Chapter 2
Asphalt Binders

2.1 Introduction

Asphalt mixtures are a composite comprising asphalt binder and mineral aggregates. Asphalt binder, also referred to as bitumen in Europe and other parts of the world, can be regarded as glue (hence the term binder) that holds the aggregate particles together in the mixture. Asphalt binders make up approximately 4–8% of the asphalt mixture by weight. From a volumetric standpoint, typical asphalt mixtures contain 9–18% of asphalt binder, 87–78% of mineral aggregates, and 3–6% of air voids. The size and distribution of air voids within the asphalt mixture is very important in order to understand mechanisms related to oxidation and moisture-induced damage and will be discussed in more detail in later chapters. Despite its low mass or volume fraction, from a cost standpoint as of this writing, asphalt binders make up approximately 40–50% of the cost of materials used to produce an asphalt mixture. Consequently, the cost of an asphalt mixture is very sensitive to the price of asphalt, which is in turn related to the price of crude oil in most cases.

The mechanical properties of an asphalt binder are time, temperature, and age dependent. Consequently, asphalt mixtures inherit these characteristics (time, temperature, and age dependency) from the asphalt binder. It is impossible to fully understand and appreciate the behavior and performance of asphalt mixtures without having some knowledge about the performance and behavior of asphalt binders. For example, consider the typical distresses in a flexible pavement: rutting (or plastic or permanent deformation), fatigue cracking, thermal cracking, and moisture-induced damage.

In terms of rutting, the resistance to deformation is provided by both the aggregate structure and the asphalt binder that holds the aggregate structure in place. The contribution of the binder to resist rutting is significant and cannot be ignored in understanding or predicting the rutting of asphalt mixtures.

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One of the mechanisms by which asphalt mixtures fail is the action of moisture referred to as stripping (other mechanisms will be discussed in more detail in Chap. 8). Stripping occurs when water displaces the asphalt binder from the surface of the aggregate particle. The ability of the asphalt binder-aggregate interface to resist this form of moisture-induced damage is dictated by the physicochemical surface properties of both the binder and the aggregate.

The relationship between the properties of the binder and distresses such as fatigue and thermal cracking is even more direct. The ability of an asphalt mixture to resist tensile stresses can almost exclusively be attributed to the asphalt binder. Although the aggregate size and distribution (gradation) may play a role in defining distribution of internal stresses within the binder, without the asphalt binder the aggregate particles would remain unbound and unable to resist any tensile stresses. Similarly, one of the key characteristics of an asphalt pavement is its ability to resist cracking due to thermal shrinkage when the temperature drops. As the air and consequently pavement temperature drops, tensile stresses develop within the asphalt mixture. Due to the inherent viscoelastic nature of asphalt binders, it is possible for the binder to relax and partially relieve these tensile stresses over time such that the cumulative tensile stresses do not exceed the strength of the binder.

The aforementioned examples demonstrate the importance of understanding the behavior and performance of asphalt binders as a first step to better understand and predict the performance of asphalt mixtures and pavements. However, one may raise the question that since asphalt binders are used exclusively with aggregates, it would be more meaningful to evaluate and understand the behavior of asphalt mixtures as a whole as opposed to evaluating one of the ingredients within the asphalt mixture. There is a twofold answer to this question.

First, since the performance of an asphalt mixture is dictated by the properties of the asphalt binder, a poor quality binder will not result in a durable asphalt mixture. In other words, it is difficult to produce a durable mixture if one of the critical ingredients of the mixture is of poor quality. Selecting and using an asphalt binder that is appropriate for a given climatic and traffic condition is necessary (but not sufficient) to ensure that the asphalt mixture does not fail during its service life.

Second, significant improvements in the durability and life-cycle cost of asphalt mixtures and pavements can be made by engineering and producing binders with superior performing characteristics. In short, when designing asphalt mixtures, it is critical to screen and use asphalt binders with superior mechanical and engineering properties. As of this writing, the practice of designing asphalt mixtures and pavements requires that both the asphalt binder and mixture meet certain performance requirements before being approved for use in construction.

This chapter is organized into four sections. The first section briefly describes the origins and production of asphalt binders. The remaining three sections go over the chemical, mechanical, and surface properties of asphalt binders. Each of these sections addresses two important questions: (1) Why the property is important in terms of mixture or pavement performance; and (2) how the property or its attributes are measured and used in engineering practice or research? A significant amount of information presented in this chapter is based on the research conducted

during and following the Strategic Highway Research Program (SHRP pronounced sharp) during the late 1980s and early 1990s. Information presented in this chapter must be considered as a starting point for individuals new to the asphalt industry, graduate and undergraduate students, and engineers in the asphalt industry who need a refresher on the basics of asphalt binder properties. For those interested in a more in-depth study of one or more of the topics listed in this chapter, a list of references for additional reading has been provided at the end of this chapter. Finally, by design, this chapter does not focus on details of standard tests or methods to characterize asphalt binders. Instead, the goal of this chapter is to explain to the readers the rationale behind the development of such methods. Detailed descriptions of the methods can be found in the list presented in the additional reading material.

2.2 Production of Asphalt Binders

Most of the asphalt binder used in commercial paving applications is produced by refining crude oil. Asphalt binder is also naturally found impregnated in rocks and minerals referred to as rock asphalt, mixed with sand and other fine minerals referred to as oil sands, or in bulk as in the case of Lake Trinidad. In the case of natural asphalts, the "refining" is mostly done by nature over a much longer period of time. Although most of this chapter is based on asphalt binder produced from the distillation of crude oil, concepts related to chemical makeup and mechanical properties can also be extended to natural asphalts.

Crude oil is formed by the decomposition of organic materials at high temperatures and pressures over millions of years. The nature of the organic material and the conditions under which the organic material decomposes dictates the chemical makeup of crude oil. In other words, the chemistry of crude oil will vary significantly depending on its source. Crude oils from different sources are generally described as heavy or light depending on the percentage of asphalt binder or heavy residue that is left behind after the distillation of lighter fractions such as gasoline and kerosene. Crude oils may also be described as sweet or sour depending on the percentage of sulfur (sweet refers to lower percentage of sulfur). Figure 2.1 illustrates typical compositions of crude oil from two very different geographical sources.

Crude oil is distilled to produce familiar products such as gasoline, kerosene, diesel, and lubricating oil. These products are also referred to as high-value refining products. The residue left behind after the distillation of the high-value products is typically referred to as short residue or in most cases straight-run asphalt binder. The chemical and mechanical properties of a straight-run binder can vary significantly depending on the source and batch of the crude oil as well as the processes used during the distillation of the crude oil. Note that the properties of the high-value products (e.g., gasoline) produced during distillation are relatively well

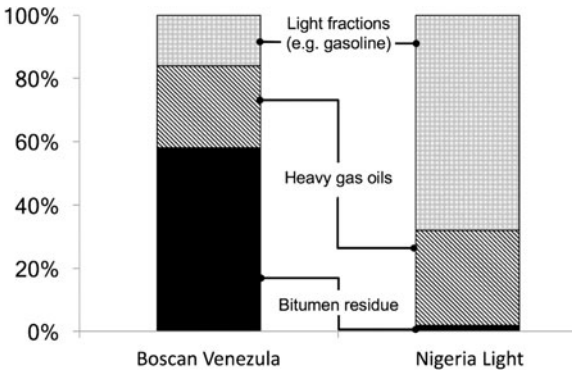

Fig. 2.1 A comparison of two different crude oil sources; the Boscan crude is regarded as sour with approximately 6% sulfur compared to the Nigerian light that has 0.2% sulfur

controlled. Consequently, the differences in the chemical makeup of different crude oil sources are amplified in the short residue or straight-run binder that is left behind after distillation.

In many cases, the properties of the straight-run asphalt binder are not suitable for paving application. This may prompt the binder producers to further process the straight-run binder to produce an end product that meets the requirements of end users for pavement applications. There are three main variables that are manipulated to produce an asphalt binder with specific properties: (i) proportioning of different straight-run binders or feedstocks, (ii) the selection of the techniques and chemical catalysts to process the straight-run asphalt binder (e.g., air blowing or half air blowing), and (iii) selection of an additive or combination of additives to modify the binder. Refineries that produce asphalt binders optimize the above variables to produce an asphalt binder that meets the requirements of the consumer with the lowest production cost. The desired properties of the asphalt binders vary with geographic region and type of application and will be discussed later.

2.3 Chemical Properties

2.3.1 The Need to Understand Binder Chemistry

This section addresses the question of why it is important for engineers or researchers working with asphalt materials to be knowledgeable, at least to some extent, about the chemistry of asphalt binders. The importance of understanding the chemistry of asphalt binders can be exemplified during the three stages of the binder's life: When the binder is produced in a refinery, when it is put to use for construction of an asphalt pavement, and when it is reclaimed after the end of the service life of an asphalt pavement.

First, consider the production of an asphalt binder. It is no surprise that the engineering properties of a material can be significantly altered by subtle changes in

the chemical composition of the material. The simplest example of this is steel. Addition of a small percentage of carbon to iron and changes in the heat treatment during production can result in significant improvements in the engineering or mechanical properties of the resulting steel. By understanding the relationship between the elemental composition of steel to its crystal structure and concomitant engineering properties, it is possible to design grades of steel that meet specific requirements for engineering applications. Also, different grades of steel can be consistently produced in different parts of the world irrespective of the source of the iron ore.

While the relationship between the chemical makeup and engineering properties is just as important for asphalt binders as it is for steel, the ability to produce different grades of asphalt binders with consistent engineering properties poses a unique set of challenges. For example, the chemical makeup of the raw material used to produce asphalt binders (crude oil) is highly dependent on the source and batch. As mentioned before, these differences are amplified in the bottom residue after the distillation of other high-value products. In addition, the chemical structure of the organic molecules that constitute asphalt binders is extremely diverse and complex. It is imperative that the personnel working with the production of asphalt binders have a thorough knowledge of the different chemical species that make up crude oils and asphalt binders as well as their relationship to the binders' engineering properties.

This section will help the reader develop a basic understanding of the chemistry of asphalt binders, and references are provided at the end as additional reading material for those interested. This knowledge will be useful for practitioners and researchers to better appreciate the differences in asphalt binders procured from different refineries or sources, even when the binders have similar mechanical and physical properties. In other words, *just because two asphalt binders have been classified to have the same "grade" based on their mechanical properties, there is no reason to expect that the two binders would have the same chemistry or would behave similarly under conditions where the chemistry of the material is important.* This knowledge is also important to appreciate the long-term implications, advantages, and limitations associated with using asphalt binders that have been modified or extended using any one of the several different environment friendly products (e.g., used oil by products, bio-binders).

After being produced at a refinery, the second stage in the life of an asphalt binder commences when it is used to produce an asphalt mixture and subsequently spans its service life in a flexible pavement. A basic understanding of asphalt chemistry is again important for researchers and practitioners alike to better appreciate:

1. the mechanisms that allow the use of chemical additives to facilitate mixing and compaction at reduced temperatures, referred to as warm mix asphalt,
2. the mechanisms that allow certain liquid additives or chemically active fillers such as hydrated lime to act as anti-stripping agents,

3. oxidative aging that occurs in the asphalt binder during production and service life of the pavement, changes in the binder chemistry due to oxidative aging and its impact on the rheological properties of the binder and distresses such as low-temperature cracking, and
4. the production and use of emulsions for application in surface treatments such as chip seals and cold asphalt mixes.

Finally, at the third stage, i.e., at the end of life stage, asphalt pavements are frequently demolished and pulverized or milled to produce fractionated black rock or recycled asphalt pavement (RAP). Since the asphalt binder in the recycled material is highly oxidized, the mechanical properties of the recycled binder must be counterbalanced by adding a binder that is less oxidized (soft binder) or by using a rejuvenator. With the recent emphasis on using higher percentages of recycled asphalt in the construction of new asphalt pavements, the knowledge of asphalt chemistry is crucial to maximize the use of recycled materials with or without rejuvenators while avoiding any short- or long-term detrimental impact. Having discussed the question of why understanding the chemistry of asphalt binders is important, the next subsection discusses the attributes that are used to describe the chemical makeup of asphalt binders.

2.3.2 Attributes of Chemical Properties and Methods of Measurement

Asphalt binders comprise a very diverse and complex range of hydrocarbons. The molecular structure of these hydrocarbons varies with the source and batch of the crude oil used to produce the asphalt binder. Owing to this diversity and complexity, it is neither feasible nor useful to identify the exact molecular structure of any given asphalt binder. Instead, a more practical approach to understand the chemical makeup of asphalt binders is to classify the molecules in the asphalt binder based on different attributes. Such classifications can then be used to discover relationships between binder chemistry and engineering properties. Four different attributes are commonly used to classify the chemical nature of asphalt binders. These attributes are:

1. elemental composition of the asphalt binder,
2. size of the molecules,
3. ionic character of the molecules, and
4. polarity of the molecules.

This section will discuss chemistry of the asphalt binder based on the above attributes as well as its implications in terms of the properties of the binder in the context of asphalt mixtures and pavements.

2.3.2.1 Elemental Composition

A typical asphalt binder comprises 90–98% by weight of hydrocarbons. The hydrocarbons exist in the form of saturated branched or unbranched alkanes and cyclic alkanes as well as unsaturated aromatics. Just as a refresher, recall that saturated hydrocarbons are molecules that do not have a carbon atom with a double or triple bond. The saturated alkanes and cyclic alkanes are also referred to as paraffins and naphthenes, respectively, in the petrochemical industry. The hydrocarbons typically have a carbon to hydrogen ratio of 1.5. This is somewhere in between the carbon to hydrogen ratio of saturated alkanes (approaching 2.0) and that of an aromatic ring structure such as benzene (1.0).

In addition to carbon and hydrogen, asphalt binders also contain other heteroatoms such as oxygen, sulfur, and nitrogen and trace metals. Although the heteroatoms constitute a small percentage by weight of the asphalt binder, they have a significant influence on the overall properties of the binder. For example, the functional groups such as pyrroles and carboxylic acids have been shown to be responsible for promoting adhesion although with different levels of resistance to debonding (resulting in stripping) in the presence of water. Oxygen and sulfur impart polarity to the molecules and are responsible for generating strong intermolecular interactions, which in turn contribute to the stiffness and strength of the binder. The oxygen content in an asphalt binder does not remain unchanged during its service life. Oxidation of the asphalt binder during production and service life results in the production of functional groups such as ketones, sulfoxides, and carboxylic acid. The typical heteroatoms and functional groups found in an asphalt binder are perhaps best summarized by Petersen (1984) and some of which are illustrated in Fig. 2.2.

Elemental composition provides the basic building blocks for any given asphalt binder. However, due to the diversity and complexity of the molecular structures, it is difficult to relate the elemental composition of the binder to it's mechanical properties. One notable exception to this is the amount of oxygen present in an asphalt binder that can be used as an indicator of the extent of oxidation in the binder. Oxidation results in the formation of polar functional groups as shown in Fig. 2.2 and reduce the ductility of the asphalt binder as well as its ability to relax. The subject of oxidation and aging in general will be revisited in the last section at the end of this chapter.

In the context of evaluating asphalt binders based on their elemental composition, the amount of oxygen in the binder can be used to track the extent of aging that the binder has experienced during production or its service life. This information can also be used to determine the rate and extent of oxidation in any given asphalt binder. The extent of oxidation in an asphalt binder is strongly related to its mechanical and rheological properties; however, such relationships may be different for each asphalt binder and dictated by its overall chemical makeup. An understanding of the oxidation process and concomitant changes in the binder properties is very important in the context of asphalt mixtures, and this topic will be revisited several more times in this and subsequent chapters.

