomenon that should be noted is that, from Table 6.5, the binders recovered from the mastics after short-term ageing (1 hour aged for gritstone mastic, 1 hour and 3 hour aged for limestone mastic) are harder than the pure bitumen for the same ageing times. However, as the ageing simulation proceeded, the recovered binders became softer than the pure binder at the equivalent ageing times. This order change might be caused by several possible factors which are introduced as follows.

Firstly, a small part of the polar components that was adsorbed by the fillers might not be completely extracted during the bitumen recovery. Figure 6.18 shows a visual comparison between the residual limestone filler from bitumen recovery and the original one. This comparison implies that some interactions between the polar components of bitumen and the mineral surface may be irreversible. In order to prove this, attempts were made to test the residual filler from binder recovery using the FTIR test and to compare the results with those of original ones. The ‘pellet’ sample preparation method, which has been introduced in Chapter 3, was adopted. In this preparation method, the tested filler was mixed with dry KBr powder and the mixed filler-KBr was then placed between two highly polished stainless steel dies inside a pellet press, where it was compressed at 25,000 Pa for 1 min to make a small pellet. A pellet of the same mass using pure KBr was similarly prepared for obtaining background comparisons. Figure 6.19 shows the test results for the original limestone filler and the residual filler from 20 hour aged limestone mastics. By comparing with the spectrum for the original filler, two new peaks (at around 790 and 1000 cm^{-1}) can be observed in the results of the residual filler, proving that some interactions between the polar components of bitumen and the mineral surface of the filler are irreversible.

Figure 6.18 Comparison of original limestone filler (left) and the residual one from binder recovery

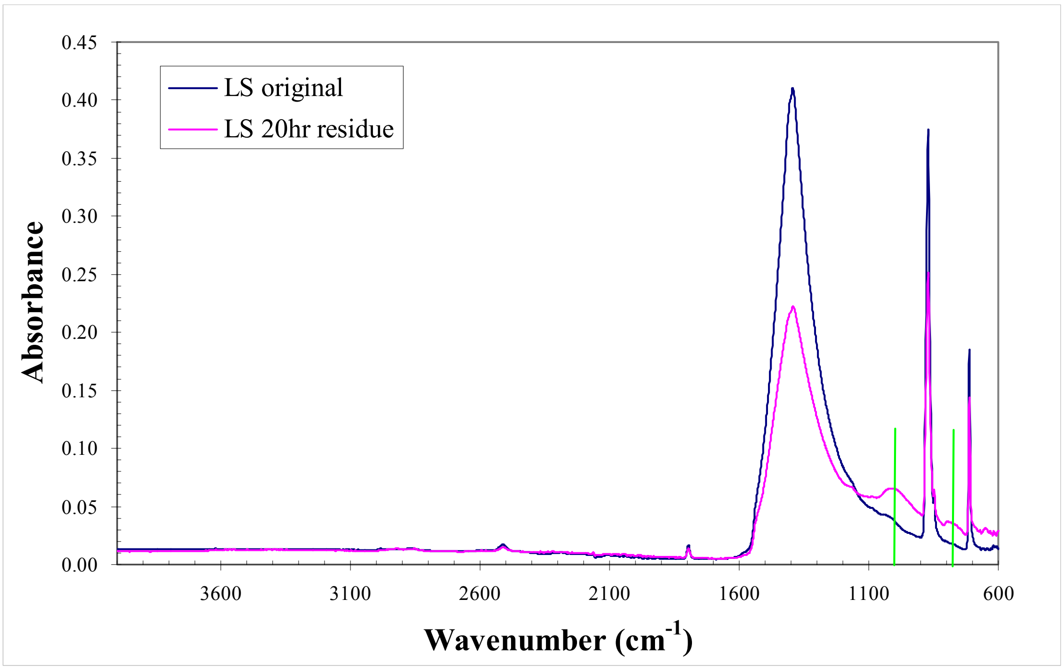


Figure 6.19 FTIR results for original limestone filler and residual filler from 20 hour aged limestone mastic

Another possible factor to which the characteristically softer recovered binders, compared to the pure binder with the same ageing time (as seen in Table 6.5), may be attributed is that fillers might have absorbed some oily and/or less polar components from bitumen during ageing, which could protect these components from oxidation and evaporation. As stated in Chapter 2, the absorption mainly results from the movement of oily components that exude from the bitumen into the mineral matters; the connection of the absorbed components to the mineral aggregate is much weaker than that of the adsorbed polar components. Therefore, these absorbed (protected) components are easier to extract during bitumen recovery, which will lead to a higher proportion of oily components in recovered binders than in aged pure binders. In this way, the binders recovered from aged mastics become softer than the pure binder with the equivalent ageing times.

According to the above analysis, the different effects of mineral fillers on the ageing of mastics and their recovered binders are summarized in Table 6.7. From this Table, it can be seen that, for a mastic with a particular filler, there are always counteractive factors affecting the ageing of both the mastic and its recovered binder. In addition, as concluded in Chapter 5, the strength of these affecting factors changes continuously as the ageing proceeds. Therefore, the development of ageing indices of mastics and their recovered binders is mainly dependent on which factor is dominant at that particular ageing stage. It is believed that the irregular development of ageing indices of mastics and their recovered binders is mainly caused by these continuously changing factors.

Table 6.7 Different effects of mineral fillers on the ageing of mastics and thier recovered binder

Factors	Effect on mastics	Effects on recovered binders
Catalysis	+	+
Adsorption	−	−
Absorption	+	−

+ Accelerating effect
− Decelerating effect

6.5 Influence of Binder Recovery Technique

The binder recovery technique through solvent extraction is a process that has been found by researchers (Branthaver et al., 1993) to have a significant effect on the properties of the recovered binder. The mastic ageing study introduced above has already given some indication about how the binder recovery technique affects the properties of recovered binders. However, there are still several uncertain aspects that need to be checked by further tests.

6.5.1 Influence of dissolving time

It was found that some heavier fractions adsorbed by fillers from bitumen were not recovered after the binder recovery. However, it was unclear whether this was because this portion of adsorption is irreversible, or this was caused by an insufficient dissolving time of mastics during the recovery. Therefore, three samples of 10 hour aged limestone mastics were recovered separately with different dissolving times: 8 hours (normal time), 24 hours and 48 hours. The complex modulus and phase angle master curves made from the DSR results for these three binders are presented in Figures 6.20 and 6.21. These coincident master curves indicate that the incomplete recovery of bitumen components was not caused by an inadequate dissolving time of bitumen in the dichloromethane solvent. Therefore, it can be concluded that the adsorption of some bitumen fractions is irrecoverable using current recovery techniques.

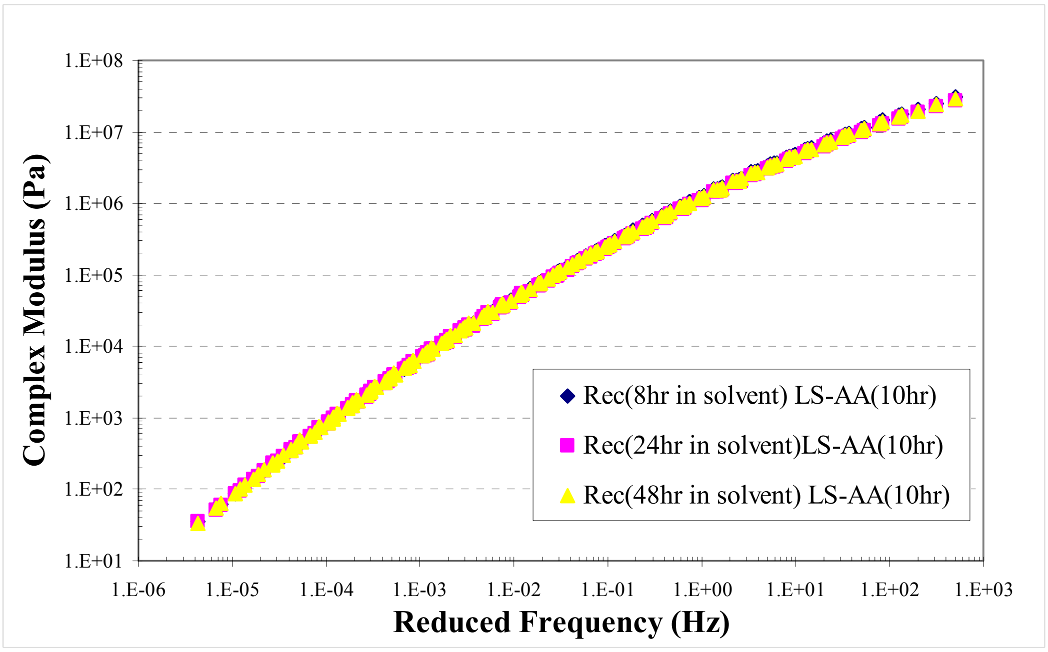


Figure 6.20 Complex modulus master curves for recovered binders with different dissolving time

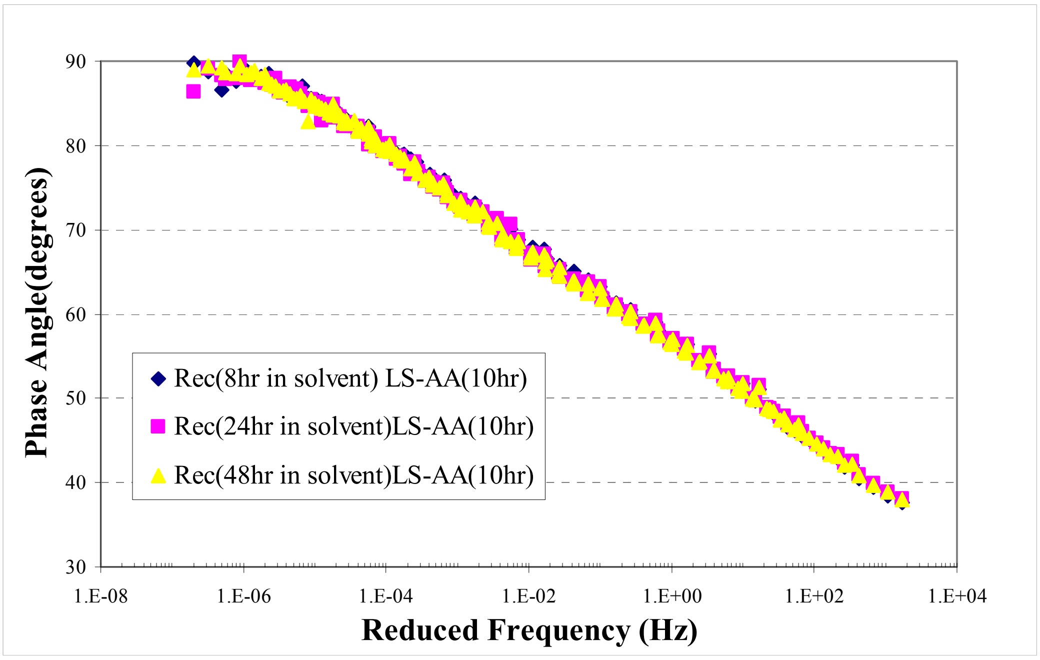


Figure 6.21 Phase angle master curves for recovered binders with different dissolving time

6.5.2 Influence of completeness of solvent evaporation

With regard to the phenomenon that some recovered binders were softer than the virgin binder, it was suggested that this could be caused by irreversible adsorption of heavier fractions and the recovery of absorbed oily fractions from the filler back to bitumen. However, there is another possible cause that could lead to this result. Some chemical compositions from the solvent that was used in binder recovery might remain in the binder, which could also result in a decreased bitumen stiffness. Therefore, a simple test was carried out to check this problem.

Instead of mastic, pure binder was dissolved in the recovery solvent. After that, the recovery evaporation system was used to remove the solvent. The DSR test was then applied to the 'recovered' binder and the test results are shown in Figures 6.22 and 6.23. From these figures, it can be seen that the 'recovered' binder did not become softer than the virgin one. Instead, the 'recovered' binder is slightly harder after completion of the recovery procedure. This phenomenon has been pointed out in a British Standard (BS EN 12697-4: 2005), which states that the use of the hot extraction methods in EN 12697-1 may harden the binder. Therefore, it can be concluded that the softening of recovered binders was not caused by the incomplete evaporation of the recovery solvent (dichloromethane).

