Blending and Diffusion of Recycled Asphalt Pavement and New Approach to Recycling Asphalt Shingle

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DEDICATION

This dissertation is dedicated to my dear wife, Xiaomei Bu, my lovely daughter, Olivia Ding, and my friends in Knoxville.

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ABSTRACT

This study proposed a series of methods to investigate the blending and diffusion process of recycled asphalt mixtures using Fourier-transform infrared spectroscopy (FTIR), fluorescence microscopy and molecular dynamic simulation. A new approach to recycling asphalt shingles in which RAS binder was extracted by a mixed solvent with certain polarity and used as common asphalt binder was also developed.

A new parameter, mean grey value (MGV), was derived from the fluorescence image and used to differentiate between recycled and virgin binders as well as their blends. The mobilization rate of plant-produced RAP mixtures was calculated on the basis of surface area proportion of aggregates with different size. Three types of asphalt mixtures, including one warm mix with foaming technology, two hot mixes with or without rejuvenator, were used to validate the proposed method.

Two asphaltic models with three components including asphaltenes, resin, and oil were built with different components ratio to investigate the diffusion between virgin and aged binders. In an inter-diffusion model of virgin and aged binders, the diffusion coefficients of binders were not only determined by the diffusion ability itself, but also influenced by the properties of the diffusion acceptor.

A new method was proposed to utilize fluorescence microscopy to determine the diffusion coefficient of aged RAP binder in recycled mixtures. The diffusion coefficient was determined by fitting the analytical solution to the laboratory concentration measurements. Comparison of the diffusion coefficient by the proposed method and that using the dynamic shear rheometer (DSR) method shows that the diffusion coefficient determined by fluorescence microscopy was of the same magnitude to, but slightly lower than that by DSR method.

The RAS binder was extracted by a mixed solvent with certain polarity and used as common asphalt binder. The use of the mixed solvent of heptane and TCE with a certain proportion through the proposed method could prepare asphalt binder with desired properties. Results indicate that soft asphalt could not dissolve RAS binder at 170 ℃. The binder blend of RAS binder and rejuvenator had a potential antiaging problem because an obvious loss of rejuvenator existed during the aging process.

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AASHTO: American Association of State Highway and Transportation Officials

ASTM: American Society for Testing and Materials"

CV: Coefficient of Variation

DSR: Dynamic Shear Rheometer

DRH: RAS binder component dissolved and extracted using heptane

DRT: RAS binder component dissolved and extracted using TCE

ER: Extracted binder using mixed solvent

EPA: Environmental Protection Agency

E*: Dynamic Modulus

FHWA: Federal Highway Administration

FTIR; Fourier Transform Infrared Spectroscopy

GPC: Gel Permeation Chromatography

G*: Complex Shear Modulus

HMA: Hot Mix Asphalt

LMS(%): Large Molecular Size Percentage

MGV: Mean Gray Value

MD: Molecular Dynamics

NAPA: National Asphalt Pavement Association

NCHRP: National Cooperative Highway Research Program

RAR: Binder blend of rejuvenator and RAS binder

RAP: Recycled Asphalt Pavement

RAS: Recycled Asphalt Shingle

RI: Refractive Index

RTFO: Rolling Thin-Film Oven

SAR: Binder blend of soft asphalt and RAS binder

SHRP: Strategic Highway Research Program

TCE: Trichloroethylene

THF: Tetrahydrofuran

TDOT: Tennessee Department of Transportation

TFOT: Thin Film Oven Test

UV: Ultraviolet

Chapter I Research Background and Objectives

1.1 Research Background

1.1.1 Recycled Asphalt Pavement (RAP)

With the ever-increasing cost of aggregate and asphalt binder, the incorporation of high percentage (> 30%) of recycled asphalt pavement (RAP) into asphalt mixtures has become more and more popular (Huang et al., 2010, Shu et al., 2008, Zhao et al., 2012, Zhao et al., 2013a). The use of RAP can produce significantly economic and environmental benefits. In 2015, RAP usage in new asphalt pavement mixtures reached 74.2 million tons, a 32.5 percent increase from 2009. More than 99 percent of asphalt pavement reclaimed from roads and parking lots was reclaimed for use in new pavements instead of going into landfills (Hansen and Copeland, 2015). It was estimated that using RAP provides a saving ranging between 14 and 34% if the RAP content varies from 20 to 50% (Zhou et al., 2013a).