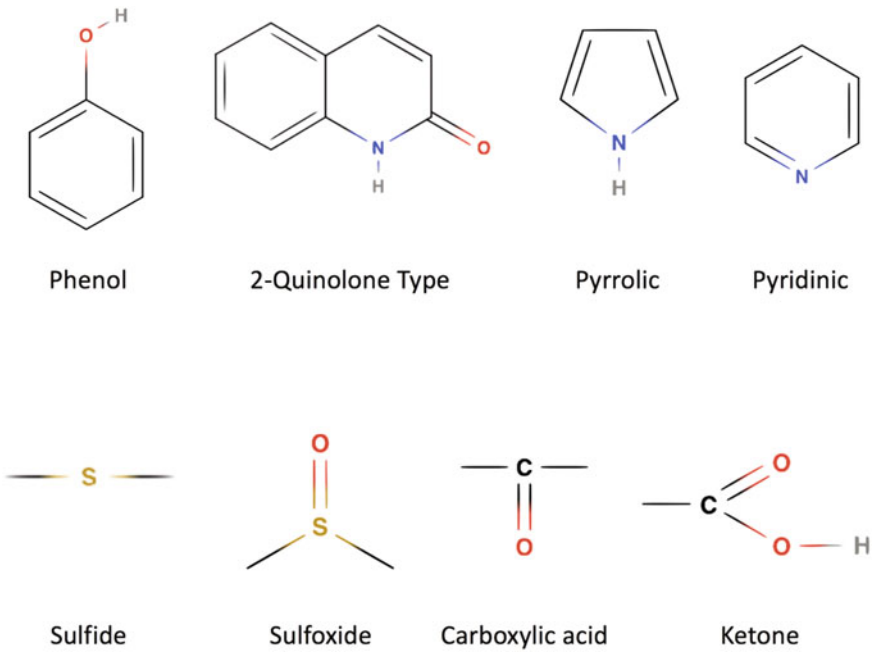

Fig. 2.2 Typical functional groups in asphalt binder (Recreated based on Petersen 1984)

On the subject of functional groups and oxidation, it is important to briefly mention one of the most commonly used techniques to quantify the concentration of different functional groups in asphalt binder, i.e., Fourier transform infrared spectroscopy or FTIR. When infrared light, typically comprising wave numbers that range from 4000 to 600 cm^{-1}, is incident on a sample of the material, molecular bonds corresponding to different functional groups absorb energy corresponding to specific wave numbers. An absorption spectrum is obtained by comparing the incident and reflected (or transmitted) infrared spectra. The absorption spectrum provides a fingerprint of the different functional groups that are present in the sample. The magnitude of the absorption peak at a given wave number is related to the concentration of the functional group that absorbs energy at that wave number in the sample. For example, the carbon-oxygen bond in the carbonyl (C = O) functional group stretches by absorbing energy corresponding to wave numbers from 1820 to 1670 cm^{-1}. Therefore, an absorption peak between these wave numbers indicates the possible presence of the carbonyl functional group; the size and area under the absorption peak is an indirect indication of the concentration of the carbonyl functional group.

The FTIR absorption spectra for a material can be obtained in either (i) transmission mode or (ii) reflectance mode. In the transmission mode, the infrared beam

passes through the sample to the detector. Liquid or gaseous samples in infrared transparent cells are typically used in the transmission mode. A very thin solid film or small amount of solid mixed with a powdered infrared transparent material (like KBr) to form a pellet can also be used in the transmission mode. If a solvent is used to carry the sample (e.g., binder in a solution form), then absorption by the pure solvent must be subtracted from the absorption spectra. In the reflectance mode, the infrared beam passes through one end of an infrared transparent crystal at a grazing angle.

The beam then reflects multiple times from the interface of the sample (solid or liquid) with the crystal surface. This type of test is referred to as attenuated total reflectance (ATR) spectroscopy (Fig. 2.3). Most FTIR instruments support both types of test modes. Although the FTIR is a powerful and easy to use technique, the results must be interpreted with caution because each functional group may have more than one characteristic absorption peak (e.g., corresponding to bond stretching

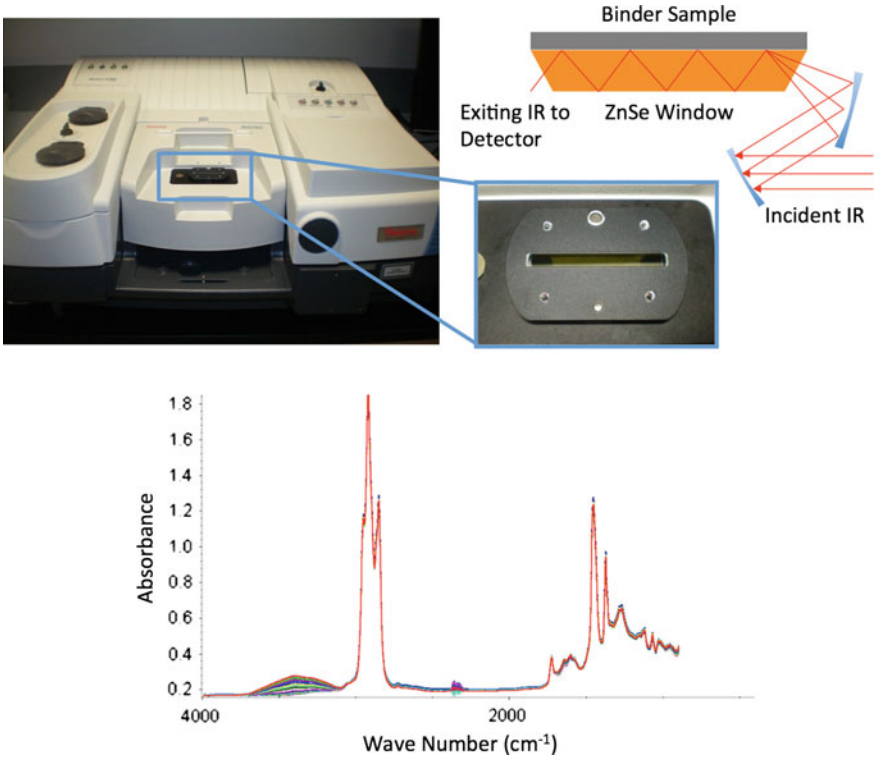

Fig. 2.3 Typical FTIR setup (*top* and *top right*) being used in the multi-bounce ATR mode; typical stack of spectra (*bottom*) for an asphalt binder exposed to water on the surface, the two highest peaks correspond to the methyl and ethyl functional groups that are predominant in asphalt binders, the several peaks with increasing intensity in the 3100 to 3700 cm^{-1} correspond to water due to diffusion in water over a period of time; peak around 1700 cm^{-1} is often used to characterize extent of oxidation (with permission from Vasconcelos 2010)

and rotating), and different functional groups may have peaks that overlap. Semiquantitative estimates must also be made carefully to account for sample-to-sample variability. As of this writing, FTIR is extensively used for research purposes (e.g., for oxidative aging kinetics). Although FTIR is not used a common tool by transportation agencies to specify or verify the chemical makeup of asphalt binders, there has been some work in this direction to promote the use of FTIR as a tool to detect and verify the polymer content in modified asphalt binders or for QA/QC to verify the use of liquid anti-stripping agent or hydrated lime in asphalt binders during mixture production.

In summary, by comparing the elemental composition (e.g., concentration of heteroatoms), it is possible to get some idea about the relative differences in functional groups between asphalt binders and expected resistance to shear, ability to bond with aggregate surfaces, and stripping in the presence of water. For any given binder, by tracking the amount of oxygen it is possible to estimate the extent to which a binder oxidizes as a function of time and temperature, also referred to as oxidation kinetics. Extent of oxidation is strongly related to the mechanical and rheological properties of the asphalt binder, although such relationships are unique for each asphalt binder and dictated by their overall chemical makeup.

2.3.2.2 Molecular Size Distribution

Attempts to relate the mechanical properties of the asphalt binder to its molecular size distribution were made during the 1960s and 1970s. The inspiration for such attempts was the observation that at the macroscopic level, the viscoelastic behavior of asphalt binders is similar to that of polymers. In the case of polymers, the mechanical properties can be modified by adjusting their molecular composition and size distribution. Therefore, it is reasonable to assume that, to some degree, the properties of the asphalt binder can also be related to molecular size distribution.

The molecular size distribution of asphalt binders is typically obtained using a method referred to as size exclusion chromatography (SEC) or gel permeation chromatography (GPC). This method entails dissolving the asphalt binder in a solvent and then pumping the solvent through a column packed with porous particles or beads. The beads are typically made of polystyrene cross-linked with divinyl benzene and are saturated in the solvent prior to use. Saturating the beads causes them to expand and form a pore structure with a broad size distribution. The asphalt binder solution is then pumped through the gel-packed column. Smaller molecules will tend to migrate into the smaller pores within the gel whereas the larger particles, owing to their size, would tend to travel in the larger spaces between the beads and within the gel. Consequently, the smaller molecules will take the longest time to travel to the outlet of the gel-packed column and vice versa. By tracking the concentration of hydrocarbons at the outlet of the GPC column over time, it is possible to obtain a distribution of molecular sizes in the asphalt binder. Figure 2.4 illustrates typical SEC results for two different asphalt binders.

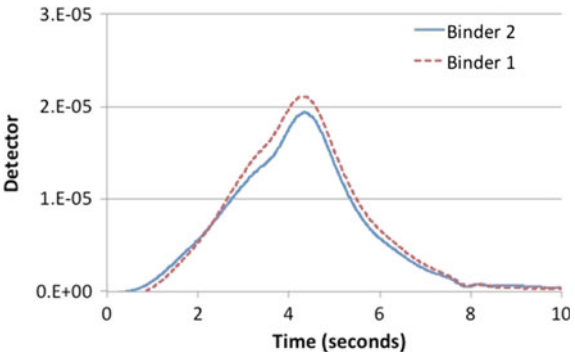

Fig. 2.4 Typical results for molecular size distribution for two binders using the SEC; B2 was oxidized version of Binder B1 and is considered to have slightly more polar and associated molecules

Careful consideration is required in comparing the results from SEC for different asphalt binders. First, results from the SEC are extremely sensitive to the particulars of the method used. Several factors influence the results from SEC. For example, results from SEC are sensitive to the choice of gel material, pore sizes in the gel material, concentration of the binder in the carrier solvent, temperature of the column, dimensions of the column, and method used to pump the solution through the column. Therefore, SEC results for different binders from different labs may not be comparable.

The second consideration is regarding the definition of molecular size itself. Molecules with high polarity have intermolecular forces that keep such molecules together. Molecules bonded by such forces are referred to as associated molecules. Although intermolecular forces are much weaker compared to intramolecular forces (e.g., a covalent bond between a hydrogen and a carbon atom), the association between molecules may be strong enough to resist separation in the solvent used as a carrier for the SEC. As a result, several smaller associated molecules may appear as a single large molecule when separated using the SEC. One may argue that since associated molecules are likely to remain as such in an asphalt binder, the SEC must be carried out using a solvent that preserves these associations.

In a study following SHRP, researchers from the Western Research Institute compared the molecular size distribution of different asphalt binders to their rheological properties. They used the SEC to separate the asphalt binder into two fractions: SEC Fraction-I and SEC Fraction-II. The demarcation between the two fractions was based on fluorescence under ultraviolet (UV) radiation at 350 nm wavelength and reported to be very distinct. The material extracted from SEC Fraction-I is often in the form of dark friable solid particles and represents the strongly associated molecules in the asphalt binder. In contrast, the material extracted from SEC Fraction-II is a dark viscous liquid comprising molecules that are not strongly associated and hence fluorescent to UV light. In terms of relationship to the mechanical properties of the asphalt binder, the phase angle δ obtained by measuring the phase shift between sinusoidal stress and strain response correlates with the concentration of the SEC Fraction-I (more on phase angle later in this chapter). In summary, the molecular size distributions from SEC can be used to compare the relative molecular associations and size distribution of different binders provided the exact same testing conditions are used during the SEC separation.

Concentration of the SEC fractions can also provide some indication of the relative elastic to viscous nature of the asphalt binder. However, the success in relating molecular weight distribution to mechanical properties is limited because although asphalt binders have similar mechanical or viscoelastic behavior as polymers, the molecular origins of such behaviors are vastly different.

2.3.2.3 Classification Based on Ionic Character

The third category to relate the chemical makeup of asphalt binders to their mechanical properties is based on the ionic character of the molecules. Ion exclusion chromatography (IEC) is used to separate the acid, base, and neutral fractions in any given asphalt binder. This method involves dissolving the asphalt binder in a solvent and pumping it through columns containing activated anion or cation resins. Molecules with a basic functional group are adsorbed on the cation resins, and molecules with an acidic functional group are adsorbed on the anion resins. Neutral fractions are eluted through the column without being absorbed by these resins. A stronger solvent is then used to desorb the basic and acidic fractions from the cationic and anionic resins. Results from the IEC can vary depending on the conditions used during chromatography, including but not limited to the type of solvent being used and the rate at which the solvent is pumped through the columns. Therefore, care must be exercised in interpreting results or comparing the results from IEC on different binders from different testing sources. Also, there are several amphoteric fractions in the asphalt binder, i.e., fractions that are both acidic and basic in nature. In sequential chromatographic columns (e.g., cation resin column followed by anion resin column), the amphoteric fractions can be adsorbed in the first column that they come into contact with.

One of the studies from SHRP (Report A-368) evaluated seven different asphalt binders based on their IEC fractions. The asphalt binders were separated into five different fractions by using solvents and adsorption resins with different strengths: weak acids, strong acids, weak bases, strong bases, and neutrals. Typical results from this study indicate that the neutral fractions make up approximately 50% of the binder by mass. Approximately 23–36% of mass fraction of the binders was weakly or strongly acidic, and approximately 13–20% of the mass fraction of the binders was weakly or strongly basic. In terms of functional groups, sulfoxides and pyrrolic functional groups were found in all polar fractions, ketones were mostly concentrated in weak acids and bases, carboxylic acids were mostly found in strong acids, quinolones were mostly found in strong acids, and phenolic functional groups were found in strong and weak acids. One of the goals of this exercise was to relate binder chemistry to ion exclusion chromatography. To this end, findings from the SHRP studies indicate that the molecular weight of the IEC neutral fraction positively correlated well with the viscosity of the binders at 25 °C. Also, the molecular weight of the strong acid fraction negatively correlated with $\tan \delta$ of the asphalt binders, where δ is the viscoelastic phase angle. However, the aforementioned correlations do not necessarily explain the mechanisms or causes that result in the viscosity building of a binder.

2.3.2.4 Classification Based on Polarity

The last form of classifying the different molecular species in an asphalt binder, and perhaps the one that has received the most attention, is based on the polarity of the molecules. Asphalt binders comprise molecules that exhibit a range of polarity from nonpolar to highly polar. As discussed previously, highly polar molecules also tend to be the most associated. Recall the aphorism from basic chemistry that "like dissolves like". In this context, if a nonpolar solvent is used with the asphalt binder, it is likely to dissolve the nonpolar molecules as well as molecules that are at least partially nonpolar leaving behind the highly polar molecules as a precipitate. In some of the earliest works related to separating the asphalt binder based on polarity, a nonpolar solvent such as n-hexane was used to separate the highly polar fractions from the less polar or nonpolar fractions. The precipitate obtained after dissolving an asphalt binder in a nonpolar solvent was referred to as asphaltene, whereas the fraction that remained dissolved in the binder was referred to as maltene. Asphaltenes are dark friable solid particles, whereas maltenes are a thick viscous fluid. Referring back to the SEC, the SEC Fraction-I typically corresponds to asphaltenes, whereas SEC Fraction-II corresponds to maltenes. Figure 2.5 shows the asphaltene and maltene fractions extracted from a typical asphalt binder.