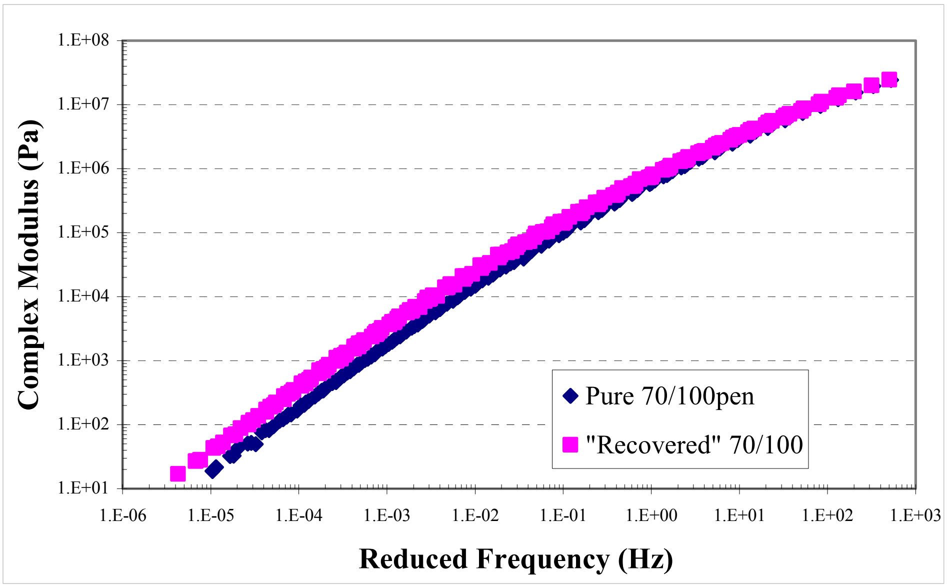


Figure 6.22 Complex modulus master curves for 70/100 pen binder and its 'recovered' binder

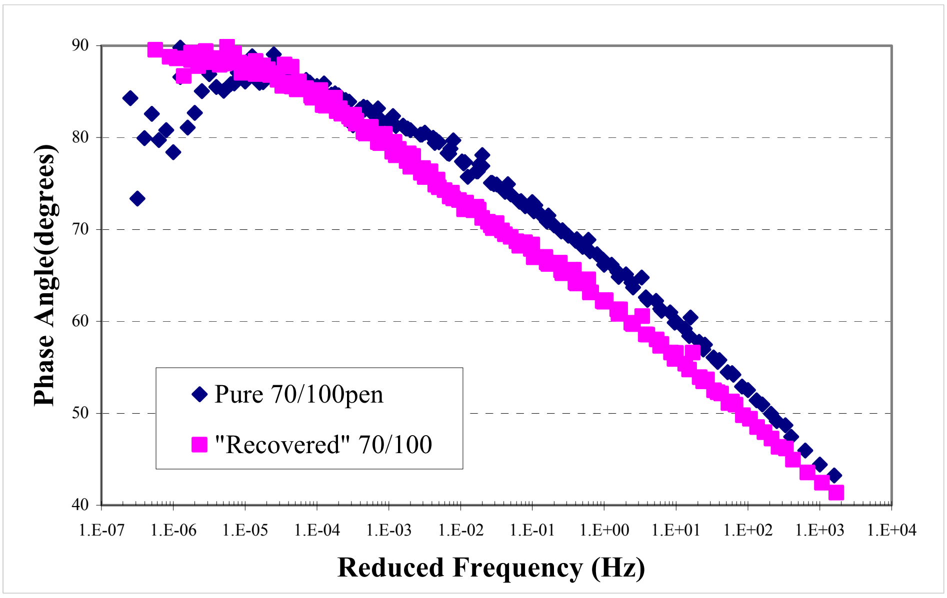


Figure 6.23 Phase angle master curves for 70/100 pen binder and its 'recovered' binder

6.7 Summary and Discussion

In this study, a pure binder and mastics containing different fillers were artificially aged in the TFOT oven at 165°C for differing ageing times (1 hour, 3 hours, 5 hours, 10 hours and 20 hours). The ageing indices in terms of complex moduli of the mastics and their recovered binders were calculated and compared with those of the pure binder. In addition, the FTIR test was applied to the binders recovered from mastics at different ageing stages so that the influence of mineral filler on the bitumen chemical changes due to the artificial ageing could be detected.

The results of the experiments indicated that the ageing properties of bitumen-filler mastics can be significantly affected by the varying types of mineral fillers they contained. In general, the mineral fillers can influence the ageing of mastics in the following ways.

Firstly, mineral fillers can catalyze the oxidation of bitumen components. This was due to higher ageing indices of the 1 hour aged gritstone mastics, the recovered binder from 1 hour aged gritstone mastics and the recovered binders from 1 and 3 hour aged limestone mastics compared to that of the pure bitumen with the same ageing time. It should be noted that, although the results of FTIR and DSR testing conducted on the recovered binders implied that the limestone fillers in this study had stronger catalytic effects on bitumen oxidation, which differed from the claim of Anderson et al. (1994) that limestone exhibits the smallest catalytic effect on bitumen oxidation, it is felt that the catalytic effects of the limestone filler in this study might not be caused by its main component ($CaCO_3$), but by some metal salts it contained. Therefore, further research utilising more limestone fillers from different sources is recommended so that the effects of limestone mineral on bitumen ageing can be exhaustively studied.

Secondly, different fillers can adsorb different amounts of polar components from bitumen which, as stated by Curtis et al. (1993), can delay the increase of the stiffness of bituminous materials upon ageing by holding the polar components of bitumen on the surface of mineral particles. In this study, the FTIR and DSR testing carried out on the recovered binder indicated that more oxygenated products were formed in the binders from limestone mastics than in the binders from gritstone mastics, whereas the ageing indices in terms of mastic complex modulus showed that stronger age hardening has happened to the gritstone mastics. This phenomenon supported the observation by Anderson et al. (1994), that limestone has the greatest adsorbing ability among most of the commonly used mineral aggregates in pavement engineering. In addition, the results of FTIR tests on the pure limestone filler and the residual ones from binder recovery showed that some parts of the adsorbed components are difficult to extract by the normal recovery techniques.

The absorption of oily components from bitumen to aggregate was summarised by Petersen (1984) as one of the main composition-related factors that can cause the age hardening of bituminous materials. However, it was found to be difficult to detect the movement of these oily components during the ageing and it is highly suspected that major parts of the absorbed oily components are recoverable by the bitumen recovery technique due to their weaker connection to the minerals than the adsorbed polar components. It is recommended that the column chromatography analysis should be used in the future studies so that the different absorbing abilities of different mineral fillers could be compared.

According to the above analysis, a simplified procedure for the ageing studies utilising binder recovery technique is summarised in Figure 6.24, from which, the problems of using binder recovery technique in bitumen ageing studies can be observed. As shown in Figure 6.24, mineral materials (fillers in this study) can adsorb polar components and absorb oily components during ageing. The results of experiments in this study implied that these absorbed and adsorbed components might have only made a tiny contribution in the build-up of the rheological properties of mastics; it was the part of bitumen (Binder②), excluding these ab/adsorbed components, that acted as the binder in the aged bitumen-filler mastics. However, analysis based on the testing results of this study also indicated that part of the adsorbed polar components and most of the absorbed oily components can be recovered by binder recovery, which means that the recovered binder (Binder③) used in the FTIR and DSR analysis is neither the binder initially used in the mixture (Binder①) nor the part which coated the outside of the filler particles (Binder②). It is, therefore, not recommended to use bitumen recovery techniques in ageing studies on bituminous materials.

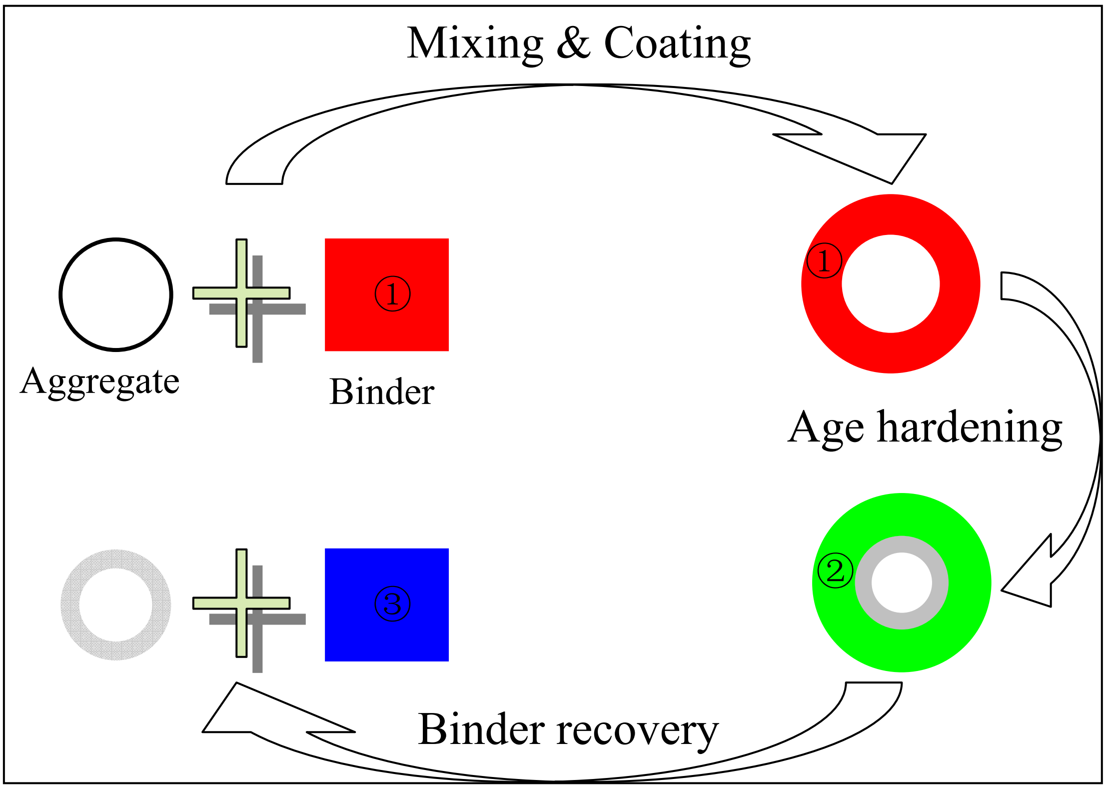


Figure 6.24 General procedure of bituminous mixture mixing, ageing and recovery

7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The principal conclusions which can be drawn from the literature review summarised in Chapter 2 of this thesis include:

- For a pavement constructed strictly according to current specifications, which attempt to account for durability, damage due to moisture and age hardening are the two main factors that can significantly affect the durability of bituminous paving materials.

- A reasonable level of age hardening in pavement layers has been commonly viewed as being beneficial. However, excessive age hardening can result in both structure failure (cracking damage) and surface failure (loss of materials at the surface layer) to the pavement.

- Due to the extremely complicated composition of bitumen, the number of factors that can influence bitumen age hardening is substantial. However, the most important aspect of a durable bitumen is its resistance to chemical composition changes, which include: loss of oily components of bitumen by volatility or absorption by porous aggregates, change in chemical composition of bitumen molecules from reaction with atmospheric oxygen and molecular structuring that produces steric hardening.

- Ageing of the binder in a bituminous mixture manifests as an increase in its stiffness. The degree of hardening is due to changes which produce an increase in the total associating polarity of bitumen, the strength of the polar associations and the dispersing capacity of the non-polar components in solvent moiety.

- Besides absorbing oily components from bitumen, mineral aggregates can affect bitumen age hardening in two added ways. Firstly, the charged and polarised aggregate surface can interact with (adsorb) polar groups (either naturally occurring or the oxidation products) in bitumen, which can decelerate the bitumen age hardening. In addition, some mineral components on the aggregate surface can catalyze bitumen oxidation. It should be noted that these ab/adsorbing and catalytic effects on bitumen age hardening vary from aggregate to aggregate.

- Oxidation catalysts are found naturally present in the more polar fractions and can promote the air oxidation of the saturate fractions. However, these polar oxidation catalysts in asphaltenes can also be adsorbed on, and therefore deactivated by, the mineral aggregate surface.

- An adequate bitumen film thickness is essential for a bituminous paving mixture to survive its design life. Whereas a thicker bitumen film will result in a low asphalt stiffness and a large construction cost. A rational bituminous paving mixture design must keep the binder content to a minimum while satisfying specification criteria (thick enough to ensure adequate resistance to age hardening and moisture damage).

The principal conclusions which can be drawn from the experimental work presented in this thesis include:

- The pure bitumen ageing study showed that different pure bitumen ageing simulation methods can harden the bitumen in different ways. Although similar results of penetration and R&B SP tests were obtained for the binders aged by RTFOT and High-shear mixer, the FTIR test indicated that more oxygenated products were formed in the RTFOT aged binder, which implied that the High-shear aged binder might have reached a similar penetration and R&B SP results by evaporating more volatiles during the 2.5 day High-shear ageing simulation. In addition, the results also indicated that DSR testing might be more sensitive to the changes in polar components within the bitumen than the empirical penetration and R&B SP tests, since the complex modulus was observed to be much higher for the RTFOT binder which, as stated above, contained larger amounts of oxygenated products.

- The study on the effects of binder film thickness on ageing showed that the binder content (film thickness) in asphalt mixtures can significantly influence the ageing of bituminous material. A fairly good correlation was obtained between the bitumen film thickness and the stiffness of both the asphalt mixture (ITSM stiffness) and the recovered binder (DSR complex modulus). It was found that, with the same ageing time, asphalt mixtures with thinner binder film thickness can be affected by age hardening more strongly, and binders recovered from these mixtures have much higher stiffness. In contrast, as the binder film thickness increased, its influence to the ageing properties of both the asphalt mixtures and bituminous binders became smaller and stabilised, which indicated that with thicker binder films, the ageing of bituminous materials will be less sensitive to the changes in film thickness.

- Evidence was provided in Chapter 5 to show that both the bitumen and aggregate types can affect the ageing characteristics of bituminous materials. It was found that, with a particular bitumen, stronger age hardening has happened to the binders in granite (acidic aggregate) mixtures than the binders in limestone (basic aggregate) mixtures. The results support the findings from the literature review that the aggregates with the least adsorption of highly polar fractions (e.g. quartzite and granite) exhibit the greatest catalytic effect in bitumen oxidation, whereas those showing the largest adsorption (e.g. limestone) exhibited the smallest catalytic effect. In addition, it was also found from this study that, for a particular bitumen, the aggregate type appears to influence whether the majority of the total age hardening occurs in the early ageing period or in the subsequent periods.

- The adsorbing and catalytic effects of mineral materials on bitumen age hardening were presented more clearly in the bitumen-filler mastic ageing study due to the extremely large specific surface area (which measures the total surface area per unit of mass) of the fillers. In addition, it was observed that the ageing indices of the limestone mastics were lower than those of the gritstone mastics, whereas the binders recovered from limestone mastics had higher ageing indices and contained more oxygenated products. This observation indicates that limestone can adsorb more polar components from bitumen (which supports the findings in literature review); and these adsorbed polar components might not have played a major role in the mastic stiffness build-up.

- Analysis based on the results of experiments in the bitumen-filler mastic ageing study showed that the binders recovered from bituminous mixtures, in which strong absorption and adsorption has happened, may be significantly different from the part of bitumen (effective binder) that acts as the binder in the mixture. It is considered that this is the main cause of the phenomenon that the ageing indices of limestone mastics are lower than those of the gritstone mastics, whereas the ageing indices of the recovered binders from limestone mastics are mostly higher than that of the binders recovered from gritstone mastics.

7.2 Recommendations

Based on the findings from both the literature review and the experimental work presented in this thesis, the following recommendations are made:

- Further investigations are necessary to extend the main findings of this research using a wider range of materials. These should embrace a wider range of paving-grade bitumens obtained from different crude oil sources with greater compositional diversity than those evaluated in this research. A wider range of mineral aggregates commonly used in bituminous paving mixtures should also be investigated. Although findings from this study have shown the influences of different mineral types (acidic and basic) on bitumen ageing, it was found that some major effects might not be caused by the main components that compose the mineral matter (e.g. $CaCO_3$ in limestone), but by some minor components the mineral matter contained. Therefore, mineral materials (fillers or aggregates) with same type but from different sources are also recommended in the future study; and their chemical compositions are suggested to be tested before the ageing study.

- Findings from the literature review showed that the aggregate can significantly promote the oxidation of the saturate fraction, and the promoting ability of aggregate surface appears to decrease with the increasing polarity of the bitumen fractions. In addition, results of experimental work in this thesis showed that the adsorption of polar components can restrain the catalytic effects of mineral aggregates on bitumen ageing. Therefore, an asphalt mixture ageing study or a bitumen-filler mastic ageing study utilising bitumens from the same source but with different proportion of polar fractions is recommended, so that the catalytic and adsorbing effects of the mineral matters on bitumen ageing can be presented more quantitatively.

- Different pure bitumen ageing simulation methods can significantly affect the bitumen ageing mechanism due to the differences in their ageing times, testing temperatures, oxygen supplies and the volumetric states of the bitumen during ageing. A study involving rheological simulation of the bitumen behaviour in different ageing methods, chemical tests for bitumen component changes and DSR rheological test is therefore strongly recommended. The rheological simulation should be able to simulate not only the rheological movement of the bitumen in different ageing methods, but also the volatile evaporations and the oxygen uptakes according to the testing temperatures, oxygen supplies and the contact surfaces of the bitumen to the air. In such a way, by combining the results of chemical and DSR testings, simulation models for different pure bitumen ageing methods might be developed.

- It was found to be difficult to control the air void contents of asphalt specimens cored from compacted slabs, which could affect the accuracy of the analysis on the effects of aggregate types on bitumen ageing. Therefore, it is recommended that the gyratory compaction method be used for asphalt specimen compaction so that the air void contents of the fabricated specimens can be controlled at a similar level.

- The bitumen-filler mastic ageing study demonstrated the catalytic and adsorbing effects of mineral fillers on bitumen ageing. However, it was felt that the catalytic effects might have been restrained due to settlement of the fillers to the bottom of the TFOT plates. Therefore, it is highly recommended that lower temperature should be used in future studies on bitumen-filler mastic ageing to prevent the fillers from settling. In addition, compressed air (or oxygen) is suggested to be supplied during the ageing simulation so that the effects of mineral fillers on bitumen oxidation can be shown more clearly. Accordingly, a bitumen-filler mastic ageing study using Pressure Ageing Vessel (PAV) with a temperature of 85°C and a pressure of 2.07 MPa is recommended in future investigation.

- Evidence was provided to show that the ageing indices of bitumen-filler mastics were all lower than those of the pure bitumen ageing after long time ageing simulation. It was also stated in the literature that most of the fillers are embedded in the bitumen and it is the bitumen-filler mastic that should be viewed as the binder for the asphalt mixture. Therefore, it would be interesting to make a comparison between a bitumen-filler mastic and a pure bitumen with similar stiffness with the mastic by mixing these two different 'binders' with the same aggregate (same type and same batching detail) and with the same 'binder content' by volume. The ageing indices in terms of asphalt mixture stiffness can be calculated and compared after different ageing times so that the effects of mineral fillers on the ageing of bituminous mixture can be investigated.

- Analysis based on the results of bitumen-filler mastic ageing study showed that the recovered binder (Binder③ in Figure 6.24) is different from the binder coating the outside of the aggregate (Binder② in Figure 6.24). It is felt that more attention should be paid to Binder② as it is this part of binder that contributes the most in the build-up of the mixture mechanical properties. Therefore, it is desirable that the bitumen should be aged on aggregate surface and its rheological properties could be tested directly without running the bitumen recovery technique. The DSR testing with modified spindles that was introduced in Section 3.4.5 is suggested to be used in the further studies. Some preliminary work has been done, which is presented in Appendix B. However, it was found that the precision of aggregate plate fabrication and details of ageing procedures still requires further improvement so that repeatable testing results could be obtained.

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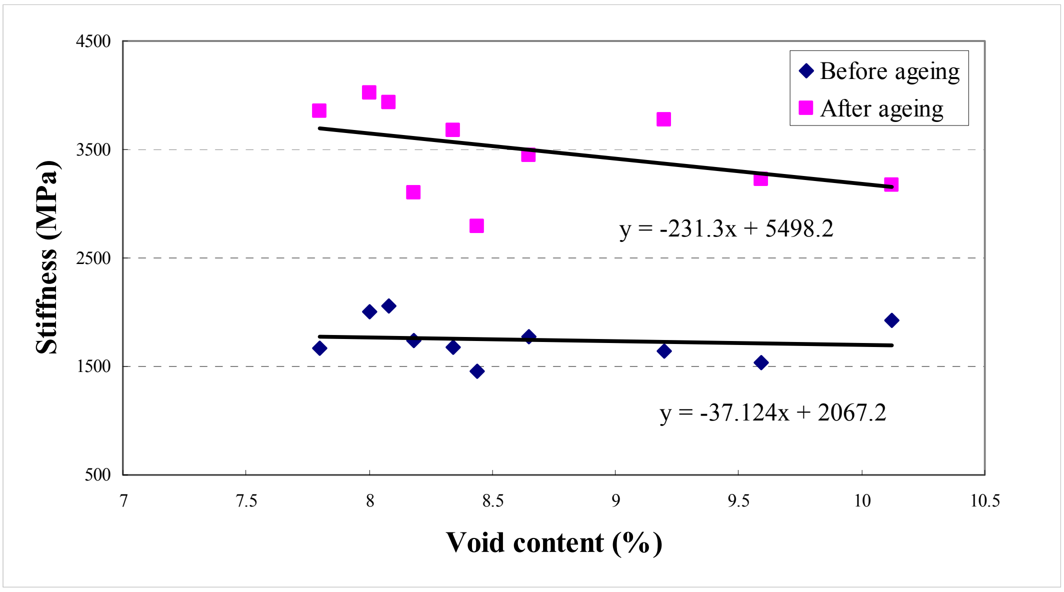
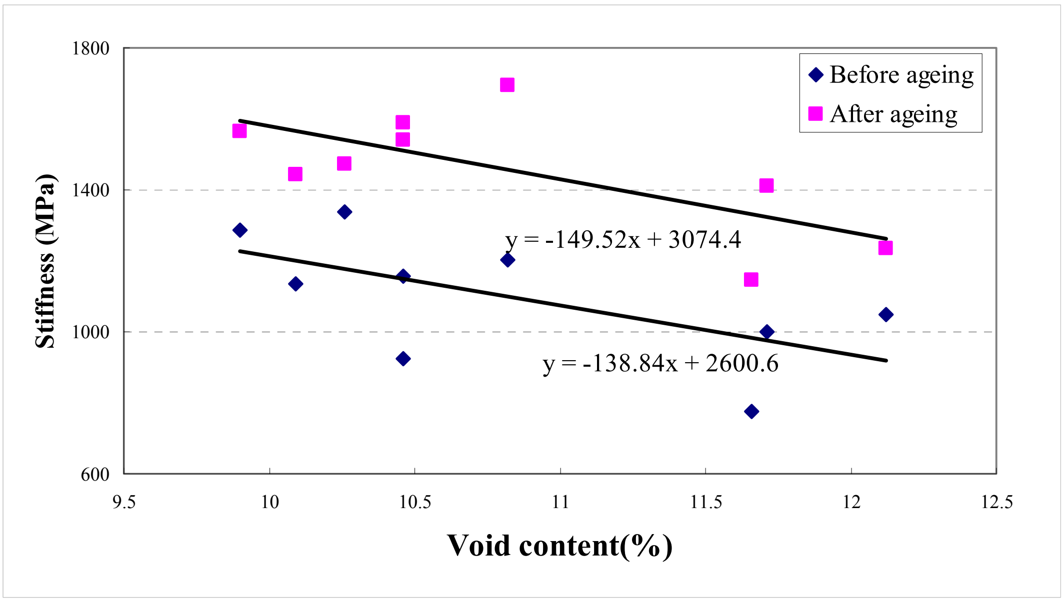
Appendix A
Plots of ITSM Stiffness Versus Air Void Content