During the late 1940s, Hubbard and Stanfield (1948) further separated the maltenes into resins and oils using other slightly polar solvents, with resins being

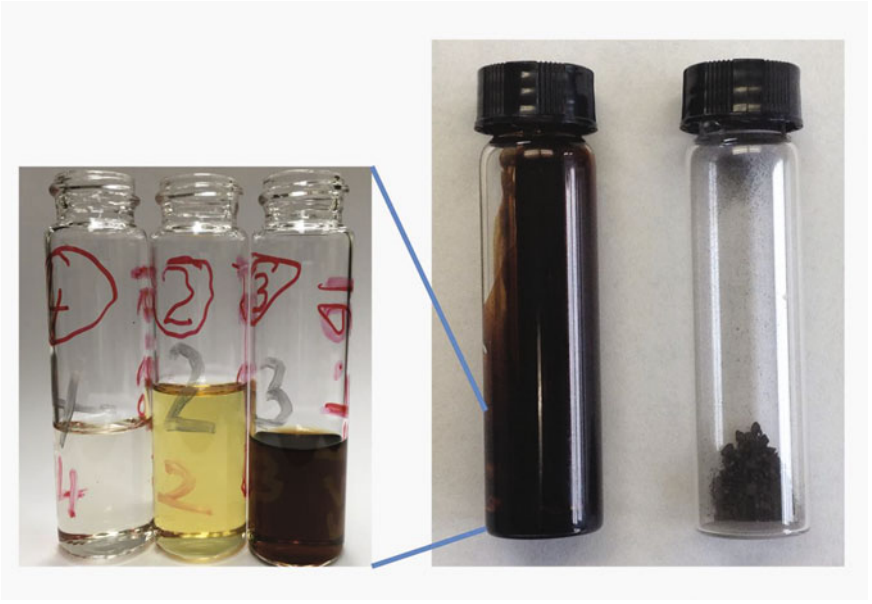

Fig. 2.5 Asphaltene (*right*) and maltene (*middle*) fractions from a typical asphalt binder separated using n-heptane; maltene further separated into Saturates, Aromatics and Resins (inset—*left* to *right*) (Photograph by A Bhasin)

slightly more polar than oils but much less polar than the asphaltenes. Finally, in the 1970s Corbett (1969) used liquid chromatography and solvents with different levels of polarity to separate maltenes into three fractions. The four fractions thus obtained are referred to in increasing order of polarity as: (S) saturates, naphthene aromatics or simply (A) aromatics, polar aromatics or (R) resins, and (A) asphaltenes. These fractions, also referred to by their acronym SARA fractions, are still being used to understand the relationship between the chemical makeup of asphalt binders and their mechanical properties. Saturates (typically 5–15% by weight) are the least polar fraction of all and have a glass transition temperature of approximately −70 °C that is approximately 40 °C below the glass transition temperature of the parent binder.

Saturates also have the lowest density of the four fractions with typical values in the range of 0.9 g/cm^3. On the other extreme, asphaltenes (typically 5–20% by weight) are highly polar dark colored solid particles at room temperatures. Asphaltenes have the highest density of the four fractions with typical values in the range of 1.15 g/cm^3. Asphaltene molecules typically have several fused aromatic rings in a plate-like structure; these molecules have been shown to stack together as micelles both experimentally and using computational modeling tools such as molecular dynamics. The aromatics and resins have polarity and properties that are in between these two extremes (saturates and asphaltenes). These four molecular species collectively work together to impart the time-dependent viscoelastic properties of the asphalt binder.

The solubility of different chemical species is typically measured using Hansen solubility parameters with units of MPa$^{0.5}$. Molecules with similar Hansen solubility parameters are more likely to remain dissolved. Saturates, aromatics, resins, and asphaltenes have a solubility range of approximately 15–17 MPa$^{0.5}$, 17–18.5 MPa$^{0.5}$, 18.5–20 MPa$^{0.5}$, and 17.6–21.7 MPa$^{0.5}$, respectively. The monotonically increasing range of solubility is also a reflection of the methodology used to separate these four fractions. The aforementioned ranges must not be considered as a definitive cutoff for these fractions but more of an approximate quantitative indicator for the polarity of the SARA fractions. As with other techniques discussed earlier, the SARA fractions are a qualitative indicator and do not have a universal definition. For any given binder, the quantitative estimates of these fractions depend on the solvents and adsorption medium used during liquid chromatography. Also, the solubility parameter, especially for asphaltenes, can be influenced by the aggregation of the different molecules and must be interpreted carefully. Having considered the asphalt binder as an ensemble of organic molecules with different structures and polarities, it is important to address the spatial assembly of such molecules.

2.3.3 Microstructure of Asphalt Binders

Figure 2.6 illustrates SARA fractions of some of the core SHRP binders. As mentioned earlier, Saturates normally compose between about 5–15 weight percent

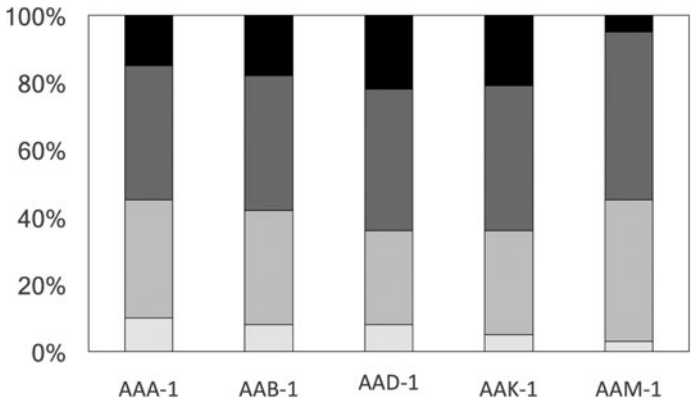

Fig. 2.6 SARA fractions for some of the binders from the core Strategic Highway Research Program, SHRP (Recreated using data from SHRP Report A-646 by Mortazavi and Moulthrop 1993)

of the paving grade bitumen (Corbett 1969). The structures are mainly aliphatic with some branching of the chains and with a solubility parameter (related to the energy required to completely remove a unit volume of molecules from their neighbors to infinite separation) between 15 and 17 $MPa^{0.5}$ (Speight 1999). The aromatics compose between about 30–45 weight percent of the bitumen and have a carbon skeleton that is slightly aliphatic with lightly condensed aromatic rings and with a notably higher molecular weight than the saturate fraction (Corbett 1969). The solubility parameter is between about 17 and 18.5 $MPa^{0.5}$ (Speight 1999).

The resins, also referred to as polar aromatics, compose between about 30 to 45 wt% of the bitumen and form a black solid at room temperature (Corbett 1969). They play a key role in the stability of the bitumen as they stabilize the asphaltene fraction. Their stability parameter lies between about 18.5 and 20 $MPa^{0.5}$ (Speight 1999). Asphaltenes generally represent between about 5 and 20 wt% of the bitumen of paving grade (Corbett 1969). Figure 2.7 presents average molecular structures of asphaltenes in oil sands. Several characteristics of the asphaltene structure may be gleaned from this figure. They contain condensed aromatic rings and more polar groups and fused aromatic structures. They also form planar molecules that can associate through π-π bonding to form staked-type structures, Fig. 2.8. The stacking phenomenon of asphaltenes has been captured by X-ray diffraction of "pure" solid asphaltenes from which the Yen model was derived as illustrated in Fig. 2.9.

Researchers have investigated the spatial organization of different molecular species within the asphalt binder since the 1940s. Knowing that the molecules that make up the asphalt binder are diverse in terms of their elemental composition, size,

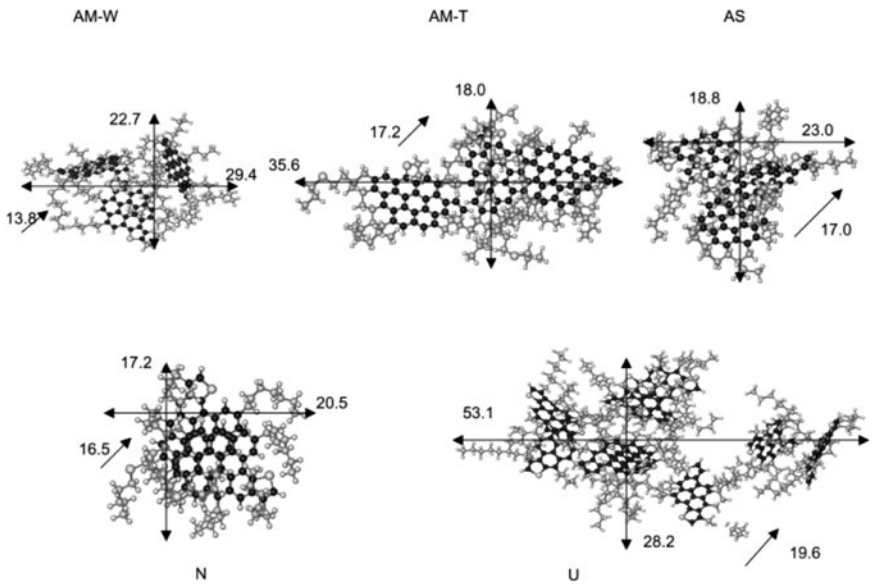

Fig. 2.7 Average molecular structures for asphaltenes from oil sands: Athabasca (Canada) asphaltenes recovered using distinct procedures (AM-W, AM-T and AS), Dahomey (Nigeria) asphlatenes (N) and Sunnydale (Utah, USA) asphaltenes. The numbers are in Angstroms (Reprinted from Fuel, 80/13, Zhao et al., Solids contents, properties and molecular structures of asphaltenes from different oilsands, pp 1907–1914, Copyright (2001), with permission from Elsevier.)

and polarity, one can imagine two possibilities for their spatial organization, henceforth referred to as the microstructure of asphalt binders. The first possibility is that different molecular species agglomerate to form well-defined structural entities within the binder. Such agglomerates may further be a function of the thermal history of the asphalt binder. The second and contrasting possibility is that the different molecular species are homogenously dispersed within the asphalt binder. The first possibility is referred to as the colloidal model, and the latter is referred to as the dispersed fluid model.

The idea that molecular species with different polarities coexist in the asphalt binder in the form of a colloid dates back to the late 1940s and 1950s from the work of Traxler and Romberg (1952). These early models proposed that asphaltenes floated in the form of micelles within a matrix of maltenes. Later studies further separated maltenes into saturates, aromatics, and resins and also demonstrated that aromatics and resins were critical in ensuring the stability of the binder. In other words, without a certain minimum percentage of aromatics and resins, the asphaltenes and saturates would simply separate. Earlier studies also proposed that these fractions created macrostructures, referred to as the sol-gel model (Pfeiffer

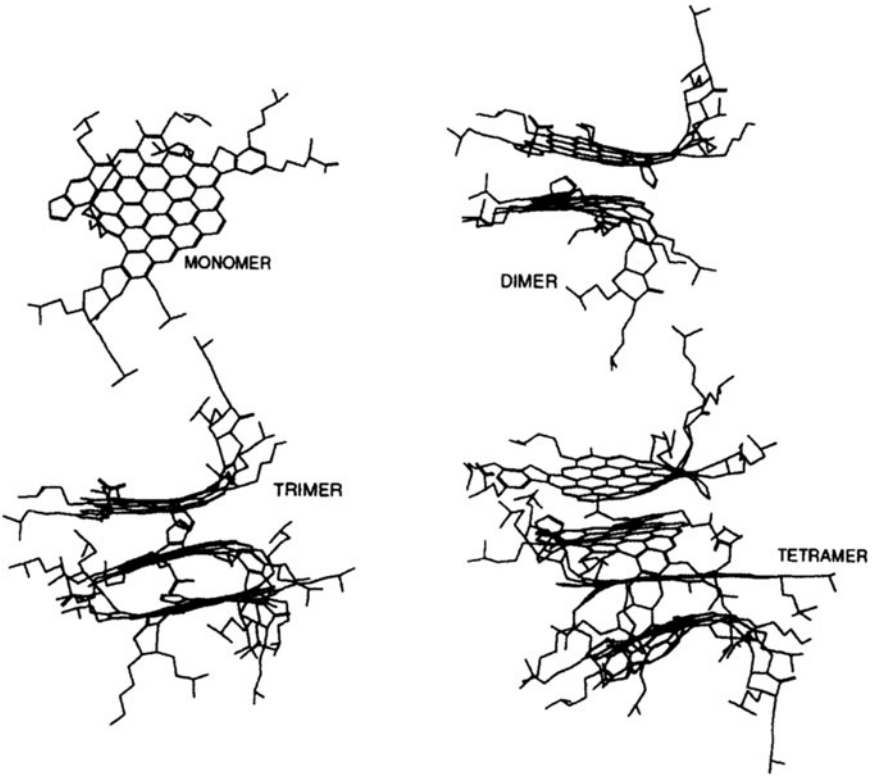

Fig. 2.8 Formation of dimer, trimer and tetramer for as Venezuelan molecule (Reprinted from Colloids and Surfaces A: Physicochemical and Engineering Aspects, 104/1, Rogel. E., Studies on asphaltene aggregation via computational chemistry, pp 85–93, Copyright (1995), with permission from Elsevier)

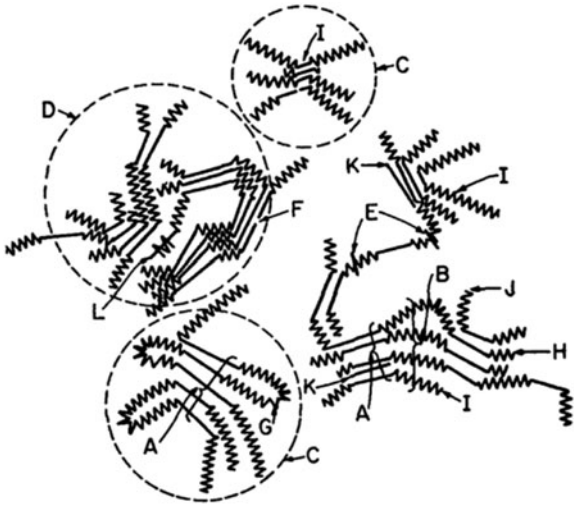

Fig. 2.9 The Yen model of "pure" solid asphaltenes (Reprinted with permission from Analytical Chemistry, Dickie, J.P. and Yen, T.F., Macrostructures of the asphaltic fractions by various instrumental methods, Vol. 39, No. 14, pp 1847–1852, Copyright (1967), American Chemical Society)

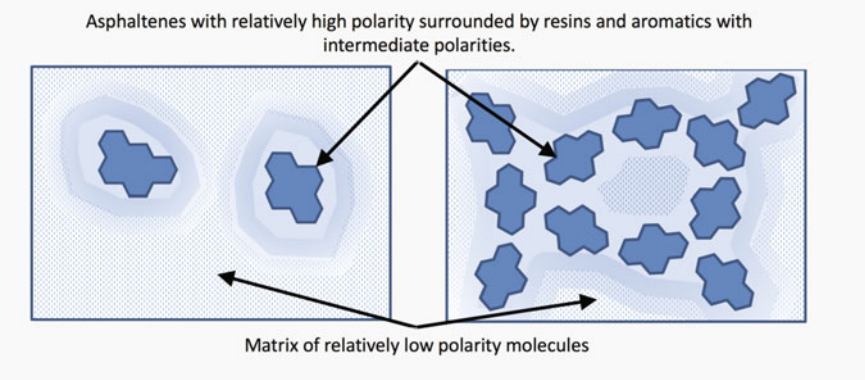

Fig. 2.10 Original colloidal model: sol and gel bitumen (Recreated based on concept from Read and Whiteoak 2003)

et al. 1940), that could be used to explain differences in the rheological behavior of bitumen from different sources. Figure 2.10 presents a schematic of the original colloidal model for sol and gel bitumens. During the most recent decade, significant experimental evidence has emerged to support the colloidal model. For example, results based on small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) indicate that asphaltenes tend to agglomerate and form micelles in asphalt binders as well as other organic solvents.

A contrasting theory to the colloidal model is the dispersed polar fluid model, which, as the name suggests, proposes that the polar molecular fractions are more uniformly dispersed within the asphalt binder. As of this writing, there seems to be increasing consensus toward the colloidal model. Readers interested in learning more about the differences between these two models for asphalt binders are encouraged to review papers by Lesueur (2009a, b) and Redelius (2006). These two papers present very thorough, and often contradicting, synthesis of observed experimental results and their interpretations supporting one or the other of the two microstructure models discussed above. For example, Lesueur (2009a, b) uses results from SAXS and SANS to support the colloidal model, whereas Redelius (2006) suggests that the SAXS and SANS cannot be used to establish whether microstructures exist, rather results from these techniques can be interpreted only if it is known a priori' that such structures exist.

A more recent body of experimental work that is being used to investigate the microstructure of asphalt binders is based on the use of atomic force microscopy (AFM). Unlike an optical (or electron) microscope, AFM scans the surface of a test specimen by "feeling" the surface of a test specimen using a very sharp conical or spherical tip attached to the end of a cantilever. The end of the tip is only a few nanometers in size and the cantilever is no more than 1 or 2 mm in length. By moving the tip over the test surface, it is possible to obtain a profile of the surface. By measuring the friction and forces of attraction between the tip and the surface, it is possible to identify whether the material underneath the tip has changed. The

latter method produces phase images highlighting the heterogeneities on the surface of the test material. Typical AFM images have a spatial resolution of a few nanometers over an image size of approximately 25 × 25 to 50 × 50 μm.