For LV_U Group



For GV_U group



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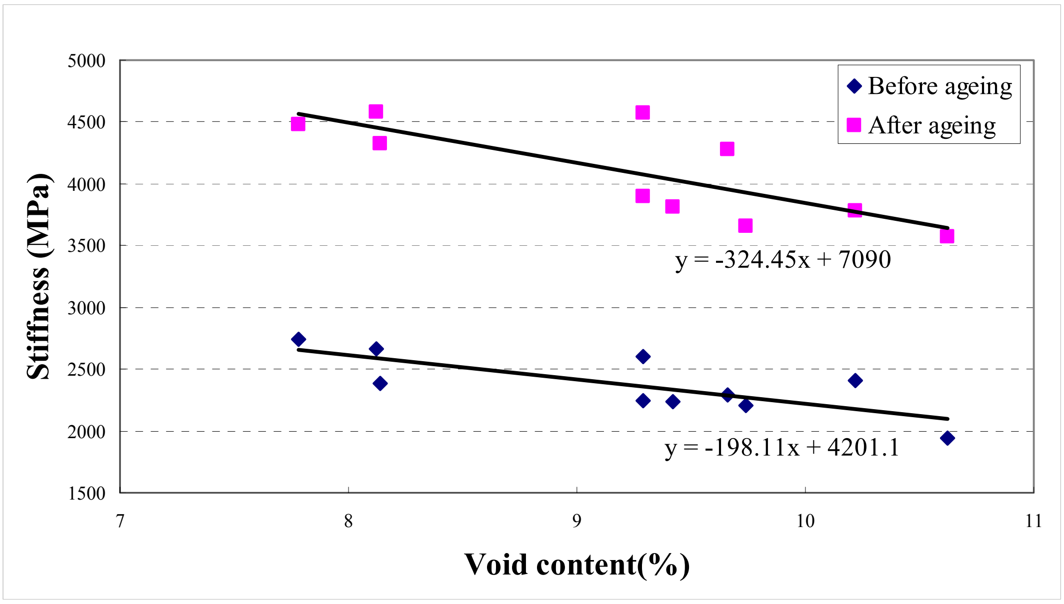

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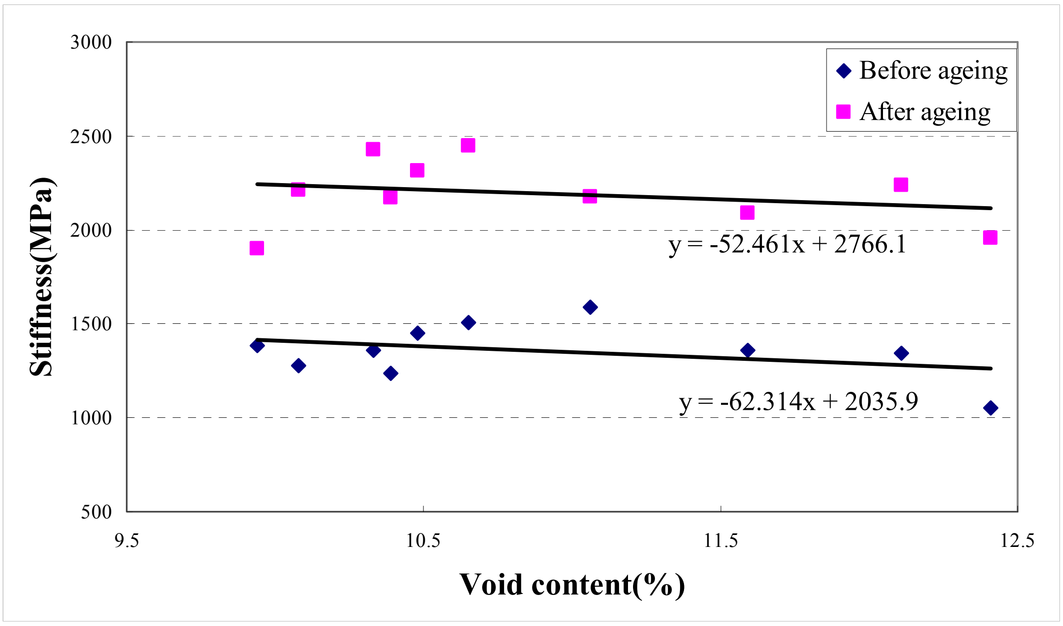
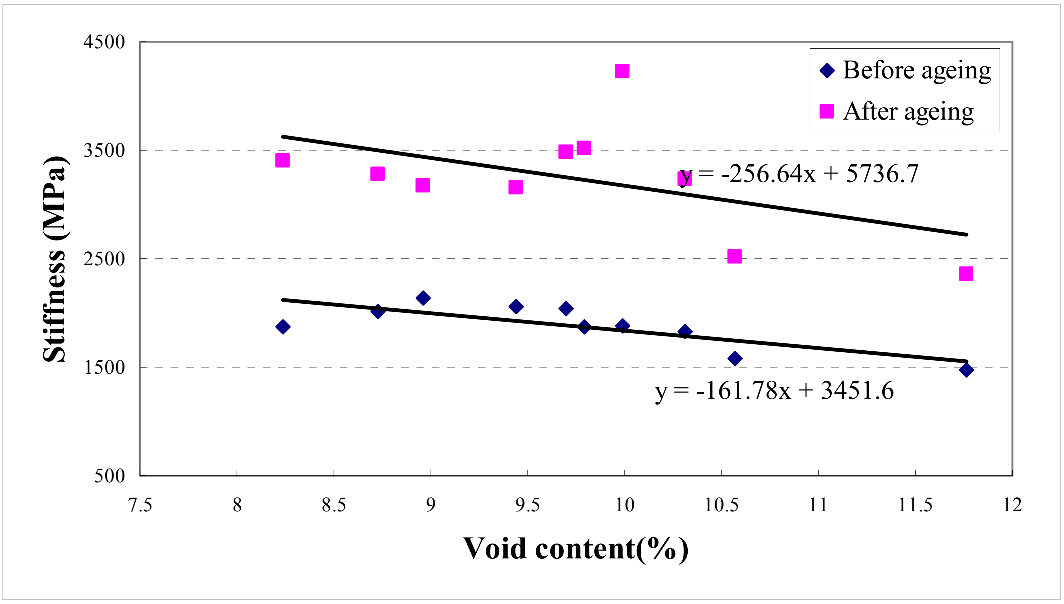


For LV_STA Group



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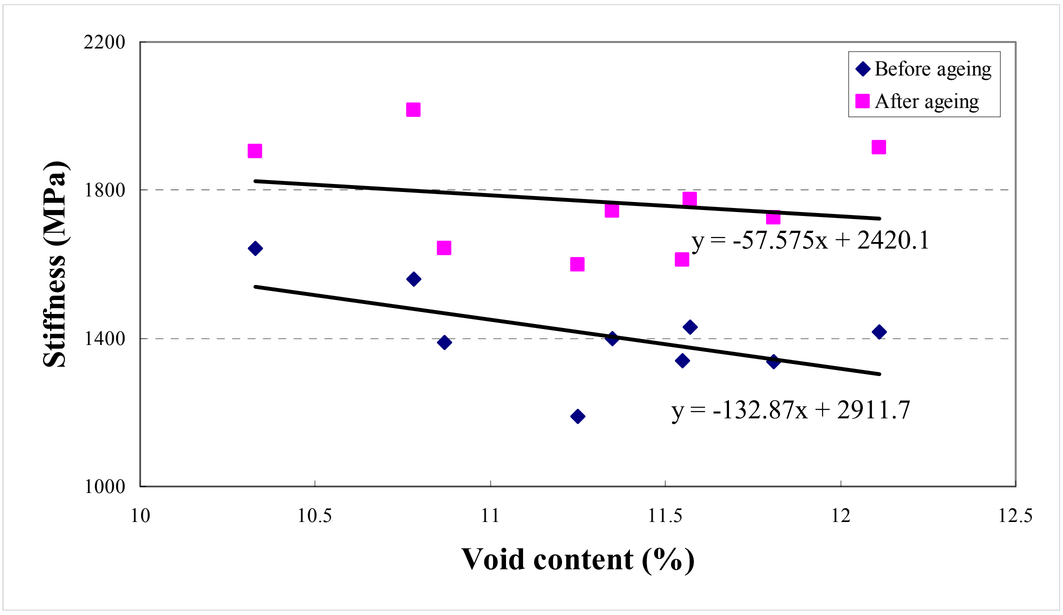

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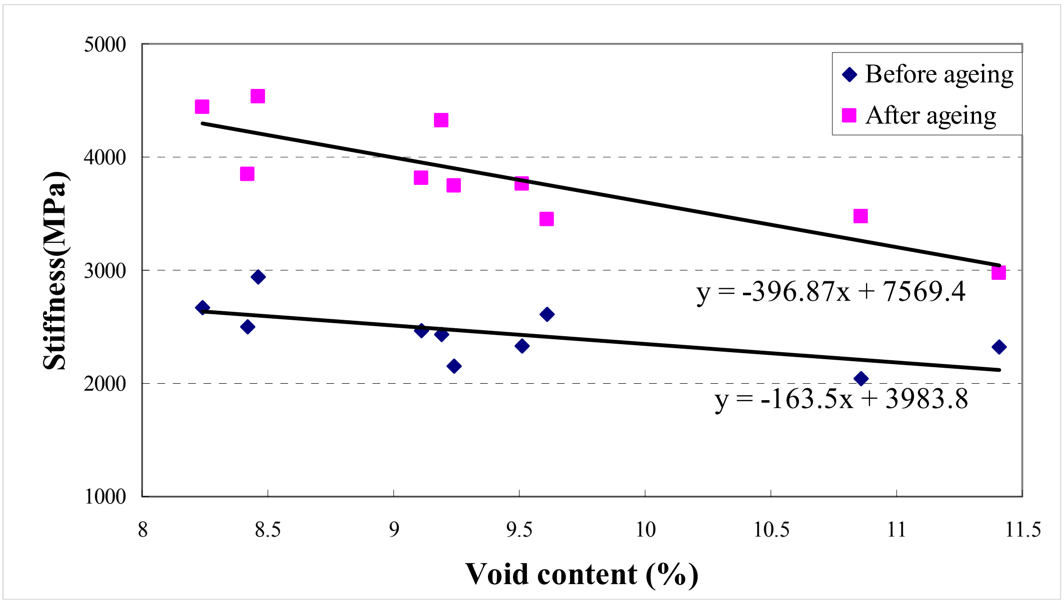

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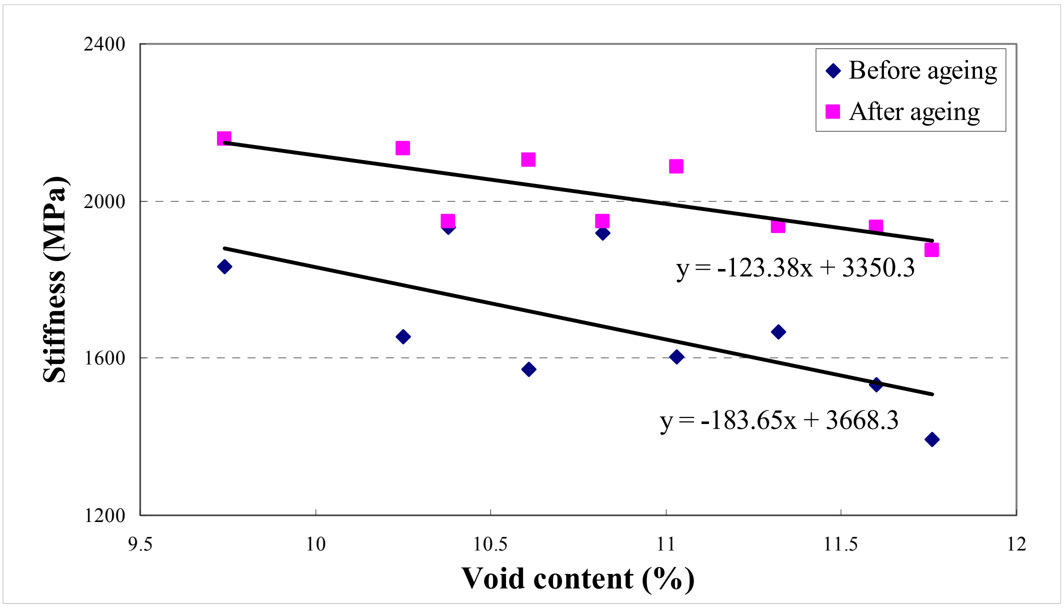


Appendix B
Development of DSR Modification for Bitumen Ageing Study

B.1 Introduction

Findings from the experimental work of this thesis have indicated that the currently used bitumen recovery technique can significantly affect the properties of recovered binder and therefore, mislead researchers in data analysis (as shown in Figure 6.24). It was recommended that the bitumen be aged on an aggregate surface and its rheological properties be tested directly without running the bitumen recovery technique. Therefore, the modified DSR spindle that was developed by Rottermond et al. (2004), as shown in Figure 3.7, was adopted by the author so that the rheological properties of bitumen both before and after ageing simulation could be measured while in contact with mineral aggregates. Two aspects of original DSR test procedure were proposed to be altered by using this modified DSR spindle: 1) reducing the gap to microns rather than millimetres and 2) incorporating mineral aggregate into the testing apparatus.

However, because of the low precision in aggregate plate fabrication and problems with zero gap setting, this proposed study was not completed and most effort was made to calibrate the modified DSR test.

B.2 Hardware Preparation

B.2.1 Fabrication of modified spindle

The modified spindle that is suitable for the tests in DSR water bath system was fabricated in a workshop. Figure B.1 is the picture of the modified set for this study. It can be seen that this modified set is almost the same as the conventional spindle and base plate, except for the additional ring with the threaded holes for the set-screws. This modification enables researchers to incorporate mineral aggregate into the testing apparatus.

Figure B.1 The modified DSR spindle

B.2.2 Fabrication of stainless steel and aggregate plates

Two stainless steel plates (5 mm thick, 25 mm diameter) were also fabricated in workshop to be used as reference plates for the aggregate ones (as shown in Figure B.2). The mineral aggregate plates were cut from 25 mm diameter cores extracted from ‘football-sized’ rock (limestone and granite rocks were used in this study), as shown in Figure B.3. Because the equipment can only cut the cores into plates with a minimum thickness of around 7 mm, one end of each plate was polished to reduce its thickness to 5 mm, as shown in Figure B.4.

Figure B.2 Stainless steel plates for modified DSR tests

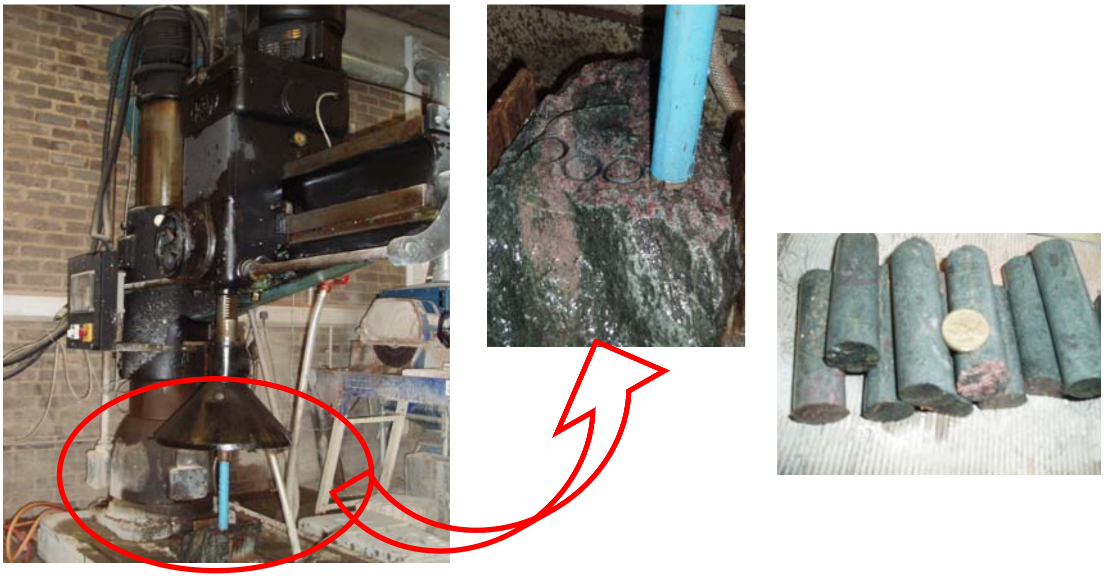


Figure B.3 Coring of aggregate cores

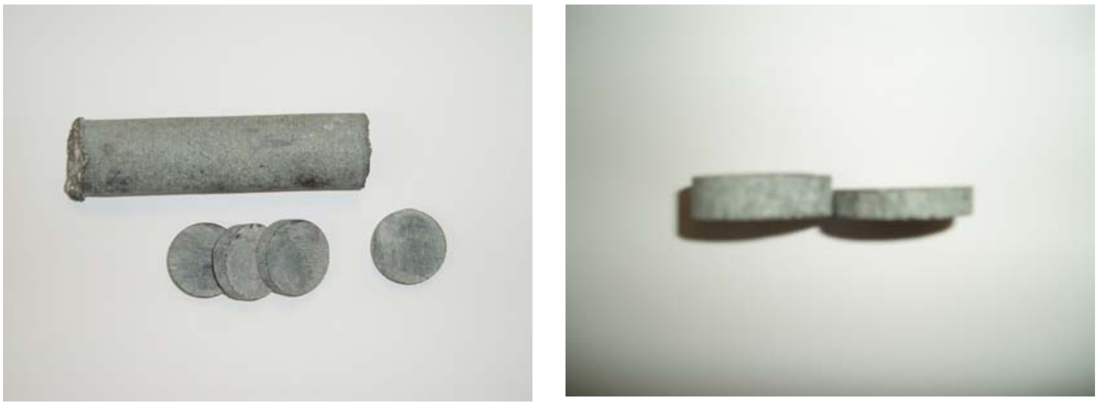


Figure B.4 Cutting and polishing of aggregate plates

B.2.3 Roughness test for the plate surfaces

The roughness of each plate surface was scanned using ‘Talysurf CLI 1000’ for purposes of comparison; the equipment and its principle are shown in Figure B.5. The test was carried out by scanning 25001 points (1μm spacing) along central diameters of the plates; the Roughness (Ra) of each plate was calculated automatically by the machine following the principle as shown in Figure B.6.

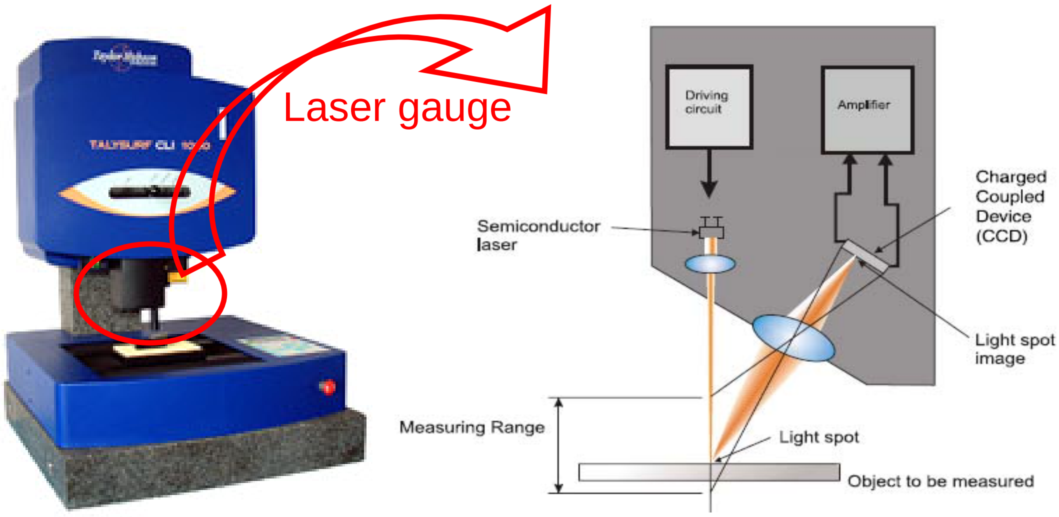


Figure B.5 Picture of Talysurf CLI 1000 and its laser gauge

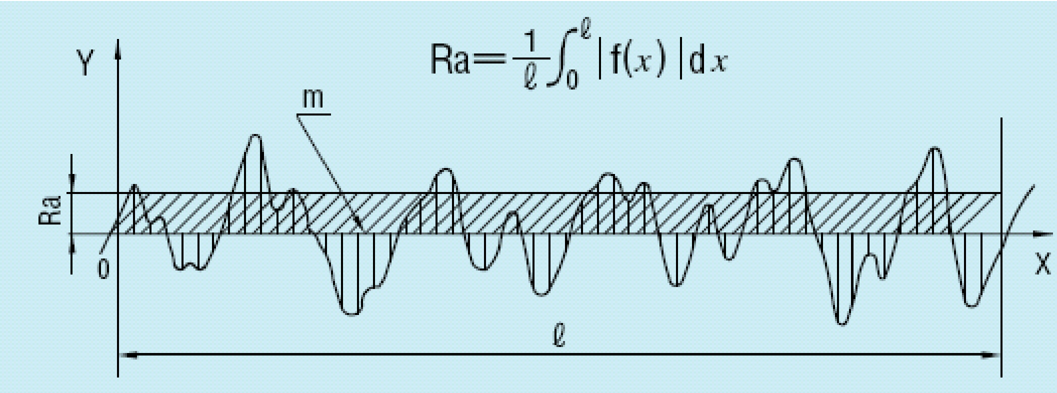


Figure B.6 The way of roughness calculation

Figures B.7 to B.9 show the scan results for the standard plate, the modified stainless steel plate and one of the aggregate plates. It can be seen that although their roughness (Ra) results are similar, the fabricated plates have a larger slope on their surfaces, which, as it will be discussed, caused testing error in this study.

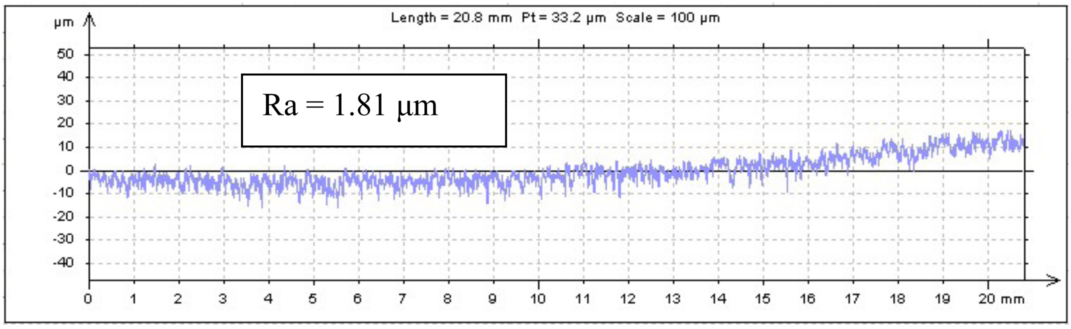


Figure B.7 Roughness scan for standard plate surface

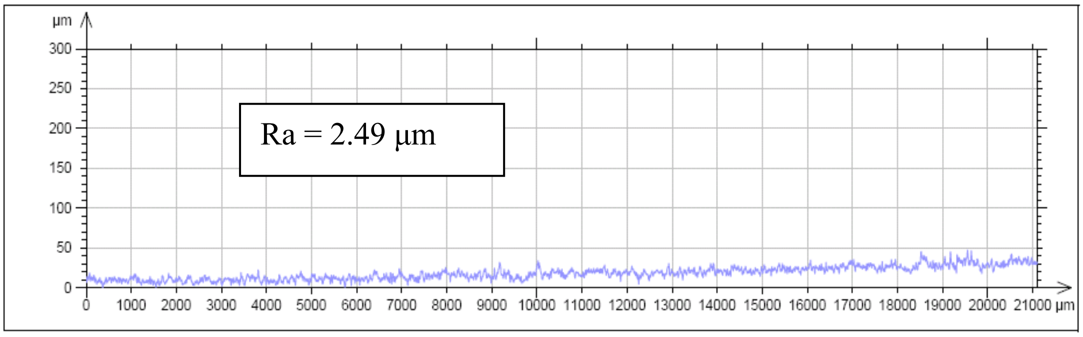


Figure B.8 Roughness scan for modified stainless steel plate surface

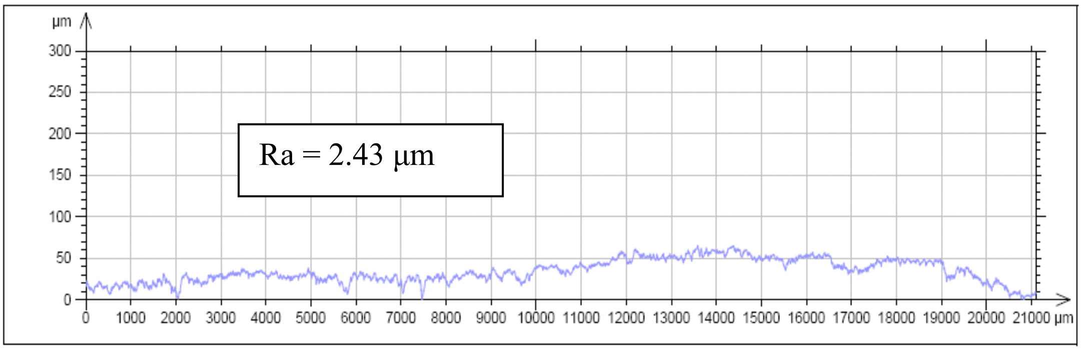


Figure B.9 Roughness scan for aggregate plate surface

B.3 Software Settings

B.3.1 Detection of problems

A frequency sweep test was carried out on the 70/100 penetration binder, using both the standard and the modified stainless steel spindle. The test conditions are listed as follows:

- Mode of loading: Controlled-strain (0.4%),
- Temperatures: 35 to 80°C (5°C intervals),
- Frequencies: 0.1 to 10 Hz,
- Plate geometries: 25 mm diameter with a 1mm gap,
- Test system: PP25 DSR (NCPE).