Loeber et al. (1996) were perhaps the first to identify the existence of two or more phases in the asphalt binder using AFM. They labeled the discrete phases as "bee structures" based on their peculiar shape. In more general terms, typical phases observed using AFM in an asphalt binder may be regarded as the matrix, inclusion, and matrix-inclusion interface (Fig. 2.11). Several independent research groups have confirmed the presence of these phases (e.g., Loeber et al. 1996). However, as of this writing there is a lack of consensus on the relationship between specific phases and molecular species in the asphalt binder. Readers must also note that the term "phase" in this context is not employed in the strictest sense. In physics and chemistry, the term phase is used to describe one of many states or configurations for a material with the same chemical composition. For example, water, ice, and steam are different phases of the same material. In the context of asphalt binders and literature relevant to AFM, the term phase may refer to a microstructural entity with entirely different chemistry. The term domain or microdomain, although not commonly used in the asphalt literature, may be more appropriate.

As mentioned before, as of this writing there is no conclusive evidence in the literature to fully explain the chemical makeup of the different domains that appear in the AFM images (Fig. 2.11). For example, Masson and coworkers suggest that the inclusions represented asphaltenes in the asphalt binders (2007). Kringos et al. (2009) and Schmets et al. (2010, 2009) suggest that the asphalt binder comprises two different phases: a wax rich phase and a continuous matrix surrounding it. They attributed the inclusions (aka "bee structures") to waxes in the asphalt binder as opposed to the asphaltenes as suggested by Masson et al. (2007, 2006). However, the wax content in most asphalt binders is typically between 0 and 7%, which is not consistent with the relative percentage of the inclusions in the AFM images.

Other researchers conducted a systematic evaluation of the different domains observed using the AFM. In one study, the microrheology of the different domains observed using the AFM before and after oxidative aging of different binders was evaluated and compared (Allen et al. 2012). Results showed that (1) oxidative aging increased the size and frequency of the inclusions, and (2) the inclusions and inclusion-matrix interface were much stiffer than the paraphase. Other studies have established that oxidative aging increases the percentage of asphaltenes through the oxidation and concomitant decrease in the concentration of resins and aromatics (Lin et al. 1995; Petersen et al. 1993; Petersen 1984). This information in conjunction with the AFM results suggests that the inclusions may be related to the presence of asphaltenes. Also, since the stiffness of asphaltenes is typically an order of magnitude higher than the aromatics or saturates, it is unlikely that the inclusions or inclusion-matrix interface are made up entirely of asphaltenes but are more likely to contain a higher concentration of asphaltenes and resins. Other studies related to the use of the AFM were conducted by different derivative asphalt binders that were produced by doping the original binder with each one of the four chemical fractions (SARA) (Allen et al. 2013). These studies also showed that the difference between

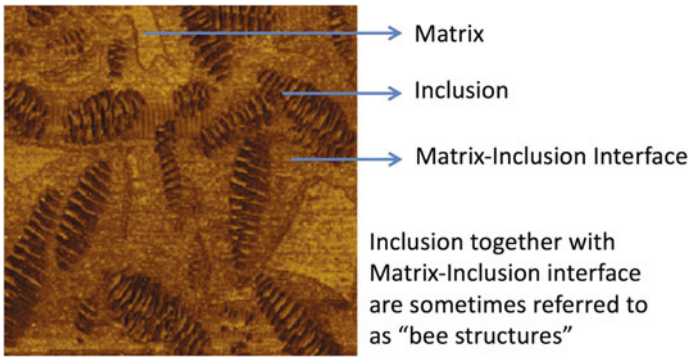

Fig. 2.11 Typical phase image obtained for an asphalt binder using AFM; the image shows different phases in the asphalt binder

the percentage of asphaltenes and saturates (the two extreme polars in the SARA fraction) was related to the size and dispersion of the catanaphase and periphase. Finally, more recent studies have shown that these structures are much smaller within the bulk of the binder compared to the surface and highly dependent on the composition and thermal history of the binder (Ramm et al. 2016).

It is possible that the inclusions and the inclusion-matrix interface may not exclusively correspond to asphaltenes or waxes as suggested by other researchers. A more realistic explanation for these phases, which is also consistent with the reported experimental evidence, is that these domains have higher concentrations of asphaltenes and resins, while the matrix has a higher concentration of saturates and aromatics. This proposed model of the asphalt microstructure reconciles the differences reported by the proponents of the colloidal model and the dispersed fluid model.

One of the major drawbacks of using the AFM is that this technique does not investigate the bulk of the asphalt binder and evaluates a test material only at its surface. Also, unless a series of functionalized tips are used with AFM imaging, the phase images cannot be used to identify the chemical composition of the asphalt binder.

2.3.4 Relationship Between Microstructure and Engineering Properties of Asphalt Binder

The ultimate goal of understanding the relationship between chemical composition, microstructure, and rheological properties of an asphalt binder is that such knowledge can eventually be used to design newer asphalt binders, binder modifiers, or eco-friendly substitutes with superior mechanical properties and performance characteristics.

Thus far, we have discussed the possible relationship between the chemical composition and microstructure of the asphalt binders but we have not fully addressed a very relevant question: Can the properties of the constituent chemical fractions be used to predict the properties of the binder without knowing the microstructural arrangement of these fractions within the binder? In other words, Why is understanding the chemical makeup and microstructure of the asphalt binder important?

To answer this question, let us consider the problem of predicting the mechanical or rheological properties of a composite (in this case asphalt binder) of different constituent materials (in this case SARA fractions). The simplest approach to solve such a problem would be to use the rule of mixtures or something similar to Einstein's model. However, studies also show that the shape, size distribution, and interfacial properties of the inclusions in a matrix significantly influence the properties of the composite (Chow 1980; Demjén et al. 1998; Verghese and Lesko 1999). One of the models that has been used with some success to predict the rheological properties of a composite of two different viscoelastic materials was proposed by Palierne (1990). Other studies have shown that even the Palierne model cannot accurately predict the composite properties, when there are more than two components in the composite (Elias et al. 2007). To summarize, in addition to the volume concentration, the microstructure of a multicomponent or multiphase material must also be known to predict the properties of the composite.

The fact that mixture models cannot be used to predict the properties of a composite binder has been well known within the industry for many years. For example, Siegmann (1950) demonstrated that the mixture of two crude stock binders from two different sources with very high and similar stiffness resulted in a composite that had a stiffness that was lower than the stiffness of the constituent binders. The only explanation for the results observed by Siegmann is that combining the crude stocks from these two chemically diverse sources resulted in a microstructure that reduced the overall stiffness of the composite binder. Other researchers (Kringos et al. 2009) have also hypothesized that the microstructure within the asphalt and the difference in the stiffness of the microstructural entities is responsible for nucleating fatigue cracks in the asphalt binder.

To further demonstrate the significance of microstructure on the properties of the composite, consider a simple 2D finite element analysis of an asphalt binder based on the geometry and microrheology obtained using AFM. Figure 2.12 illustrates the creep compliance of the different phases within the binder as well as the creep compliance of the composite. The colored overlay on the AFM images shows regions of stress concentration, where the local stress intensity is two to five times the far field stress.

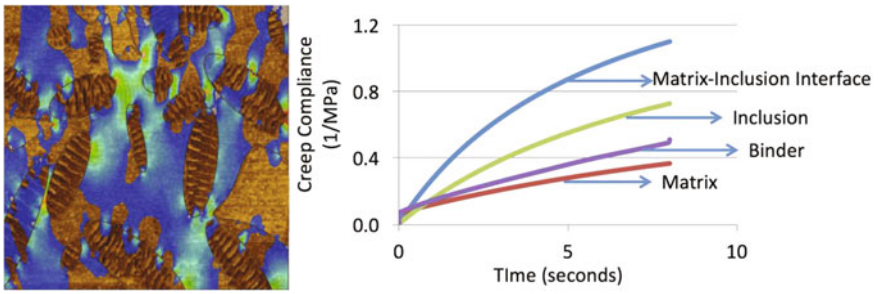

Fig. 2.12 Results from a simple 2D finite element analysis that demonstrate the influence of microstructure on the overall properties of the binder

2.3.5 Concluding Thoughts on the Chemical Properties of Asphalt Binders

In summary, the chemical makeup of asphalt binders and their microstructure (defined as the spatial arrangement of different chemical species within the binder) significantly influence the engineering properties of the binder. Although chemical properties of asphalt binders discussed in the preceding sections are typically not used for purchase specifications or as an input in the design of asphalt binders, mixtures, or pavements, this information is extremely useful to better understand several aspects related to binder selection and mixture design. For example, the knowledge of binder chemistry is important to understand the effect of binder oxidation on mixture performance, role of chemical and other additives to enhance binder and mixture properties, and handling of recycled asphalt materials in design of new asphalt mixtures. These and other aspects will be discussed in the following sections and chapters. Engineers and researchers involved in the production and modification of asphalt binders should treat the aforementioned section as a simplified starting point for further reading.

2.4 Aging in Asphalt Binders

Understanding aging in asphalt binders is very important to appreciate the significant changes that occur in the mechanical response of the asphalt binder during the various stages of its life starting from asphalt mixture production in a hot-mix plant to end of service life in an asphalt pavement, and beyond as the binder may be used in the form of recycled asphalt material incorporated in new asphalt mixtures. Typically the term “aging” of asphalt binders generally refers to oxidative aging of binders. However, in a more general sense the term aging may sometimes also be used to describe the hardening of asphalt binders due to steric hardening (that is

reversible), oxidative aging, loss of volatiles from the binder, or any combination of these factors. This section briefly describes these processes. The importance of aging in characterizing the properties of asphalt binders and composites cannot be over emphasized. Although the subject of aging is introduced here only briefly, it will be a recurring theme throughout this book as we investigate its influence on physical and mechanical properties of asphalt binders and composites.

2.4.1 Steric Hardening

Steric hardening is also referred to as reversible aging and can occur at intermediate to low temperatures. At intermediate temperatures (typically around 5–25 °C), steric hardening is typically driven by the polar nature of the molecules. Recall from the previous section that asphalt binders comprise molecules with varying degrees of polarity. Note that polar molecules also tend to have opposite charges at different ends. For example, consider the pyridine molecule as shown in Fig. 2.13. The nitrogen atom imparts polarity to this molecule, with one end of the molecule being positively charged and the other being negatively charged.

Molecules above absolute zero possess some amount of energy that keeps them in constant motion. As a result, over time, polar molecules within the material tend to rearrange themselves such that the opposite charges between two adjacent polar molecules are aligned next to each other. This results in the formation of secondary bonds or associations between the polar molecules and a concomitant increase in the capacity of the material to resist deformation; engineers recognize this as an increase in stiffness. As a corollary, the breakdown of these secondary bonds or associations causes the material to loose its stiffness or become soft. Secondary bonds are weak bonds and require very little energy to be disrupted. This energy can be provided in the form of thermal energy by heating the binder or in the form of external work by applying stress. Steric hardening is also referred to as reversible aging, since the formation of secondary bonds between molecules and concomitant increase in stiffness can be reversed by heat or work.

Steric hardening or reversible aging also takes place at lower temperatures (typically below 0 °C), albeit via a different mechanism. At lower temperatures, neutral or apolar molecules (and typically molecules with few or no branches) tend to reorient themselves into a well-organized structure. This organization typically tends to increase the overall stiffness of the asphalt binder. This process is typically referred to as crystallization of naturally occurring “waxes” in the asphalt binder. The resulting increase in stiffness is also referred to as physical hardening in some literature. In fact, a temperature sweep conducted using a differential scanning calorimeter can be used to detect the energy released during the crystallization of the these molecules. Similar to steric hardening at intermediate temperatures, physical hardening at low temperatures is also easily reversed with an increase in temperature. The existence of this form of hardening must be recognized while measuring engineering properties of the material. For example, certain studies have

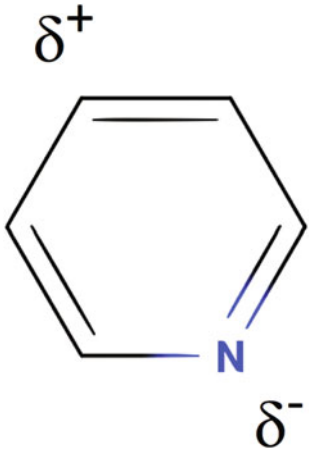

Fig. 2.13 Structure of polar pyridine molecule showing regions of positive and negative charge

shown that asphalt binders conditioned at low temperatures (approximately −5 to −10 °C) continue to show an increase in stiffness with an increase in the conditioning time up to a certain limit.

2.4.2 Volatilization and Oxidative Aging

Asphalt binder experiences oxidation during two stages of its life: (1) during mixture production and placement and (2) during its service life. During production and placement, a process that can last typically for a few hours, hot or warm mix asphalt binder is maintained at very high temperatures (typically above 100 °C) in the form of a thin film coating aggregate particles in a loose mix. These conditions (high surface area, high temperature, and easy access to oxygen from air in a loose mix) result in significant oxidation of the asphalt binder by the time it is placed and compacted in the field. Also during this time, some of the lighter and more volatile fractions escape from the asphalt binder. Oxidation of the binder continues during the service life of the asphalt pavement albeit at a much slower rate, since the temperatures are relatively lower and access to oxygen is limited.

As the name suggests, oxidative aging occurs due to the oxidation of unsaturated bonds typically in the aromatics and resins fraction of the binder. Unlike steric hardening, oxidation results in a change in the molecular structure that cannot be easily reversed. The addition of an oxygen atom to a molecule also typically results in an increase in its polarity. As a result, over time the aromatic and resin molecules are consumed to form more asphaltene like polar molecules. This in turn leads to the formation of larger and more associated groups of molecules that increase the stiffness and decrease the ductility of the binder. Since oxidative aging and concomitant changes in the properties of the asphalt binder and mixture continue to occur over the service life of the pavement, it is imperative that any approach to

predict the performance of a mixture or pavement structure take into consideration this continually changing nature of the asphalt binder.

2.4.3 Simulating Aging in Asphalt Binders

Asphalt binders are typically evaluated for their mechanical properties at different levels of aging. For practical purposes, three different points or levels of aging are defined for asphalt binders: (1) unaged, (2) short-term aged, and (3) long-term aged. As the name suggests, unaged binder is the binder as received from the refinery by the contractor responsible for producing the hot mix asphalt. The viscosity of the unaged binder is of interest, because it dictates the workability of the asphalt mixture during production at the hot mix plant. The short-term aged binder refers to the binder immediately after placement in the field. In this sense, short-term aging encompasses aging that occurs during the few hours starting from mixture production at the hot mix plant, transport to the construction site, until placement and compaction. Recall that although the short-term aging occurs only for a duration of a few hours, the loss of volatiles and extent of oxidation is significantly higher on account of: (1) the high mixing temperatures and (2) excessive exposed surface area of the binder-coated aggregates in the loose mix. Finally, long-term aged binder reflects the state of the binder in the mixture at the end of the expected service life of the pavement. The duration of time between the short-term aged state and the long-term aged state is several years, but in this case the oxidation occurs at typical service temperatures of the pavement.

Several methods have been developed over the years to simulate short-term and long-term aging in asphalt binders in a laboratory environment in a short accelerated time frame. Two of the most common methods are the rolling thin film oven (RTFO) and pressure aging vessel (PAV) to simulate short-term and long-term aging, respectively. The RTFO is a device (typical device shown in Fig. 2.14) that injects a stream of hot air (typically at 163 °C) into an open mouthed bottle filled with asphalt binder. The bottle or bottles filled with the asphalt binder are placed on a rack that constantly rotates. The rotation helps the binder film flow over itself, thus avoiding a scenario in which only the surface of the binder is oxidized. The aging is carried out typically for 85 min, and the binder sample is weighed before and after aging to estimate the mass percent of volatiles that escape from the binder. At the end of the test, the binder sample is treated as a short-term aged binder. A very important consideration here is that the binder industry typically uses standard temperature and duration for producing these so-called short-term aged binders and for subsequent grading of the binder. Given the fact that the binders used in the field may be produced using a hot mix asphalt or warm mix asphalt technology (at 20–30 °C lower than hot mix asphalt), transported over varying distances for construction at elevated temperatures, and possibly even stored in a heated silo for extended durations, it is unlikely that a universal standard time and temperature for RTFO aging would result in an accurate representation of the binder

aged in the field. On the other hand, when the binder is being produced in a refinery, there is no way for the producer to ascertain the circumstances or technology that will be used to produce and place the asphalt mixture in the field. As a result, despite this limitation the RTFO is still used as a standard benchmark to physically produce a short-term aged sample of the asphalt binder.