For comparison, the test results have been presented in the form of complex modulus master curves (as shown in Figure B.10). It can be seen that at low frequency (high temperature), the complex modulus result for the modified stainless steel spindle becomes higher and unstable.

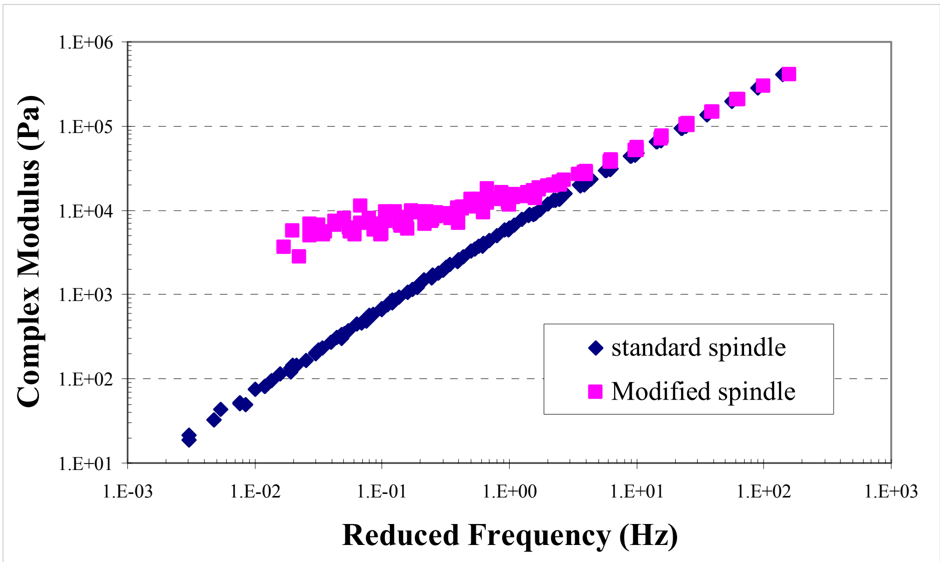


Figure B.10 Complex modulus master curves for 70/100 pen binder with different spindles

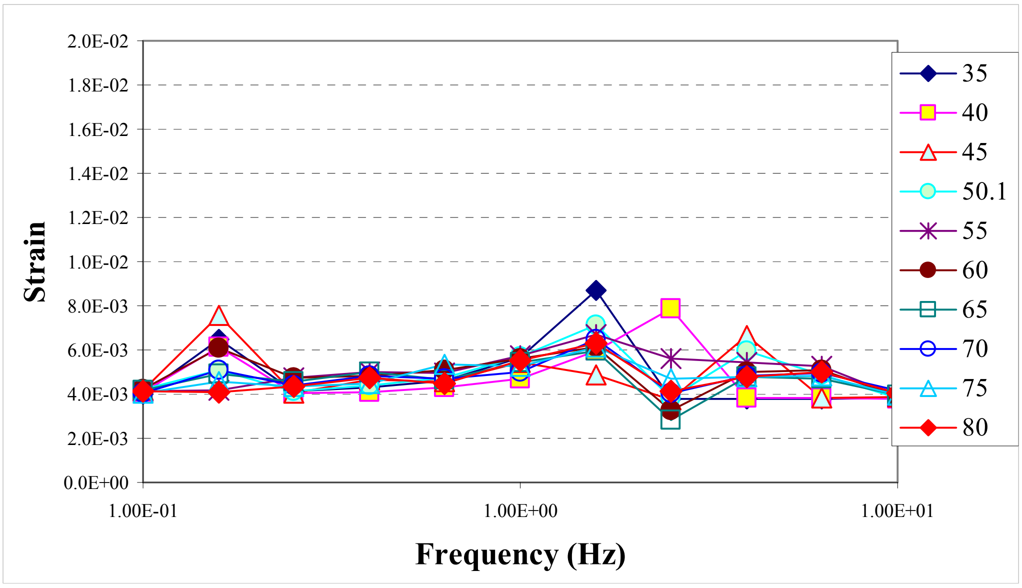


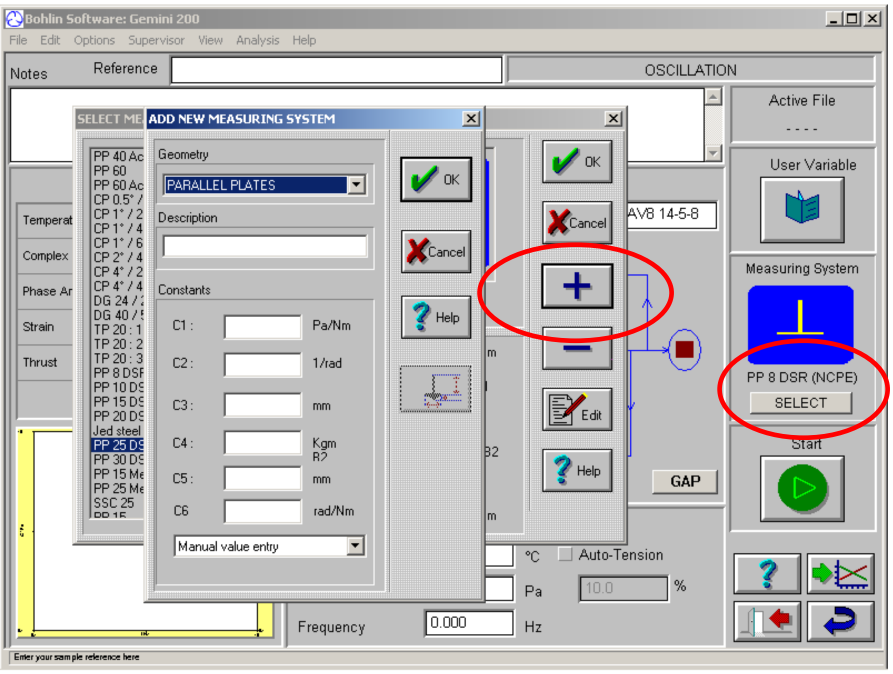
Figure B.11 Statistic data of strain in the modified spindle test

From the statistical data of strain in the modified spindle test (as shown in Figure B.11), it can be observed that the strain is stabilised at about 0.4% during the test, which means the stress (σ) and torque is higher than is expected at high temperature. By comparing the differences between these two tests, it is not difficult to ascertain the most possible reason which can lead to this error: the heavy upper spindle for the modified test (68.236 g compared with 28.27 g for the standard).

B.3.2 Internal constants for DSR

It was found the software for DSR test does have several internal parameters related to the properties of upper spindle (as shown in Figure B.12) and it has some functions which enable users to edit the existing systems and/or to add a new system for new test spindles (also seen from Figure B.12). A general explanation for the six different form factors is given as follow:

- C1 - This is the torque to shear stress conversion value, with units of $1/m^3$.
- C2 - This is the angular displacement to shear strain conversion value with unit 1/rad. It is also the conversion factor for angular speed to shear strain rate.
- C3 - This is a switch for variable gap measuring geometries. Its value is 0 for fixed gap geometries like cone and plate systems. A C3 value of 1 indicates to the software that the geometry gap can be variable. It will then use the gap from the gap panel in the calculations (so essentially, the software will calculate the gap correction for the user).
- C4 - This is the inertia constant. It represents the inertia of the geometry (not including the shaft in the chuck as this is constant across the range and is included in the bearing inertia value. It has units of kgm^2.
- C5 - This is the truncation height for systems with a fixed gap based on the virtual tip of the cone on the end of the geometry. Cone systems have a truncation on their tip and so they are set back from the plate by the amount taken from the tip. This is typically 30 to 150 microns.
- C6 - This is the compliance factor for the measuring geometry, unit 1/Pa. It is used in compliance correction in the oscillation test.



Geometry: PARALLEL PLATES

Description:

Constants

C1 : Pa/Nm

C2 : 1/rad

C3 : mm

C4 : Kgm R2

C5 : mm

C6 rad/Nm

Manual value entry

AV8 14-5-8

Measuring System: PP 8 DSR (NCPE)

°C

Pa

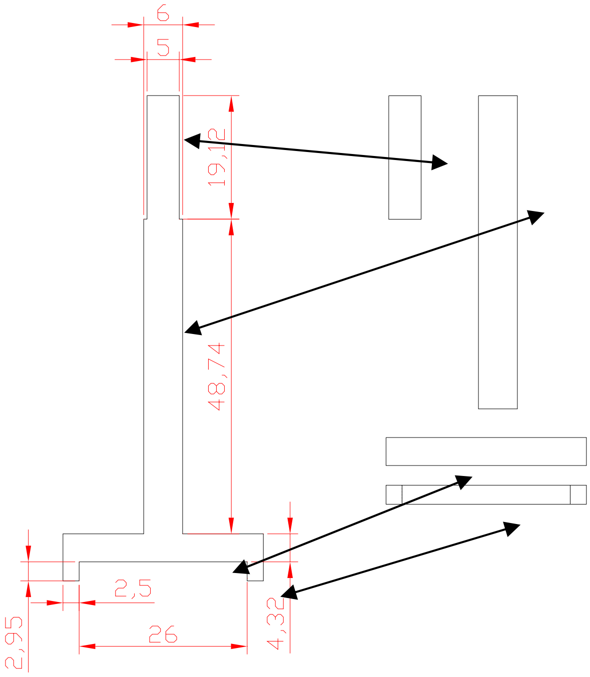
10.0 %

Frequency 0.000 Hz

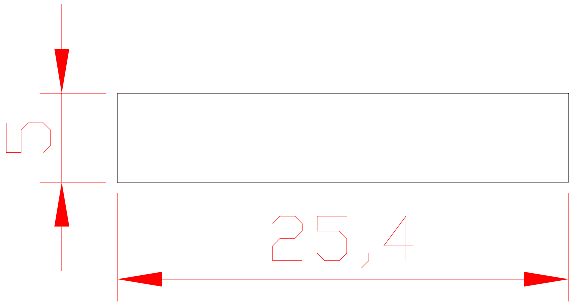
Figure B.12 Testing systems for DSR tests

B.3.3 Calculation of the constants

Figure B.13 shows dimensions of the modified spindle and its plate. According to the dimensions and the introduction above, parameters for the new testing system was calculated.



a) Dimensions of the modified spindle



b) Dimensions of the plate

Figure B.13 Dimensions of the modified spindle and its stainless steel plate (mm)

1) C1

This is the torque to shear stress conversion value, with units of $1/m^3$. In DSR test for bitumen, consider a bitumen ring of width “δr”, a distance “r” from the centre of the disk(as shown in Figure B.14). The torque (δT) required to generate this shear stress is given by:

$$\delta T = \sigma(r) 2\pi r^2 \delta r \tag{B-1}$$

Therefore, the total torque for a plate of radius “R” is:

$$T = \int_0^R 2\pi\sigma(r)r^2 dr \tag{B-2}$$

In a DSR test, the shear strain rate for the position with a distance “r” from centre of the disk is given by:

$$\dot{\gamma} = \frac{\dot{\theta} \cdot r}{h} \tag{B-3}$$

where:

$\dot{\gamma}$ = the shear strain rate;

$\dot{\theta}$ = deflection angle rate;

h = gap between parallel plates.

Therefore, the sear stress can be given by:

$$\sigma(r) = \eta(r)\dot{\gamma} = \eta(r)\frac{\dot{\theta} \cdot r}{h} \tag{B-4}$$

where:

$\eta(r)$ = the shear viscosity of the bitumen, which is a constant for the bitumen in linear range.

By combining equation (B-2) and equation (B-4), it will give:

$$T = \int_0^R 2\pi\eta \frac{\dot{\theta} \cdot r}{h} r^2 dr = 2\pi\eta \frac{\dot{\theta}}{h}\left[\frac{r^4}{4}\right]_0^R = \frac{1}{2}\pi\eta\frac{\dot{\theta}}{h}R^4 = \frac{\pi}{2}\sigma_{\max}R^3 \qquad \text{(B-5)}$$

Therefore, C1 is equal to $\frac{2}{\pi R^3}$, which, for this modified spindle, is 310791(1/m3).

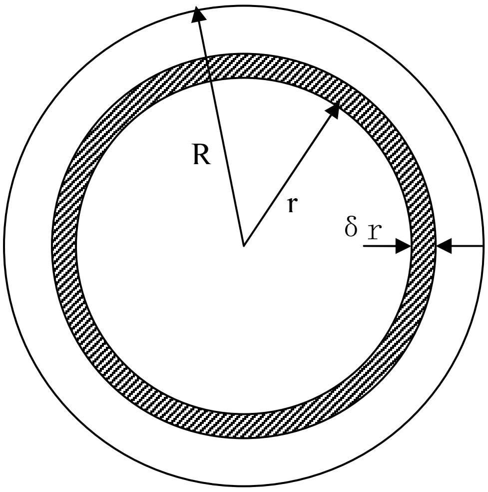


Figure B.14 DSR testing plate

2) C2

This is the angular displacement to shear strain conversion value. It is known that the shear strain is given by:

$$\gamma_{\max} = \frac{\theta \cdot R}{h} \qquad \text{(B-6)}$$

Because the gap between parallel plates can be set by users in the DSR test and the software will adjust it automatically, C2 is defined as the radius of plate by the software introduction. Therefore, C2 = 12.7 for this modified spindle.

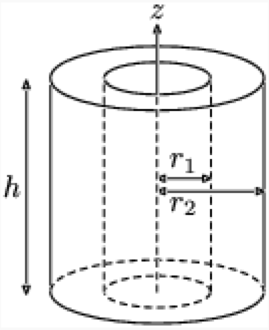
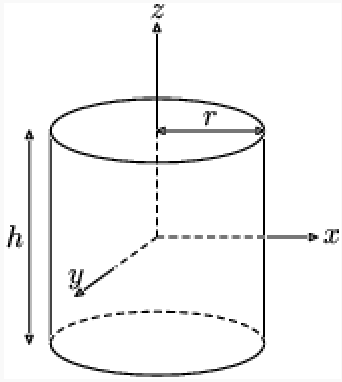
3) C3

Because the gap for binder DSR test will vary from one test to another, C3 = 1.

4) C4

C4 is the moment of inertia (I) for the modified spindle and its plate (excluding the shaft in the chuck). Moment of inertia, also called mass moment of inertia or the angular mass, (SI units kg m^2), is the rotational analog of mass. That is, it is the inertia of a rigid rotating body with respect to its rotation. The moment of inertia plays much the same role in rotational dynamics as mass does in basic dynamics. The calculation methods for the moment of inertia of cylindrical tube and solid cylinder are listed in Table B.1.

Table B.1 List of moment of inertia

Thick-walled cylindrical tube with open ends, of inner radius r_1, outer radius r_2, length h and mass m		$I_z = \frac{1}{2}m\left({r_1}^2 + {r_2}^2\right)$
Solid cylinder of radius r, height h and mass m		$I_z = \frac{mr^2}{2}$

As it can be seen from Figure B.13, C4 for this modified spindle and its plate will be the moment of inertia of the spindle (excluding the top part as it is in the chunk) together with the moment of inertia of the plate. The mass for the spindle and plate are 47.731 g and 20.532 g respectively, therefore, C4 in this case is 6.12E-6 kgm^2.

5) C5 & C6

C5 and C6 in the bitumen DSR test are both 0.

B.3.4 Experimental adjustment for C4

As stated above, the biggest difference between the standard spindle and modified spindle is mass, which is related to the internal constant of C4.

It can be observed from Figure B.10 that the test error only appears at high temperatures, which means the effect of moment of inertia is not very significant until the binder becomes very soft. Therefore, some flux oil was used to see the C4 effects in the extreme condition. A single frequency (at 25°C, 1Hz with a gap of 250 μm) test was applied to the flux oil, using both the standard spindle and the modified spindle with stainless steel plate. Figures B.15 and B.16 show the phase angle and complex modulus results for tests with different spindle-test system combinations (as listed in Table B.2). It was found that, with the calculated C4 (6.12E-6 kgm^2), the phase angle result for modified spindle is too large when comparing with the result for the standard spindle with standard system. Therefore, C4 was adjusted until both the complex modulus and phase angle results for the modified spindle were similar to the ones for the standard system (when C4 = 2.6E-6 kgm^2).

At the same time, a frequency sweep test was applied to a 70/100 penetration bitumen under the same condition listed at the beginning of this subsection, using the spindle-system combinations listed in Table B.2. The master curves for the complex modulus and phase angle (reference temperature: 50°C) are presented in Figures B.17 and B.18. It can be seen that the test results with both the calculated and adjusted C4 are acceptable. However, considering the situation for some extremely soft binder, it is decided that the adjusted one will be used in the future study.

The C4 for the modified spindle with aggregate plates were calculated based on the differences in the mass between the stainless steel and aggregate plates.

Table B.2 List of test conditions

No.	Spindle	C4(kgm^2)
1	Standard spindle	6.8E-7 (standard NCPE system)
2	Modified spindle	6.8E-7
3	Modified spindle	6.1E-6 (Calculated C4)
4	Modified spindle	2.6E-6 (Adjusted C4)

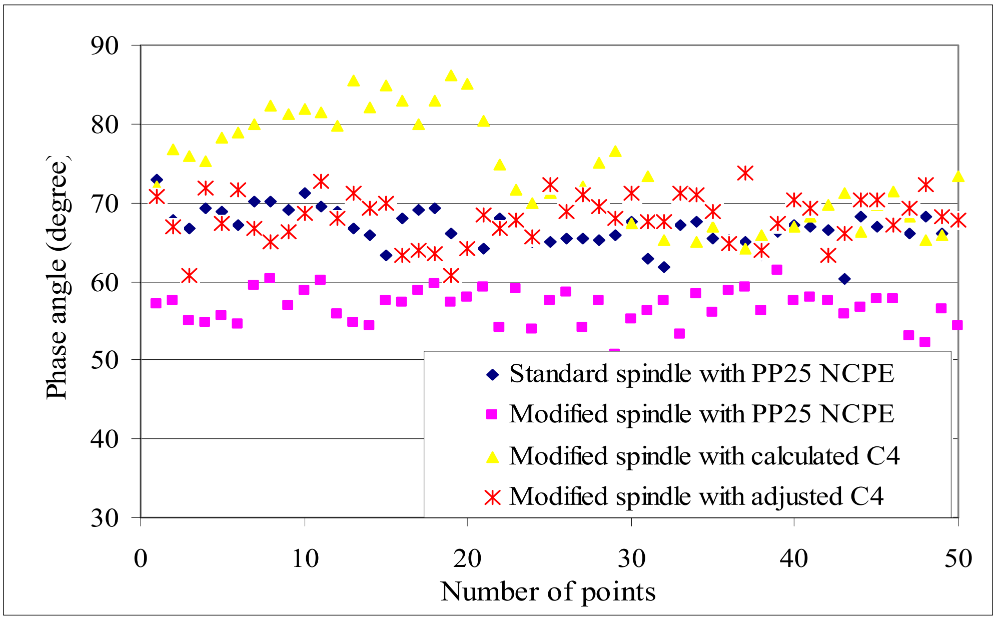


Figure B.15 Phase angle for flux oil (at 25°C, 1Hz with a gap of 250µm)

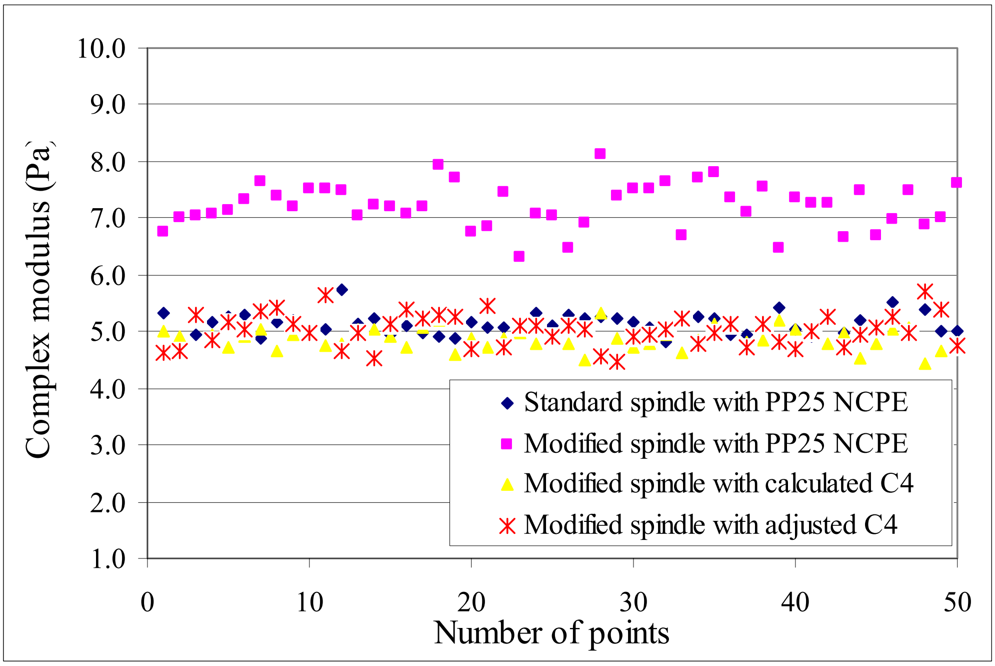


Figure B.16 Complex modulus for flux oil (at 25°C, 1Hz with a gap of 250µm)