The sample aged using the RTFO is further aged with the pressure aging vessel or PAV to simulate long-term aging (typical device shown in Fig. 2.15). The RTFO binder sample is placed as a thin film on a metal tray in the PAV. The sample is then subjected typically to a temperature of 100 °C at 300 psi (2.07 MPa) pressure for 20 h in the presence of air which naturally contains oxygen. The aging temperature may vary based on climatic conditions. The high temperature and pressure accelerate oxidation in the binder to simulate several years of aging. Similar to the RTFO, the conditions used for PAV are standardized, which helps with the grading and specification of the asphalt binder but is not always the most accurate representation of what occurs in the field. Also, there has been some criticism that the PAV aging does not really simulate the claimed 7–10 years of aging. For example, some recent studies have aged the asphalt binder under atmospheric conditions at realistic high pavement temperatures (e.g., 60 °C) and compared the binder to the PAV-aged binder to suggest that the PAV does not age the binder as severely as claimed. Another criticism about the PAV aging method is that the high temperature and pressures may trigger reactions that would normally not occur in the pavement at the typical service temperatures (recall from basic chemistry that certain reactions have an energy barrier or threshold that needs to be crossed for the reaction to occur).

2.5 Mechanical Properties

2.5.1 Scope

In the previous sections, we have emphasized the need to be knowledgeable of binder chemistry (at least to some extent) in order to better understand and appreciate the mechanical behavior of asphalt binders and consequently asphalt mixtures. This section will first discuss the challenges and differences in characterizing the properties of an asphalt binder, which are also applicable for asphalt mixtures. This will be followed by an overview of the methods typically used to characterize the time, temperature, and age dependent properties of an asphalt binder. This section is a starting point for readers who are being introduced for the first time to asphalt binders or for practicing engineers who are interested in refreshing their knowledge on the basics of rheology that are the basis for current standards. For readers interested in details of the current industry standards and protocols used to grade asphalt binders, a list of easily downloadable references is provided at the end of this chapter. Readers interested in a more in-depth

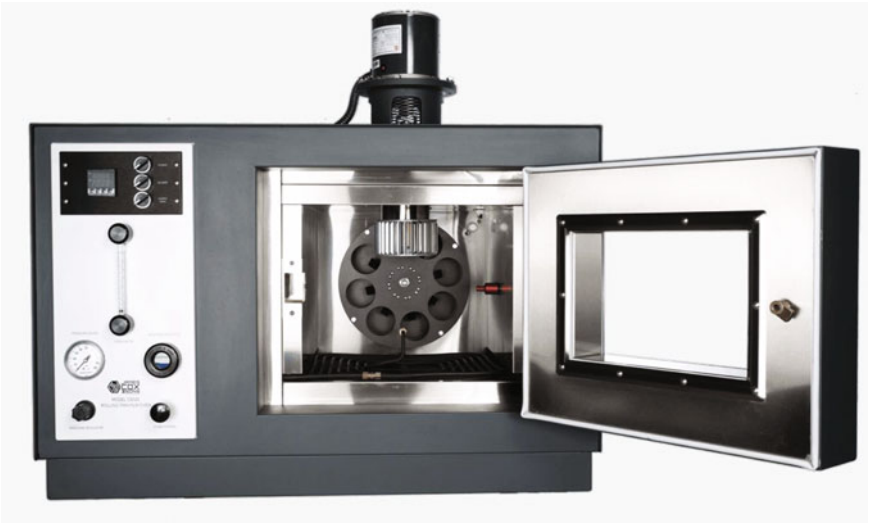

Fig. 2.14 Image of a typical RTFO device for short-term aging (Image courtesy of James Cox and Sons, USA)

mathematical analysis of the methods described in this chapter can refer to Part II of this book. *Note that the information presented in this section and chapter is for a reader interested in having the basic working knowledge of the methods used to characterize asphalt binders and model its response. A more detailed and mathematically rigorous account of these models is revisited again in Part II and Chap. 13 of this book. A slight overlap of information and repetition is by design to enable the readers to appreciate the application of the mathematical methods in the context of the material (asphalt binder or mixture) as well as in the context of the general principles of mechanics.*

2.5.2 *Significance of Mechanical Properties of Binder and Challenges*

Characterizing and reporting binder properties is far more complex compared to other construction materials. To illustrate this, let us once again use the example of steel and contrast the design of an asphalt pavement to the design of a steel structure in three areas: material characterization, structural design, and failure.

First, in terms of material characterization, steel used in construction can typically be considered to be linear elastic within its service range. In other words, steel has a well-defined modulus and tensile strength that does not vary with rate of loading, typical service temperatures, or age of the structure (exceptions to this may be

Fig. 2.15 Image of a typical PAV device for long-term aging (Image courtesy of Gilson Company Inc., USA)

designing structures that resist high temperatures in the event of a fire). In contrast, the mechanical properties of asphalt binders and concomitantly those of asphalt mixtures are highly dependent on time histories or rate of loading (e.g., traffic speeds or rate of cooling), temperature of the environment, and age of the material.

Second, in terms of structural design, a steel structure can take any simple or complex geometric form. The job of a design engineer is to calculate stresses at different locations within the structure and to determine the cross sections of steel members. In contrast, an asphalt pavement always has a geometry of a slab; the only design variable that can be manipulated by design engineer is the layer

thickness and in some cases the use of an interface layer with special properties between these layers (e.g., geosynthetics or other membranes).

Third, in terms of failure criteria, steel structures oftentimes fail due to lack of serviceability (e.g., unacceptable deflection) much before they fail due to lack of strength (e.g., fracture or plastic failure). In contrast, failure in asphalt pavements due to lack of serviceability occurs much after failure due to lack of strength. For example, microcracks and concomitant weakening of the pavement or small amounts of plastic deformation are allowed to a certain extent as long as it does not severely deteriorate the pavement structure and ride quality.

In summary, the most challenging aspect of designing a pavement structure is not the complexity of the structure but rather the complexity of the stress-strain behavior that is dependent on the time or rate of loading, the temperature of the material, and the age of the binder. More importantly, flexible pavement structures are allowed to accrue small amounts of damage (e.g., plastic deformation or rutting and microcracking) before they become unserviceable. Therefore, characterization of the stress-strain response of the material in an undamaged state as well as the characterization of damage evolution (as a function of time or rate of loading, temperature, and age) in asphalt materials is critically important and perhaps the most challenging aspect of material and pavement design.

2.5.3 Time Dependency

Asphalt binders are observed to be time dependent or viscoelastic in nature. The term viscoelastic indicates that the material response is somewhere in between that of a viscous fluid and an elastic solid. The stress-strain behavior of an isotropic linear elastic solid in one dimension is typically given as $E = \sigma/\in$, where E is the modulus of elasticity, σ is the stress, and $\in$ is the strain. Also, recall the behavior of a simple Newtonian fluid, wherein the shear stress is directly proportional to the strain rate. This relationship is typically denoted as $\eta = \tau/\dot{\gamma}$, where η is the shear viscosity, τ is the shear stress, and $\dot{\gamma}$ is the shear strain rate. Asphalt binders are typically shown to have a stress-strain response that is a combination of an elastic solid and a viscous fluid (although not necessarily a Newtonian fluid). As a result, any model that describes the stress-strain relationship of an asphalt binder will inevitably include time or rate of loading. The influence of time decreases with a decrease in temperature. This will be discussed in more detail in the next subsection.

The time or rate dependency of asphalt binders is typically modeled and measured either in time domain or frequency domain. The two most common tests used in the time domain are the creep test and relaxation test. These two tests yield the creep compliance and relaxation modulus of the material, respectively. *The test used in the frequency domain is the frequency sweep test that yields the complex or dynamic modulus of the material.* Note that the tests discussed here are typically considered to represent the linear viscoelastic response of the material without any damage. In other words, *these tests are typically conducted by applying a stress or*

strain of magnitude that is not large enough to induce significant permanent damage to the material. A more detailed mathematical description of these behaviors and test methods is discussed in Part II of this book (Chaps. 11 and 12).

The creep test involves applying an instantaneous constant load or strictly speaking stress to the test specimen and measuring its deformation over time. The material property measured using such a test is referred to as the creep compliance, $D(t) = \varepsilon(t)/\sigma_0$, where σ_0 represents the constant stress applied during the creep test, and $\varepsilon(t)$ denotes the measured strain that changes with time. The creep compliance $D(t)$ can be represented using any mathematical function that appropriately describes the observed material behavior. For example, mechanical analog models are sometimes used to model the measured response. Such models comprise one or more elastic springs and viscous dashpots configured in series or parallel or a combination of the two such the overall mechanical model can mathematically simulate the measured response of the material. Another approach is to use simple phenomenological models to model the measured creep behavior. For example, the power law model $D(t) = D_0 + D_1 t^m$ or the Prony series of the form $D(t) = D_0 - \sum_{i=1}^{n} D_i e^{t/\tau_i}$ are often used to model the measured creep compliance of the material as a function of time. The terms D_0, D_i, m, and τ_i are constants that are unique to the material and obtained by fitting the experimentally measured response to the model. It is important to emphasize during this discussion that one should not decide a model a priori and then use it to represent the material behavior. Ideally, it is important to first observe the material response under well-controlled laboratory conditions and then identify the best (and simplest) model that can be used to represent the material response (revisited in more detail in Chap. 13).

A variation of the creep test is the creep-recovery test. In this case, the constant load is instantaneously removed after a specific duration of loading time and the strain recovery of the material is recorded. The observed strain from such a test is often decomposed into components such as elastic or instantaneous strain typically denoted as ε_e, time dependent or viscoelastic strain typically denoted as ε_{ve}, and permanent or irrecoverable viscoplastic strain typically denoted as ε_{vp}. As a side note, in some literature time dependent elastic and viscoelastic mean different things; the former refers to the time dependent elastic behavior with complete recovery of strain after removal of all loads at some point in time whereas the latter suggests that there is some extent of permanent strain after the application of loads. The existence or relative magnitude of these components depends on the material being tested as well as the test conditions. In the context of asphalt materials, the irrecoverable or viscoplastic strain is regarded as the source for distresses such as rutting. The constitutive models for materials that are intended to incorporate damage must include terms to account for such strains. Figure 2.16 presents a schematic of the creep compliance test with typical response for a viscoelastic material and an elastic material.

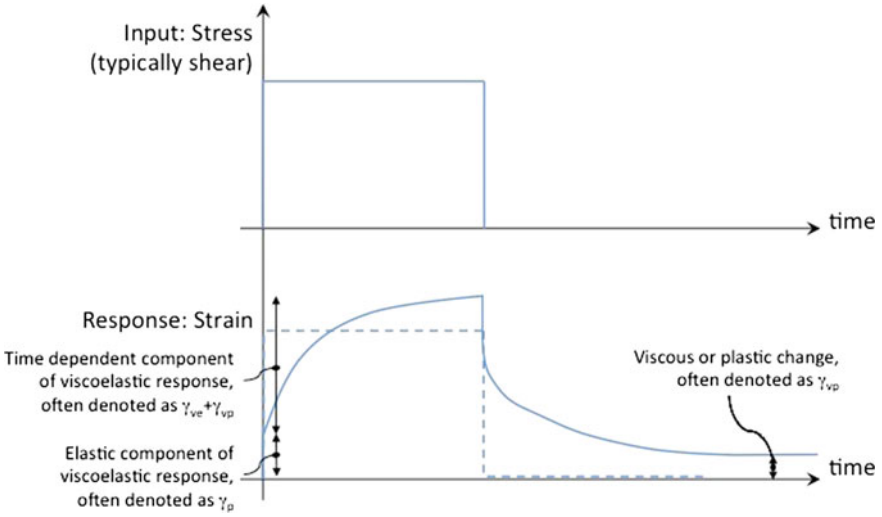

Fig. 2.16 Typical response from a creep-recovery test

The relaxation test involves applying an instantaneous constant deformation or strictly speaking strain to the test specimen and measuring the reaction stress over time. The material property measured using such a test is referred to as the relaxation modulus, $E(t)$, given by $E(t) = \sigma(t)/\in_0$, where $\in_0$ represents the constant strain applied during the relaxation test, and $\sigma(t)$ denotes the measured stress that relaxes with time. Similar to the creep compliance, the relaxation modulus $E(t)$ can also be represented using mechanical analog models or phenomenological models such as the power law or the Prony series. Note that the power law or Prony series will have a different sign for some of the coefficients because of the decreasing nature of the relaxation modulus with time. Figure 2.17 presents a schematic of the relaxation test with typical response for an elastic and viscoelastic material.

The frequency sweep test involves applying several cycles with either constant stress amplitude or constant strain amplitude in a sinusoidal waveform. A constant stress amplitude is applied and the resulting strain amplitude is measured and recorded over time or vice versa. When subject to stress (or strain) following a sinusoidal waveform, the strain (or stress) response of a viscoelastic material reaches a steady state after a few load cycles. It is important to remember that this property is measured only when the material has reached a steady state response. During this steady state, a constant time lag is observed between the stress and strain waves. The time lag, Δt, or phase shift is expressed in the form of a phase angle, δ, in degrees given as $360^\circ f\Delta t$ or $360^\circ\omega\Delta t/2\pi$, where f is the frequency of the sinusoidal wave in Hz or ω is the angular frequency in radians/second. Also, once the material response has reached steady state, the magnitude of complex modulus, $|E^*|$, is defined as $\sigma_0/\in_0$, where σ_0 and $\in_0$ are the stress and strain amplitudes, respectively. Note that the complex modulus is also sometimes referred

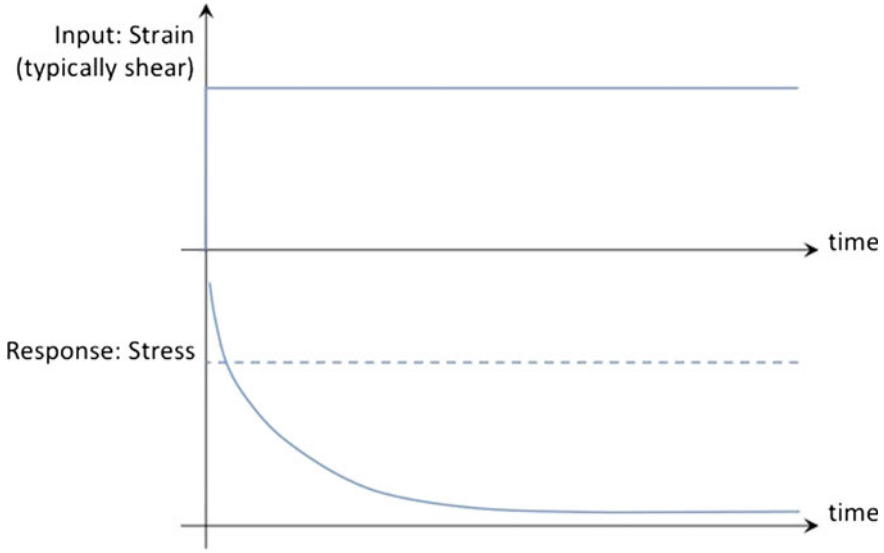

Fig. 2.17 Typical response from a relaxation test

to as dynamic modulus in the common asphalt literature, however, strictly speaking from a mechanics point of view the term dynamic modulus is not appropriate. The notation G^* may be used in lieu of E^*, when the test is conducted in a cyclic shear mode as opposed to a cyclic tension or compression mode. Figure 2.18 presents a schematic of the dynamic modulus test.