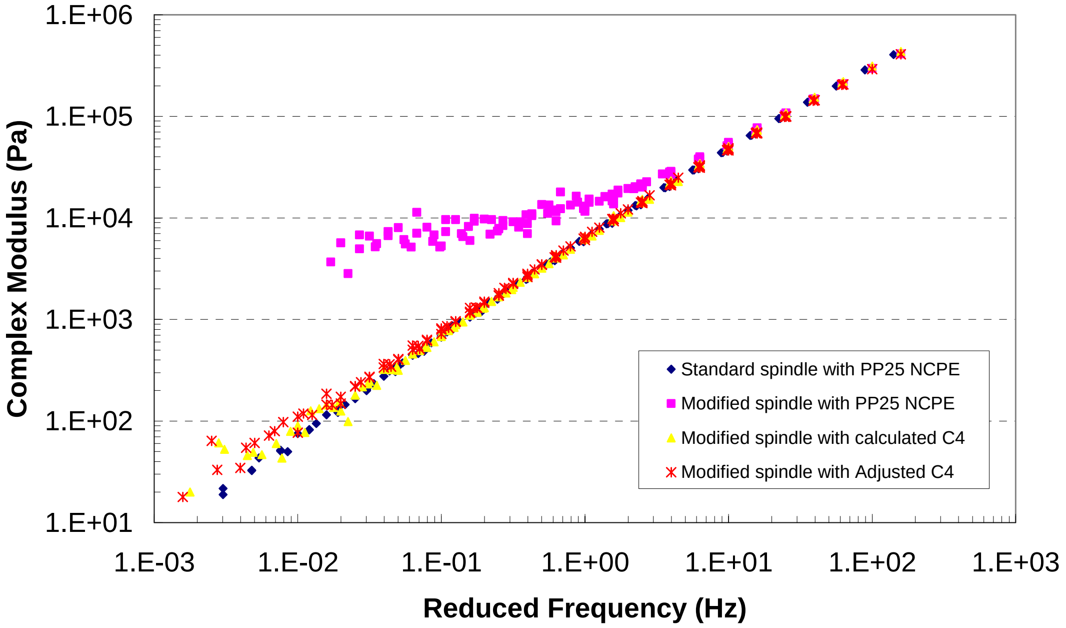


Figure B.17 Master curves for complex modulus

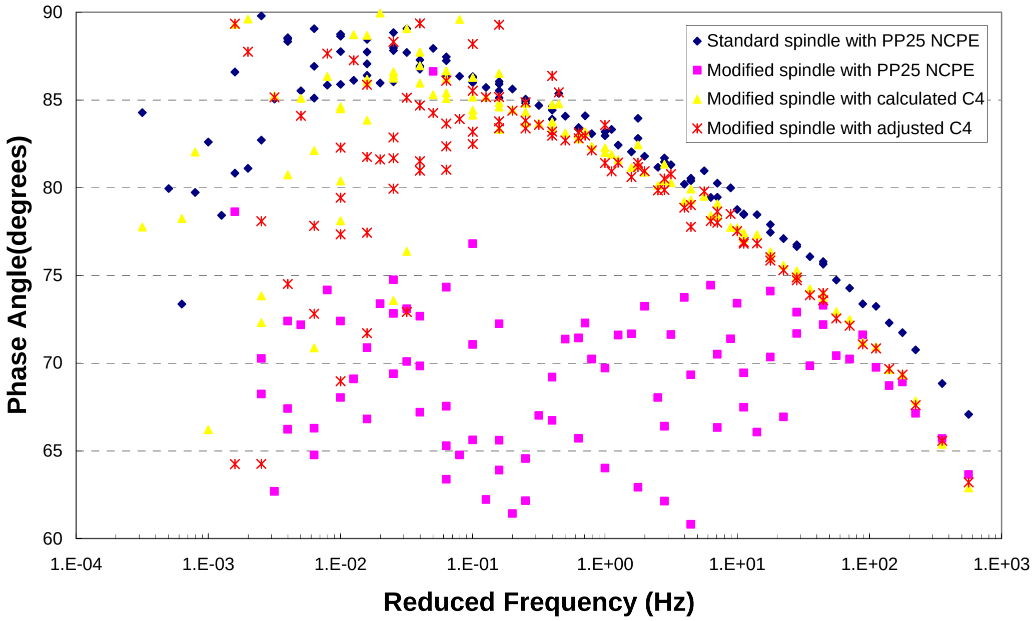


Figure B.18 Master curves for phase angle

B.4 Gap Sensitivity of DSR Test

It has been recommended by researchers (Rottermond et al., 2004) that reduced gap size for the DSR test should be adopted so that binders could be tested in a thin layer (micrometres instead of millimetres) that is close to the real situation when they are used in asphalt mixtures. It is also declared by the DSR manufacturer that conducting the DSR test in a thinner thickness could make the result more accurate. However, tests carried out by author showed that, when the DSR testing gap is reduced, the test results become more sensitive to the accuracy to which the plates are set parallel. It can be seen from the surface scan results shown in Figures B.7 to B.9 that even for the standard plate, after hundreds of times use, there is a slope appearing along the diameter of plate.

B.4.1 Single frequency tests with varying gaps

In this study, single frequency tests (0.4 Hz, 50^{o}C) were carried out on a 70/100 penetration bitumen, using the standard plate, modified stainless steel plates, modified limestone plates and modified granite plates. Two testing gaps were used for each spindle: 1 mm and 0.05 mm. Table B.3 shows the testing results.

It can be seen from Table B.3 that for all the plates (especially for the fabricated aggregate plates), when the testing gap was reduced from 1 mm to 0.05 mm, there was a reduction in the tested G* value.

Table B.3 Single frequency test with different spindles and different testing gaps

Plate	Standard		Mod. steel		Mod. limestone		Mod. granite	
Gap (μm)	1000	50	1000	50	1000	50	1000	50
G* (Pa)	2520.7	1838.4	2524.3	1581.6	2234.4	514.2	2463.4	565.7

B.4.2 Analysis and discussion

It is believed that this phenomenon is caused by the uneven plate surface. A quantitative analysis was undertaken based on a simplified plated system.

As shown in Figures B.7 to B.9, the slope along the plate diameter results in a difference in the plate thickness (d). Because the DSR testing gaps are set based on the zero-gap position, where when the upper plate is contacting the lower plate, this slope can further lead to a difference in the thickness of tested binder. Three simplified models of such situations are shown in Figure B.19. From this figure, it can be seen that, with a gap setting of *h*, the tested binder between two uneven DSR plates can be shaped in number of ways.

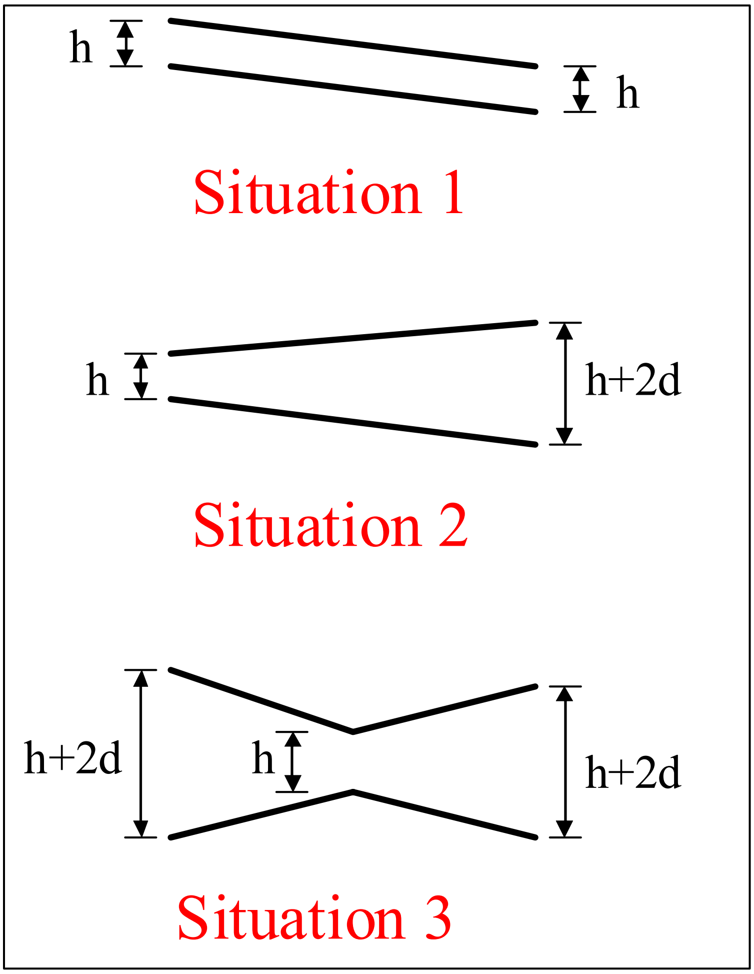


Figure B.19 Simplified models for DSR uneven testing plates

A theoretical analysis based the situation 2 shown in Figure B.19 has been conducted by author as follows:

In a DSR test, the relationship between the shear strain (γ) and deflection angle (θ) can be expressed as follows:

$$\gamma = \frac{r \times \theta}{h} \Rightarrow \theta = \frac{\gamma \times h}{r}$$

Therefore, when the testing strain limit (γ) is set for the machine, the machine knows that a deflection angle of θ should be applied to the upper plate. However, with a testing gap of h, for the binder at the position with a gap of (h+2d), the strain (γ') and stress (σ') would be

$$\gamma' = \frac{r\theta}{h+2d} \Rightarrow \sigma' = G^*\gamma' = G^*\frac{r\theta}{h+2d}$$

where:
G^* = the real value of the bitumen complex modulus.

Therefore, the average stress for the whole circle can be assumed as:

$$\bar{\sigma} = \frac{\sigma+\sigma'}{2} = \frac{G^*\gamma + G^*\gamma'}{2} = \frac{G^*\frac{r\theta}{h} + G^*\frac{r\theta}{h+2d}}{2} = G^* r\theta \frac{h+d}{h(h+2d)}$$

In addition, the relationship between torque (T) and stress in the DSR test is:

$$T = \frac{\pi\sigma \times r^3}{2},$$

so the torque needed for a set strain of γ ,in “Situation 2” is:

$T' = \frac{\pi\bar{\sigma}\times r^3}{2}$, which, in the machine’s view, is the torque that should be used to calculate the stress σ; thus, $\bar{\sigma}$ becomes the outcome stress of the test, and is used by the machine to calculate the Complex Modulus (G*’):

$$G^{*\prime} = \frac{\bar{\sigma}}{\gamma} = \frac{G^* r\theta\frac{h+d}{h(h+2d)}}{\frac{r\times\theta}{h}} = G^*\frac{h+d}{h+2d}$$

where:
G’* = the outcome complex modulus for the binder with a real complex modulus of *G**.

Similarly, the result for the test in Situation 3 can be calculated as:

$$G^{*\prime} = G^*\frac{h}{h+2d}$$

Based on the analysis above, for a binder with a stiffness of 2500 Pa, and assuming that it was tested by the plates in Situation 3 with a plate thickness difference of 50 µm, the testing results for different test gaps would be as shown in Figure B.20. It can be seen that as the testing gap is reduced, the testing result becomes more sensitive to the uneven surfaces.

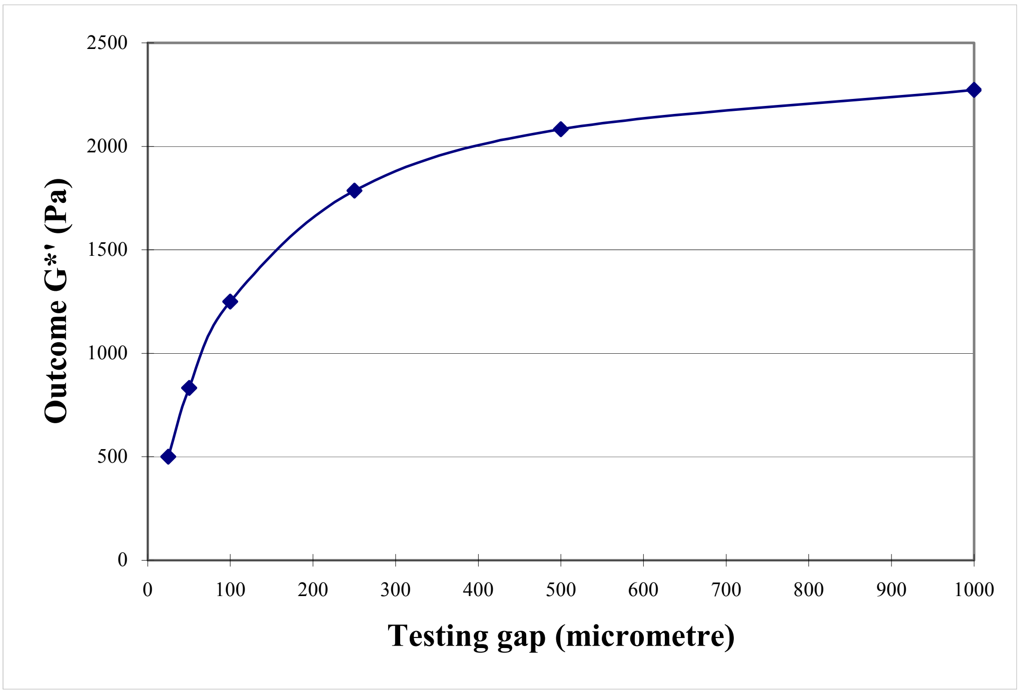


Figure B.20 The effects of uneven plate surface to the testing results