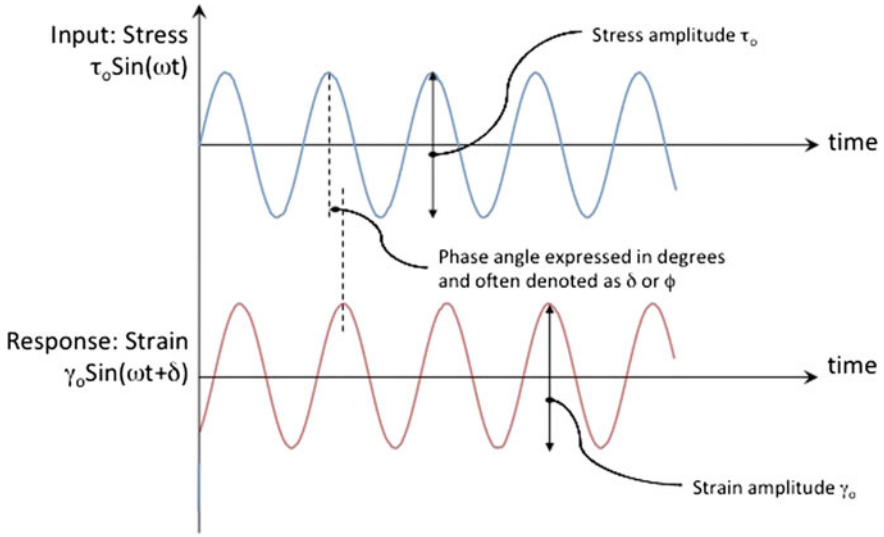

Fig. 2.18 Typical input and response at one frequency for a dynamic modulus test

The complex modulus is also sometimes expressed using complex notation as $E^* = E' + iE''$, where the tangent of the phase angle $\tan\delta = E''/E'$ and the magnitude of the complex modulus E^* is given as $|E^*| = \sqrt{E'^2 + E''^2}$. The term E' denotes the storage or elastic part of the modulus that is in complete sync with the applied load. The term E'' denotes the loss modulus or fluid part of the modulus, that is, 90° out of phase with the applied load. A more detailed mathematical description of these terms can be found in Chap. 13. Also, note that the complex modulus and phase angle are functions of the frequency f or angular frequency ω. Therefore, strictly speaking these terms are measured at multiple frequencies and must be represented as $E^*(\omega)$ and $\delta(\omega)$. Tests conducted at multiple frequencies are referred as frequency sweep tests. The typical protocol for such tests involves subjecting the test specimen to several cycles at a given frequency of sinusoidal loading with a small stress or strain amplitude. The material response from the last few cycles in steady state is then used to determine the modulus and phase angle at that frequency. The process is repeated at several different frequencies. The applied stress or strain amplitudes are usually very small to ensure that the specimen does not experience any permanent change or damage during the process. In addition to complex modulus, the term complex compliance denoted by $|D^*|(\omega)$ or $|J^*|(\omega)$ is also sometimes used. Complex compliance is simply the ratio of the strain amplitude to the stress amplitude, and its magnitude is the inverse of the complex modulus.

It is important to briefly describe the interrelationship between creep compliance, relaxation modulus, complex modulus, and complex compliance. These four metrics are material properties, and therefore it is expected that these be related to each other for a given material. This is true as long as the material is evaluated within its linear viscoelastic limits (i.e., limits within which the stress and strain response are proportional to each other for a given time history). In other words, if any one of the four properties $E(t)$, $D(t)$,$|E^*|(\omega)$, or $|D^*|(\omega)$ is known, then the other three properties can be determined. For example, the magnitude $|E^*|(\omega)$ and $|D^*|(\omega)$ are inverses of each other at any given frequency and one can easily be obtained from the other. Along the same lines, although the properties $E(t)$ and $D(t)$ are not numerical inverses of each other at any given time, one can be obtained from the other by using appropriate mathematical transformations. Also, properties in the frequency domain such as complex modulus or compliance can be obtained using hereditary integrals from properties measured in the time domain such as creep compliance or relaxation modulus. In fact, hereditary integrals can also be used to obtain the response for any arbitrary loading history if either the relaxation modulus or creep compliance is known. For example, asphalt mixtures (although not asphalt binders) are traditionally evaluated using a resilient modulus test, wherein a haversine pulse with 0.1 s loading time is applied followed by a rest or dwell time of 0.9 s. The response of the material under such a loading history can be calculated (assuming the material is linear viscoelastic) if any of the four basic material properties are known. *In fact, uniaxial forms of the hereditary integrals (Eqs. 2.1 and 2.2) are the most basic constitutive models to obtain stress response over time*

given a strain history or vice versa. For a linear elastic material subjected to uniaxial stresses, the stress is computed as the product of the elastic modulus and the given strain or the strain is computed simply as the ratio of the given stress to the elastic modulus. Equations 2.1 and 2.2 are analogous to this relationship for a time-dependent material. A more detailed description of the hereditary integral and interconversion between these four metrics can be found in Chap. 13.

$$\sigma(t) = \int_0^t E(t-\tau)\frac{\partial \varepsilon(\tau)}{\partial \tau}d\tau \tag{2.1}$$

$$\varepsilon(t) = \int_0^t D(t-\tau)\frac{\partial \sigma(\tau)}{\partial \tau}d\tau \tag{2.2}$$

Finally, readers must note that while this information is being presented in the context of mechanical properties of an asphalt binder, it is also applicable to characterize the basic undamaged properties of asphalt mixtures, which will be discussed in subsequent chapters.

2.5.4 Temperature Dependency

In the previous subsection, we reviewed the methods and metrics that are typically used to characterize the time-dependent stress-strain relationship of asphalt binders. In this section, we will review the temperature dependency of asphalt binders with some introduction of the mathematical tools and methods that are used to model such dependencies.

The creep compliance, relaxation modulus, and complex modulus described in the previous section are very sensitive to the temperature of the binder. For example, it is not unusual for the complex modulus to increase by four or five orders of magnitude as the temperature is gradually decreased from a typical maximum in-service temperature to a typical minimum in-service temperature. Perhaps the most straightforward way to handle the temperature sensitivity of the asphalt binder is to define the basic material properties such as relaxation, creep compliance, and complex modulus as functions of both time (or frequency) and temperature denoted by T, e.g., $E(t,T)$ or $D(t,T)$ or $|E^*|(\omega,T)$. However, several materials including asphalt binders exhibit a behavior referred to as being thermorheologically simple. This provides a more elegant approach to quantify and work with the temperature sensitivity of asphalt binders.

Consider, for example, Fig. 2.19. The figure shows complex modulus, $|G^*|(\omega)$, collected from a frequency sweep test on a binder at five different temperatures. As expected, at any given frequency of loading, an increase in temperature tends to soften the material and consequently reduce the complex modulus. Further observation of the data reveals that there is a smooth overlap of data shifted from different temperatures. If the data at different temperatures were to be horizontally

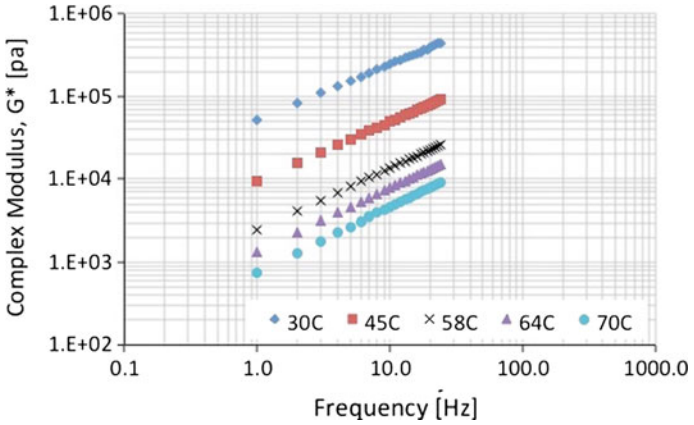

Fig. 2.19 Typical complex modulus of an asphalt binder at five different temperatures plotted against frequency

shifted on the log frequency axis, it is observed that all data eventually fall on a single smooth curve. In this example, let us define 58 °C as our *reference temperature*. Now leaving the data from 58 °C as it is, let us *horizontally* shift data from the relatively higher temperatures to the right and data from the relatively lower temperatures to the left. This horizontal shifting is carried out such that all data fall on a continuous smooth curve as shown in Fig. 2.20. This curve is referred to as the master curve. Note that all data from a given temperature are subjected to the same horizontal shift. Also individual data points from any given temperature

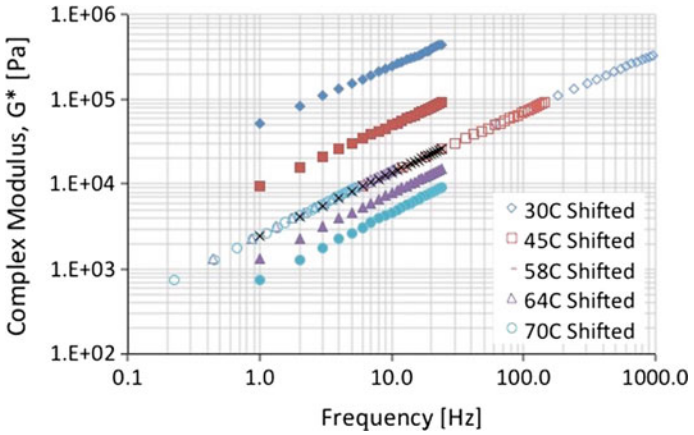

Fig. 2.20 Typical master curve obtained by horizontal shifting of the data from different temperatures

do not necessarily coincide with specific data points at the reference temperature, but rather these points overlap to form a smooth curve constructed using the data at the reference temperature as the basis. Materials that demonstrate this characteristic, wherein the data from different temperatures can be horizontally shifted onto a reference temperature to generate a single continuous smooth curve, are referred to as *thermorheologically simple materials*.

The magnitude of horizontal shift for data from any given temperature, T, is referred to as the *shift factor* and is typically denoted by the term a_T. Based on the method used to shift the graph, it is also easy to see that the horizontal shift $\log(a_T) = \log(f_r) - \log(f_T)$, where f_T is the frequency of any given data point at the test temperature T and f_r is the frequency at which the data point lands on, after being shifted to the reference temperature T_r. The term f_r is referred to as the *reduced frequency*. Finally, the shift factors for different temperatures are used to construct a shift factor versus temperature relationship. Figure 2.21 illustrates this relationship for the data shown in Figs. 2.19 and 2.20. Also note that by definition, at the reference temperature this line passes through an ordinate of zero since there is no shifting of the data involved at the reference temperature.

The master curve obtained based on the process described above can be fitted to an appropriate mathematical form that best represents the shape of the smooth curve obtained after shifting. A common mathematical form used for this purpose is the sigmoidal function shown in Eq. 2.3. The terms α through δ in Eq. 2.3 are shape parameters, and ω_r is the reduced angular frequency. The sigmoidal function has an upper and lower asymptote and is more appropriate for asphalt mixtures than binders. This is because asphalt mixtures tend to have a lower asymptote for the modulus even at very low frequencies (or high temperatures) due to the interaction between aggregate particles. A model that is more common in the area of asphalt binders is the Christensen-Anderson model or a generalized form

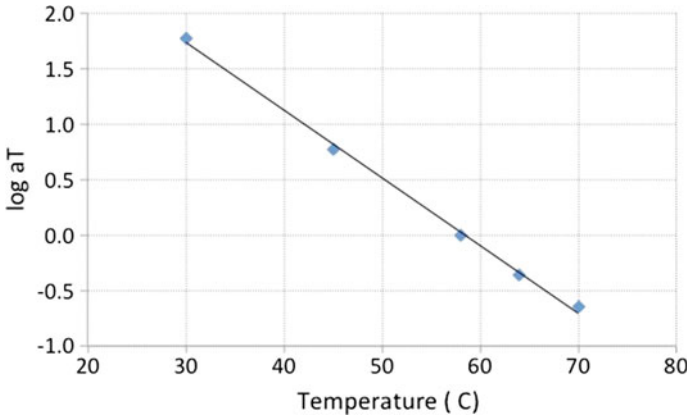

Fig. 2.21 Shift factor for time–temperature superposition derived by shifting data shown in Fig. 2.21

Christensen-Anderson-Marasteanu (CAM) model shown in Eq. 2.4. The parameters G_g is related to the glassy modulus of the binder, ω_c is the cross-over frequency (the frequency at which the loss and storage modulus are the same), and w and v are fitting parameters.

$$\log|G^*|(\omega) = \delta + \frac{\alpha}{1 + e^{\beta + \gamma \log \omega_r}} \tag{2.3}$$

$$|G^*|(\omega) = G_g \left[1 + \left(\frac{\omega_C}{\omega_r}\right)^v\right]^{-w/v} \tag{2.4}$$

Similar to the master curve, the shift factor versus temperature relationship can be fitted to any appropriate mathematical function that best describes the data. For example, researchers in the area of asphalt binders and mixtures have typically used polynomial models. However, it is important to briefly discuss a couple of forms of this relationship that have received a lot of attention in the literature (on asphalt and polymeric materials). First is the WLF equation named after its discoverers (Williams, Landel, and Ferry) and shown in Eq. 2.5. The terms C_1 and C_2 are fitting or shape parameters. The term T_g is the glass transition temperature, which is also used as the reference temperature. Broadly speaking, the glass transition temperature is the temperature below which the material behaves as a solid elastic material (the term glassy behavior is used to represent a solid amorphous material) and can be measured using techniques such as dilatometry, differential scanning calorimetry, or by conducting a temperature sweep using a dynamic shear rheometer. The WLF equation was extensively used by polymer researchers, because the parameters C_1 and C_2 were almost similar for several different polymers with values of approximately 17.4 and 51.6, respectively. Aklonis briefly describes the rationale for the generality of this model based on the concept of free volume. Another model that is also used to describe the shift factor versus temperature relationship is the Arrhenius model shown in Eq. 2.6. In this equation, the parameter k is obtained from fitting the data. The Arrhenius model has been shown to work better than the WLF model for temperatures below the glass transition temperature.

$$\log a_T = \frac{-C_1(T - T_g)}{C_2 + T - T_g} \tag{2.5}$$

$$\ln a_T = k\left(\frac{1}{T} - \frac{1}{T_r}\right) \tag{2.6}$$

The master curve along with the shift factor versus temperature relationship can be used to determine the modulus of the material for any given combination of frequency and temperature. As an example, consider a scenario where one is interested in the complex modulus at 6 Hz and 40 °C for the binder shown in Figs. 2.19 and 2.20. In this case, the first step would be use the model from

Fig. 2.21 to determine the shift factor $\log(a_T)$ at 40 °C, which is approximately 1.2 in this case. This shift factor would then be used to obtain the reduced frequency f_{Tr} based on the frequency of interest f_T using the expression described above; in this case, the reduced frequency would be 95 Hz. Phenomenologically, this means that the complex modulus of the binder at 95 Hz and reference temperature (58 °C in this case) would be the same at the complex modulus at 6 Hz and temperature of interest (40 °C in this case). Note that since the reference temperature is higher than the temperature of interest, the reduced frequency will have to be increased to compensate for the reduced stiffness associated with the higher temperature. The reduced frequency can now be used with the master curve (Fig. 2.20) to obtain the complex modulus of approximately 7×10^4 Pa. The convenience of using this approach is that once the mathematical forms for the functions shown in Figs. 2.20 and 2.21 are known, and the complex modulus at any given temperature and frequency can easily be computed using a simple expression.

Despite, which does not work well at temperatures substantially below the glass transition temperature, it is instructive to understand the derivation of the WLF equation. Aklonis et al., 1972, take us through the derivation. To begin with, the Doolittle equation for viscosity of a liquid (Doolittle 1951) is used to give an expression of viscosity based on two constants, A and B. In the Doolittle equation (shown below as Eq. 2.7), η refers to viscosity, V is the total volume of the system, and V_f is the free volume of the system.

$$\ln \eta = \ln A + B\left(\frac{V - V_f}{V_f}\right) \tag{2.7}$$

This equation demonstrates that viscosity is intimately connected to mobility and mobility to free volume; as free volume increases, viscosity rapidly decreases. Rearrangement of Eq. 2.7 gives:

$$\ln \eta = \ln A + b\left(\frac{1}{f} - 1\right) \tag{2.8}$$

where f is the fractional free volume, V_f/V. With the assumption that above the glass transition (normally used as the reference temperature), fractional free volume increases linearly, one can state:

$$f = f_g + \alpha_f\left(T - T_g\right) \tag{2.9}$$

where f is the fractional free volume at T, any temperature above T_g, f_g is the fractional free volume at T_g, and α_f is the thermal coefficient of change of the fractional free volume above T_g. If we then rewrite the Doolittle equation in terms of Eq. 2.9, we see that with some algebraic manipulation:

$$\log \frac{n(T)}{\eta(T_g)} = \log a_T = -\frac{B}{2.303 f_g}\left(\frac{T - T_g}{\left(\frac{f_g}{\alpha_f}\right) + T - T_g}\right) \tag{2.10}$$

The concept of increased mobility as a function of temperature and free volume is clear and evident, and one can now understand the form of the celebrated WLF equation. In Eq. 2.10, $C_1 = \frac{B}{2{,}303 f_f}$ and $C_2 = \left(\frac{f_g}{\alpha_f}\right)$.

2.5.5 Age Dependency

In addition to the time and temperature dependency, properties of the asphalt binder are also dependent on the age of the binder. Typically, the term aging in the context of asphalt binder during its service life refers to oxidative aging that was discussed in the previous subsections. Oxidative aging results in a change in the chemical composition of the asphalt binder, which in turn results in a change in its rheological properties. In general, oxidation results in the production of more polar molecules, which tend to associate more than the unaged binder. As a result, the stiffness of the binder increases with oxidative aging. This aspect must be carefully considered while using models and approaches to characterize the performance of asphalt binders and mixtures over the long term. In general, properties of the aged binder are measured at discrete aging stages (unaged, short-term aged, or long-term aged). There has been some work, although mostly from a research point of view at the time of this writing, to extend to time-temperature master curve concept to incorporate aging with shift-factors for aging.

2.5.6 Typical Measurement Techniques

In this section, we will discuss the instruments and hardware typically (but not exclusively) used to measure the mechanical properties of the asphalt binder. The dynamic shear rheometer (DSR) and the bending beam rheometer (BBR) are often used to characterize the mechanical properties of asphalt binders.

The DSR can be used to obtain both time- and frequency-dependent properties at different temperatures, i.e., creep compliance, relaxation modulus, and complex modulus. There are two different geometric configurations that are typically used to test asphalt binders with a DSR. The first and the most common is a cylindrical specimen, approximately 1–2 mm thick, between two parallel plates with the top plate being subjected to torsion and the bottom plate being fixed. The choice of the diameter of the plate and specimen is dictated by the torsion capacity of the instrument as well as the test temperature and aging condition of the binder. Long-term aged or significantly oxidized binders at intermediate or low temperatures (approximately 10–20 °C) are considerably stiffer than unaged or short-term aged binders tested at high temperatures (approximately 50 °C or above).

Consequently, a smaller diameter plate (8 mm) and thicker sample is more appropriate to test the former. Researchers have recently experimented using plates and specimen as small as 4 mm in diameter to test asphalt binders at much lower temperatures. For a parallel plate geometry, the shear strain rate at any point is given as $\dot{\gamma} = r\Omega/h$, where r is the radius from the axis of rotation, h is the height of the specimen, and Ω is angular speed of the top plate. Since the shear rate depends on the distance from the axis of rotation, the specimen is subjected to different strain rates and stresses at different radial positions within the specimen. As a result, it is important that this method be used to characterize a material within its linear viscoelastic limit (more on this discussed later). In some cases, it may be possible to use the method in nonlinear range, but the discussion of such conditions is beyond the scope of this chapter. For materials that exhibit significant nonlinear response, cone, and plate geometry is recommended. Figure 2.22 illustrates the parallel plate and (less commonly used) cone and plate geometries.

Consider a binder specimen that is to be evaluated after long-term aging and/or at low temperatures (typically below 0 °C). Under these conditions, the stiffness of the binder is typically much higher compared to the stiffness of the short-term aged binder or binder at elevated temperatures. Also, consider the fact that typical DSRs that are commercially available have a limited torque capacity. Consequently, if one were to use the typical 8 or 25 mm diameter and 1or 2-mm-thick sample that is long-term aged particularly at low temperatures with the DSR, the instrument will not be able to induce adequate deformation to the specimen required to make repeatable measurements. For such scenarios, some researchers have tried using a very small diameter specimen (e.g., 4 mm) with the DSR. While theoretically the use of a smaller diameter reduces the torque required to achieve a certain level of deformation, other factors must be carefully considered. For example, if the compliance of the test specimen is in the same order of magnitude as the compliance of the testing frame, then depending on the location of the displacement transducers, the instrument may record cumulative deformations that occur in the loading frame and the test specimen. One must always be on the lookout for such artifacts while making such measurements. Owing to the above limitations, the binder industry typically employs a different device, the bending beam rheometer or BBR, to make measurements for long-term aged binder at low temperature.

The bending beam rheometer or BBR is comprised of a loading frame immersed in a temperature-controlled bath of typically ethylene glycol mixed with water

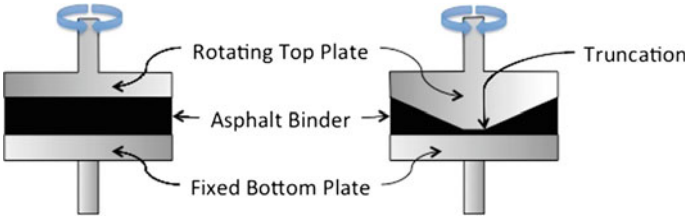

Fig. 2.22 Schematic of the parallel plate and cone and plate geometry for testing with a DSR

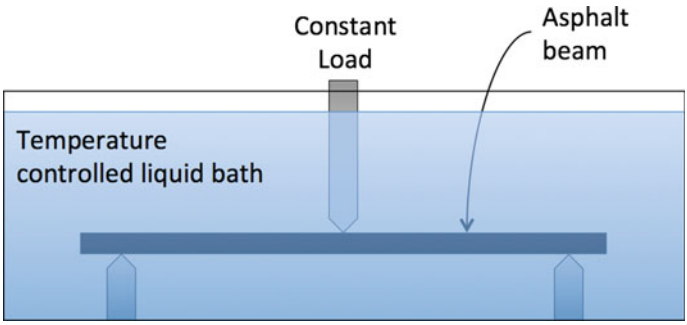

Fig. 2.23 Schematic of the bending beam rhoemeter

(Fig. 2.23). The load frame is designed to apply a constant load at the center of a beam specimen with rectangular cross section that is simply supported at its two ends. The loading axis also measures the deformation at the center of the specimen over time. Recall the relationship between load P, deformation δ, and stiffness S, for a simply supported rectangular beam with width b, depth d, and span l (Eq. 2.11). Notice in Eq. 2.9 that the stiffness and deflection are expressed as a function of time as $S(t)$ and $\delta(t)$, respectively. This is because of the time-dependent nature of the material. By estimating the change in stiffness of the material over time, it is possible to get some estimate of the ability of the material to relax. A couple of things must be noted with the use of BBR. First, the information collected in the manner as shown in Eq. 2.9. is an indicator of material behavior but not a true fundamental material property (such as creep compliance, relaxation modulus, or dynamic modulus). However, with the appropriate use of boundary conditions and mathematical analysis the data from the BBR can be used to estimate the creep compliance or relaxation modulus of the material. Second, the most common types of BBR currently available are not capable of performing tests in the frequency domain. However, it is possible to replicate this arrangement in a universal testing machine to conduct such and other tests (e.g. Four point bending, notched fracture etc.).

$$S(t) = \frac{Pl^3}{4bd^3\delta(t)} \tag{2.11}$$

At this point, we have discussed some of the basic material properties that are used to characterize a viscoelastic material such as the asphalt binder, i.e., creep compliance, relaxation modulus, and dynamic or complex modulus. We have also discussed the influence of temperature and age on these properties as well as some of the common laboratory methods used to measure these properties (DSR and BBR). However, not all of these properties are measured all the time to characterize asphalt binder for routine use. In the following section, we will briefly discuss the metrics based on these fundamental measures of material behavior that are currently being used to grade asphalt binders.

2.5.7 Desired Binder Properties to Produce Durable Asphalt Mixtures and PG System

The optimal rheological properties of an asphalt binder that will result in a durable mix are dictated by the geographic location and the type of mix. Simply put, asphalt binders cannot be produced using a one-size fits all approach. The most recently developed industry standard, referred to as the Superpave performance grade or PG specifications, requires that the rheological properties of an asphalt binder (with appropriate aging) must meet certain criteria at the highest, intermediate, and lowest service temperatures to prevent premature failure due to rutting, fatigue cracking, or low-temperature cracking, respectively. In summary, an asphalt binder rated as PGXX-YY is capable of being used in asphalt pavements with a maximum pavement temperature of XX and a minimum pavement temperature of -YY. The methodology is briefly described here, and the readers are encouraged to try the exercise questions at the end of this chapter to get a better understanding of the process.

The high-grade temperature XX is determined as the maximum temperature at which the binder fails a high-temperature criterion. In fact, there are two criteria, one each for unaged and laboratory short-term aged (or RTFO aged) binder and the lower of the two is used after rounding to the nearest lower six-degree increment (the increments are in steps of 6° starting from 46 °C). The current criterion for high temperature is a minimum value of $|G^*|/\sin\delta$ to mitigate rutting at the maximum pavement temperature measured on unaged and short-term aged (partially oxidized) binder at 10 rads/second. Here, $|G^*|$ is the magnitude of the complex shear modulus, and δ is the phase angle measured using a DSR (recall discussion related to Fig. 2.18). As of this writing, the industry is also considering to replace the above criterion with a maximum requirement of the nonrecoverable compliance J_{nr} measured at high temperatures as an indicator of the binder's susceptibility to permanent deformation. The nonrecoverable compliance is measured using a creep-recovery test with a DSR (Fig. 2.22) on short-term aged asphalt binders by applying cycles of constant shear stress for 1 s followed by zero shear stress for 9 s. The nonrecoverable compliance is defined as the ratio of the permanent or nonrecoverable strain (difference between residual strain at the end of the recovery period and the strain at the beginning of the creep period for any given cycle) to the applied stress (see Fig. 2.16).

The low-grade temperature YY is determined as the minimum temperature at which the binder fails a low-temperature criterion. In fact, there are two criteria, one based on stiffness and one based on rate of relaxation and the temperature corresponding to the higher of the two is used after rounding to the next highest six-degree increment. The creep compliance of long-term aged (significantly oxidized) asphalt binder at low temperatures is related to the low-temperature cracking resistance of the asphalt mixture. Binders with lower stiffness and higher rate of relaxation will tend to develop lower tensile stresses as the pavement cools. Consequently, an aged binder must meet a maximum stiffness and minimum rate of

relaxation criteria at the lowest expected service temperature. The stiffness and rate of relaxation are measured using the BBR (recall discussion around Fig. 2.23).

Although the grade is set based on the high and low temperatures, the binder must also meet an intermediate temperature requirement. The intermediate temperature is typically defined as 4 + the average of the sum of high and low temperatures in Celsius, although agencies have adopted other variations of this definition. The current requirement in the PG specification for intermediate temperature is a maximum value of $|G^*| \sin \delta$ at the intermediate service temperature to mitigate fatigue cracks, where $|G^*|$ is the complex shear modulus and δ is the phase angle measured on long-term aged (oxidized) binder at 10 rads/second measured using a DSR.

Note that the above tests and criteria are typically used to determine and assign a performance grade or PG to a binder produced in a refinery. Since refineries produce several different PGs, the user is then required to select the appropriate PG binder for their specific project. This is typically done by first estimating the maximum and minimum pavement temperature based on historical air temperature data. In some cases, this may involve "grade bumping" if the traffic speed and/or volume is higher than the typical speeds and volumes used as a basis for the high-temperature grade. Simply put, if the traffic speed is slower than typical (e.g., weigh stations) or traffic volume is higher (e.g., busy interstate highways), then one or two higher grades than the high-temperature grade based on pavement temperature alone are recommended for use.

Readers are also encouraged to work through the examples provided at the end of this chapter to get a better understanding of how the PG is determined for a binder and the selection of the appropriate PG binder for a specific construction project. Readers are also referred to additional reading material for a more detailed description of the standard test methods and criteria used in the PG specification.

2.5.8 *Limitations of the PG System*

Although the PG specification was a significant improvement over the previous characterization methods such as the penetration grade, there are two major shortcomings of this approach. First, recall that in the subsection on time dependency earlier we had mentioned that the "tests are typically conducted by applying a stress or strain magnitude that is not large enough to induce significant permanent damage to the material". A common criticism of the PG specification is that it is based on the stiffness of the binder at different critical conditions measured using smaller magnitudes of stresses or strains and not strength. While stiffness (even time dependent stiffness) characterizes the load deformation or stress-strain response of the material, it does not characterize the failure limit or capacity of the material to deform prior to failure initiation and propagation. Several studies have shown binders with very similar performance grade often have failure characteristics that are very different from each other. Improvement of the aforementioned tests and

criteria for specification is a subject of several ongoing studies. For example, the nonrecoverable compliance, J_{nr}, discussed in the previous paragraph as a replacement for $|G^*|/\sin\delta$ is a step in this direction, i.e., to evaluate the material for its ability to resist permanent deformation at high stresses.

Second, and the more challenging criticism to overcome, is that rheological properties measured at specific temperature and aging conditions do not fully reflect the performance of the binder in the mixture. This is particularly important for aspects related to binder performance that have to do with its physicochemical interactions with the aggregate or other chemical additives included in the mix. For example, binders with the same PG can have very different chemical compositions and may react differently with different mineral aggregates or additives such as liquid anti-strip agents resulting in very different performance characteristics. These issues will be discussed in more detail in subsequent chapters.

2.6 Properties of Liquid Asphalt Binder

In the previous section, we discussed properties of asphalt binder that are relevant during its service life in an asphalt pavement. In this last short section, we will briefly discuss properties of asphalt binder that are relevant, while the asphalt binder is mixed with aggregates in an asphalt mixture production plant and being transported to the construction site.

The two most important properties of an asphalt binder that dictate its ability to coat aggregate particles are its viscosity and surface tension. Perhaps a simplified albeit clear explanation of the interplay between these two properties on wetting and coating is given by Wulf et al. (2000): "without going into details surface tension can be regarded as the driving force and viscosity as the resistance of wetting". In the asphalt industry, viscosity of the asphalt binder is routinely used as a measure of its workability during asphalt mixture production and placement. In most cases, standards and specifications dictating the temperatures for mixing and compaction of asphalt mixtures are based on the premise that achieving a certain binder viscosity will ensure that the mixture remains workable. For example, according to the current Superpave specifications mixture production must be carried out when the binder viscosity is within 0.15–0.19 Pa-sec as measured using a rotational viscometer with a specific spindle diameter and rate of rotation (20 rpm). Figure 2.24 illustrates a schematic of the rotational viscometer along with a photograph of a typical device. The working assumption in this case is that at this viscosity the binder is fluid enough to adequate coat the surface of the aggregate particles. It is also recommended that the mixture be placed and compacted when the binder viscosity is between 0.25 and 0.31 Pa-sec measured as before. The working assumption in this case is that in this viscosity range the mixture is workable to be placed, spread, and compacted to achieve target densities, while at the same time it is not prone to segregation.

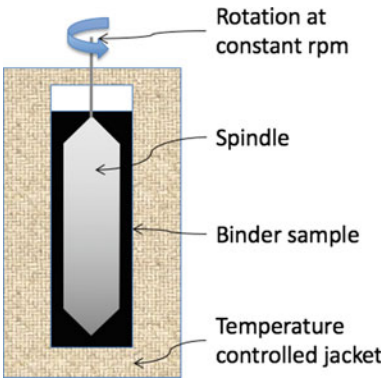

Fig. 2.24 Schematic and photograph of a rotational viscometer

Since each binder has a different viscosity-temperature relationship, in practice, the recommended viscosities need to be translated into production and compaction temperatures. Typically, a rotational viscometer is used to develop a viscosity-temperature relationship for the asphalt binder by measuring the binder viscosity at multiple temperatures. Figure 2.25 shows such a relationship and its use to determine the mixing and compaction temperatures for a typical asphalt binder. However, before we conclude this discussion, it is important to point out a couple of important considerations. First, the shear rate of 20 rpm used in typical viscometer measurements is not representative of typical conditions encountered by the mix during production. Second, mechanisms other than viscosity (e.g., surface tension) also dictate the ability of the binder to wet and coat the aggregate surfaces during production. These two considerations have important implications

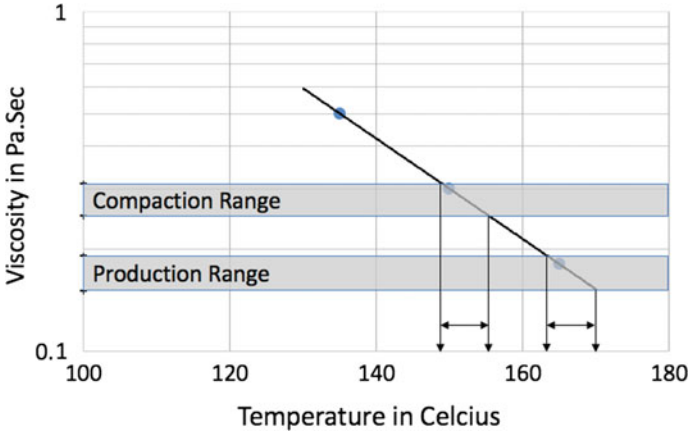

Fig. 2.25 Typical temperature viscosity relationship for an asphalt binder and determination of mixing and compaction temperatures

particularly in the context of the polymer-modified binders and warm mix asphalt, as discussed below.

In the case of polymer-modified binders, the viscosity of the binder is not only temperature dependent but also shear rate dependent. This is referred to as nonNewtonian fluid behavior or sometimes as shear-thinning or shear-thickening behavior depending on whether the increase in shear rate reduces or increases the viscosity, respectively. This behavior is routinely encountered even in daily life. For example, corn starch in water is an excellent example of a shear-thickening liquid. In this context, asphalt binders, particularly polymer-modified binders are highly rate dependent. Therefore, the use of 20 rpm in a viscometer can sometimes result in viscosities and temperatures that are not realistic representations of what happens to the binder in the production facility. In this case, either higher shear rates during viscosity-temperature relationships or experiential data must be used to determine the optimal mixing and compaction temperatures. Readers interested in additional information can refer to the findings from a study focused on this subject (West et al. 2010).

There are several technologies that are used to produce warm mix asphalt or WMA that is produced and compacted at temperatures that are about 20–40 °C below the conventional HMA temperatures. In some cases, it has been observed that the WMA technology does not facilitate mixing by reducing binder viscosity at the lower WMA production temperatures. Instead, other mechanisms such as lubricity (Baumgardner et al. 2012) and the reduction of surface tension (Osmari et al. 2015) allow mixture production. As of this writing, these dimensions of improving workability are still a subject of research, while viscosity of the binder continues to serve a benchmark for its workability.

2.7 Exercises

2.1. You are given two different asphalt binders. Binder A has very high percentage of asphaltenes and Binder B has very low percentage of asphaltenes.

   a. Which of these binders is likely to have a lower stiffness and why?
   b. Two mixtures are prepared using the exact same aggregate gradation and binder content using Binders A and B. Identify with reasoning, the problems that are likely to occur with each of these two mixtures. Also, explain when these problems would become more likely in terms of the pavement age.
   c. If you were told that both binders are from the same source, except that one of them is oxidized, which one of these two binders would you consider to be oxidized and why?

2.2. In static creep experiment, the normal strain on a specimen (material A) subjected to 100 Pa stress was measured over time. The resulting data is

provided in an accompanying data file. Calculate the parameters for the power law model for creep compliance, $D(t) = D_0 + D_1 t^n$. Plot the data and your predicted compliance over time to make sure the two matches reasonably. Do not forget to add the appropriate dimensions for compliance.

2.3. Assume you now have three new time dependent materials, B, C, and D. The compliance of all of these materials follows power law. The properties of these materials are as follows: (8 points)

Material	D_0	D_1	n
A	x	y	z
B	$0.5x$	y	$2z$
C	$2x$	y	$0.5z$
D	x	y	0

Note You will find out the values of x, y, and z from solving the previous question.

Plot the strain for materials A, B, C, and D on the same graph for time t = 0–3 s. Use time steps for 0.1 s for these plots. Answer the following questions:

a. If a person not familiar with time-dependent or viscoelastic materials were to ask, which of the four materials has the highest stiffness, what would be the answer? (Hint: the answer will change with time)
b. Which of the four materials is relatively more time dependent than others?
c. Which of the four materials can be classified as an elastic solid?
d. Does higher "n" value indicate that the material is more time dependent or less time dependent?

2.4. If you are conducting a dynamic test on the materials discussed above and you are also recording the phase angle. Rank the phase angles for the material and test conditions below and provide reasoning for your ranking.

Test number	Material	Frequency (Hz)
1	A	5
2	A	1
3	D	0.1
4	D	25

(*Note* You should be able to estimate the exact phase angle for material D)

2.5. Consider a material that follows power law and the creep compliance is given as $D(t) = 15t^{0.45}$ 1/MPa. A monotonically increasing stress is applied at the rate of 0.02 MPa/sec (i.e., $\sigma(t) = 0.02t$). What is the strain after 2 s? (Hint: Recall the discussion on hereditary integrals and also at some point to make things easier to solve you may have to substitute a variable of integration).

2.6. This exercise is to determine the PG or performance grade of a random binder based on laboratory tests.

Based on a specification system, the high-temperature grade of the binder is defined as follows: The lower of (i) the maximum temperature above which the $|G^*|/\sin\delta$ of the unaged asphalt binder falls below 1.00 kPa and (ii) the maximum temperature above which the $|G^*|/\sin\delta$ of the short-term aged or RTFO-aged asphalt binder falls below 2.2 kPa. Note that, the final temperature must be rounded to the next lower temperature step in six-degree increments starting from 46 C; i.e., the final high temperature will be rounded down and noted as one of 46, 52, 58, 64, 70, 76, or 82.

The low-temperature grade of the binder is defined based on a creep test conducted using the long-term aged or PAV-aged binder as follows: 10 °C below the higher of (i) the minimum temperature below which the stiffness of the binder is higher than 300 MPa and (ii) the minimum temperature below which the rate of relaxation at 60 s is lower than 0.3. Note that, the final temperature must be rounded to the next higher temperature step in six-degree increments starting from −10 C; i.e., the final low temperature will be rounded up and noted as one of −10, −16, −22, −28, or −34 C.

Using the above two criteria, determine the high and low PG grade of the binder if the following measurements were made and provided to you.

DSR with unaged binder			DSR with RTFO-aged binder			BBR with PAV-aged binder		
Temp. in C	|G*| in kPa	Phase angle in degrees	Temp. in C	|G*| in kPa	Phase angle in degrees	Temp. in C	Stiffness in MPa	m-value at 60 s.
64	3.7	79.4	64	6.1	75.9	−24	817	0.214
70	2.0	80.8	70	2.5	78.2	−18	453	0.442
76	1.1	82.2	76	1.1	80.4	−12	251	0.670

For the above exercise, use an interpolation scheme that best fits the data provided as needed. Typically, $|G^*|/\sin\delta$ and temperature follow a straight line on a log-linear scale; similarly, stiffness from BBR and temperature also follow straight line on a log-linear scale. The rate of relaxation or *m*-value is typically found to follow a linear relationship with temperature. Note that in practice, most binder grading specifications also require that a criterion be met at the intermediate temperature for the PAV-aged binder as well as other requirements related to safety and mass loss.

2.7 You need to select a PG binder for the construction of a flexible pavement. The following is some of the information about the construction site.

Longitude 99.43		
Latitude 31.83		
Elevation 528 m		
Low air temperature	Mean = −12 °C	Std. Dev. = 4 °C
High air temperature	Mean = +38 °C	Std. Dev. = 2 °C

Consider that the maximum pavement temperature is at 20 mm below the surface of the pavement. Also, the relationship between the maximum air temperature and pavement temperature is given as follows:

$$T_{pavement} = 54.32 + 0.78T_{air} - 0.0025\,Lat^2 - 15.14\log_{10}(H + 25) + z(9 + 0.61\sigma_{air}^2)^{1/2}$$

The above equation is an empirical model based on data collected from a long-term pavement performance (LTPP) study supported by the Federal Highway Administration (FHWA) of the USA. The term *Lat* refers to the latitude, H is the depth from surface of the pavement in mm, and σ_{air} is the standard deviation in the 7-day mean air temperature in centrigrate. Also for the purpose of this exercise, consider that the minimum pavement temperature is the air temperature at the surface of the pavement. The high-temperature binder grades start at 46 °C in increments of 6 °C and low-temperature grades start at −10 °C decreasing in increments of 6 °C.

a. What the PG binder grade you would recommend if you wanted to achieve 50% reliability in your design? (Hint: recall that z is zero for 50% reliability for high temperature and for low temperature this indicates using the mean value of the temperature).
b. What the PG binder grade you would recommend if you wanted to achieve 98% reliability in your design? (Hint: recall that z is 2.055 for 98% reliability for a normal distribution; for low temperature use, the mean and standard deviation and assuming a normal distribution find the temperature such that the air temperature is above this temperature 98% of the time).
c. The traffic scenario for the project is such that the traffic is slow and higher in volume compared to the typical scenario that was used to develop PG specifications. One high-temperature "grade bump" is recommended for each of these scenarios. What is the final grade of the binder you would recommend?

2.8 You have two binders for which you have obtained a temperature-viscosity relationship. For Binder 1 the mixing temperature range is 150–160 C and for Binder 2 the mixing temperature range is 180–190 C. Based on what you have read, do you think any of these two binders are polymer modified? If so, which one of the binders do you think is polymer modified and what is your recommendation to select a mixing temperature for this binder.

2.9. What are risks of mixing at temperatures higher and lower than the recommended mixing temperature?

Additional Reading

Robertson, R. E. (2000). *Chemical properties of asphalts and their effects on pavement performance*.

Redelius, P. G. (2006a). The structure of asphaltenes in bitumen. *Road Materials and Pavement Design, 7*(sup1), 143–162.
Lesueur, D. (2009a). Evidence of colloidal structure of bitumen. *Advances in Colloid and Interface Science, 145*(1–2), 42–82.

References

Aklonis, J. J., MacKnight, W. J., & Shen, M. (1972). *Introduction to polymer viscoelasticity* (pp. 52–53). Wiley Interscience.
Allen, R. G., et al. (2013). Identification of the composite relaxation modulus of asphalt binder using AFM nanoindentation. *Journal of Materials in Civil Engineering (ASCE), 25*(4), 530–539.
Allen, R. G., Little, D. N., & Bhasin, A. (2012). Structural characterization of micromechanical properties in asphalt using atomic force microscopy. *Journal of Materials in Civil Engineering, 24*(10), 1317–1327.
Baumgardner, G. L., Reinke, G. R., & Brown, J. (2012). *Lubricity properties of asphalt binders used in hot-mix and warm-mix asphalt pavements*. Turkey: In Eurasphalt and Eurobitume Congress.
Chow, T. S. (1980). The effect of particle shape on the mechanical properties of filled polymers. *Journal of Materials Science*, *15*(8), 1873–1888. Retrieved from http://link.springer.com/article/10.1007/BF00550613.
Corbett, L. W. (1969). Composition of asphalt based on generic fractionation, using solvent deasphaltening, elution-adsorption chromatography, and densimetric characterization. *Analytical Chemistry, 41*(4), 576–579.
Demjén, Z., Pukánszky, B. & Nagy, J. (1998). Evaluation of interfacial interaction in polypropylene/surface treated $CaCO_3$ composites. *Composites Part A: Applied Science and Manufacturing*, *29*(3), 323–329. Retrieved from http://www.sciencedirect.com/science/article/pii/S1359835X97000328.
Dickie, J. P., & Yen, T. F. (1967). Marcrostructuare of the asphaltic fractions by various instrumental methods. *Analytical Chemistry, 39,* 1847–1852.
Doolittle, A. K. (1951). Studies in Newtonian flow. I. The dependence of the viscosity of liquids on temperature. *Journal of Applied Physics, 22*(8), 1031–1035.
Elias, L. et al., 2007. Morphology and rheology of immiscible polymer blends filled with silica nanoparticles. *Polymer*, *48*(20), pp. 6029–6040. Retrieved from http://www.sciencedirect.com/science/article/pii/S0032386107007665.
Hubbard, R. L., & Stanfield, K. E. (1948). Determinatio of asphaltenes, oils, and resins in asphalt. *Analytical Chemistry, 20,* 460–465.
Kringos, N. et al. (2009). A thermodynamical approach to healing in bitumen. In A. Loizos et al. (Eds), *Advanced testing and characterisation of bituminous materials* (pp. 123–128). Rhodes, Greece: Taylor & Francis Group, Boca Raton, Florida.
Koots, J. A., & Speight, J. G. (1975). Relation of petroleum resins to asphaltenes. *Fuel, 54*(3), 179–184.
Lesueur, D. (2009b). Evidence of colloidal structure of bitumen. *Advances in Colloid and Interface Science, 145*(1–2), 42–82.
Lesueur, D. (2009c). The colloidal structure of bitumen: Consequences of the rheology and on the mechanisms of bitumen modification. *Advances in Colloid and Interface Science, 145*(1–2), 42–82.
Lin, M. S., et al. (1995). The effects of asphaltenes on asphalt recycling and aging. *Transportation Research Record, 1507,* 86–95.
Loeber, L., et al. (1996). New direct observations of asphalts and asphalt binders by scanning electron microscopy and atomic force microscopy. *Journal of Microscopy, 182*(1), 32–39.
Masson, J.-F., Leblond, V., & Margeson, J. (2006). Bitumen morphologies by phase-detection atomic force microscopy. *Journal of Microscopy, 221*(1), 17–29.

Masson, J. F., et al. (2007). Low-temperature bitumen stiffness and viscous paraffinic nano-and micro-domains by cryogenic AFM and PDM. *Journal of Microscopy, 227*(3), 191–202.

Mortazavi, M., & Moulthrop, J. S. (1993). *The SHRP materials reference library*. SHRP Report A-646. National Research Council. Washington, D.C.

Osmari, P. H., Arega, Z. A., & Bhasin, A. (2015). Wetting characteristics of asphalt binders at mixing temperatures. *Transportation Research Record: Journal of the Transportation Research Board*, *In Press*.

Palierne, J. F. (1990). Linear rheology of viscoelastic emulsions with interfacial tension. *Rheologica Acta*, *29*(3), 204–214. Retrieved from http://link.springer.com/article/10.1007/BF01331356.

Petersen, J. C. (1984). Chemical composition of asphalt as related to asphalt durability: State of the art. *Transportation Research Record: Journal of the Transportation Research Board, 999,* 13–30.

Petersen, J. C., et al. (1993). Effects of physiochemical factors on asphalt oxidation kinetics. *Transportation Research Record, 1391,* 1.

Pfeiffer, J. P., & Saal, R. N. J. (1940). Asphaltic bitumen as colloid system. *The Journal of Physical Chemistry, 44*(2), 139–149.

Ramm, A., Sakib, N., Bhasin, A., & Downer, M. C. (2016). Optical characterization of temperature-and composition-dependent microstructure in asphalt binders. *Journal of Microscopy*, *262*(3), 216–225.

Read, J., & Whiteoak, D. (2003). *The shell bitumen handbook* (5th ed.). London: Thomas Telford Publishing.

Redelius, P. G. (2006b). The structure of asphaltenes in bitumen. *Road Materials and Pavement Design, 7*(sup1), 143–162.

Rogel, E. (1995). Studies of asphaltene aggregation via computational chemistry. *Colloids and Surfaces A, 104,* 85–93.

Schmets, A., et al. (2009). First-principles investigation of the multiple phases in bituminous materials: the case of asphaltene stacking. In A. Loizos et al. (Eds.), *Advanced testing and characterisation of bituminous materials* (pp. 143–150). Boca Raton, Florida: Taylor & Francis Group.

Schmets, A., et al. (2010). On the existence of wax-induced phase separation in bitumen. *International Journal of Pavement Engineering, 11*(6), 555–563.

Siegmann, M. (1950). Manufacture of asphaltic bitumen. In J. P. Pfeiffer (Ed.) *The properties of asphaltic bitumen* (pp. 121–154). Amsterdam: Elsevier.

Speight, J. G. (1999). *The chemistry and technology of petroleum*. Springer.

Traxler, R. N., & Romberg, J. W. (1952). Asphalt, a colloidal material. *Industrial & Engineering Chemistry*, *44*(1), 155–158. Retrieved from http://dx.doi.org/10.1021/ie50505a045.

Vasconcelos, K. L. (2010). *Moisture Diffusion in Asphalt Binders and Fine Aggregate Mixtures. Doctoral dissertation*, Texas A&M University

Verghese, N. E., & Lesko, J. J. (1999). *Fatigue performance: The role of the Interphase* (pp. 336–348). New York, NY: CRC Press.

West, R. C., Watson, D. E., Turner, P. A., & Casola, J. R. (2010). *Mixing and compaction temperatures of asphalt binders in hot-mix asphalt*. Washington D.C.

Wulf, M., Uhlmann, P., Michel, S., & Grundke, K. (2000). Surface tension studies of levelling additives in powder coatings. *Progress in Organic Coatings, 38*(2), 59–66.

Zhao, S., et al. (2001). Solids contents, properties and molecular structures for various asphaltenes from different oilsands. *Fuel, 80,* 1907–1914.

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