1.1.2 Recycled Asphalt Shingle (RAS)

Due to the quality and content of asphalt binder (20 to 35% by weight) and also the environmental pressure, asphalt shingles has been recycled into pavement construction to replace some asphalt binder and fine aggregates (Krivit, 2007). According to National Asphalt Pavement Association, the usage of recycled asphalt shingle (RAS) into pavement in the U.S. achieved a total of 2 million tons in 2015, which is a 175 percent increase since 2009 (Hansen and Copeland, 2015). However, there have been concerns over the influence of using RAS on the performance of pavement. The air-blown process and the further aging during the service life has significantly stiffened the RAS binder and the using of the stiff aged binder from RAS into asphalt mixture can cause a series of pavement issues such as cracking failures (Zhao et al., 2013a, Zhou et al., 2013b). Therefore, the percentage of RAS usually is limited to less than 5% in practice (Zhao et al., 2014).

1.1.3 Current Challenges for the Utilization of RAP

With more RAP recycled into asphalt mixtures, some associated concerns also emerge. A major concern is whether or not the aged RAP binder can truly blend with virgin binder and is available to coat aggregates. Lack of a clear understanding of blending and diffusion between virgin and recycled asphalt has been a major issue in determining the effective asphalt binder in asphalt mixtures containing RAP and the uniformity of asphalt binder in the recycled mixtures. RAP binder has experienced a service life of aging and become stiff and brittle. When RAP is added into new aggregate and binder, it can negatively impact the performance of asphalt mixtures if the aged binder is not fully blended with virgin binder.

Although the degree of blending between virgin and RAP asphalt is dependent on such factors as mixing conditions and constituent asphalt chemistry, complete or nearly complete blending is often assumed to achieve the maximum cost savings potential. However, the poor performance of some high-RAP mixtures has prompted the study on the degree of blending that actually occurs in high-RAP mixtures (Ding et al., 2016a, Ding et al., 2016b, Bowers et al., 2014, Huang et al., 2005).

1.1.3.1 Blending Efficiency of RAP

Blending efficiency can be quantified using a term mobilization rate, which is defined as the percentage of aged binder that can be mobilized and blended into virgin binder to coat aggregate particles.

The blending efficiency of aged binders has been studied by many researchers in the laboratory. Researchers usually used particular virgin aggregates to mix with RAP and virgin binder to make mixtures(Zhao et al., 2013a, Zhao et al., 2013b), then visually detected and separated them from RAP aggregates and tested the amount of aged binder that was mobilized and transferred from RAP to virgin aggregates during mixing. The feasibility of this approach depends on the fact that virgin and RAP aggregates could be separated after the mixing process. However, for plant-produced mixtures, it is almost impossible to visually detect and separate virgin aggregates from RAP particles when both are similar in size and shape.

The methods for determining blending efficiency are based on two major categories of asphalt properties: chemical properties and mechanical properties. Mechanical property method involves measuring dynamic modulus (Al-Qadi et al., 2009), binder content (Shirodkar et al., 2011, Bennert and Dongré, 2010), and so on. Chemical property methods use such chemical testing techniques as gel permeation chromatography (GPC) (Zhao et al., 2015a, Bowers et al., 2014, Zhao et al., 2013a, Zhao et al., 2014, Zhao et al., 2015b), Fourier transform infrared (FTIR) (Bowers et al., 2014) and fluorescence microscopy (Navaro et al., 2012) to determine the RAP binder content in a blend of virgin and RAP binders. Among the above-mentioned chemical techniques, GPC and FTIR methods need to extract asphalt binder from aggregate particles to make samples for further testing. Therefore, the heterogeneity of binder on aggregate cannot be determined. In addition, the process of using chemical a chemical solvent to dissolve asphalt binder makes the test time-consuming and complicated. The extraction and recovery process may also affect the accuracy of the test result. Therefore, a new method without tedious binder extraction and recovery is more desirable for determining the blending efficiency of RAP binder.

1.1.3.2 Diffusion between Virgin and Aged Asphalt

In reality, aged asphalt in RAP asphalt is a thin film of binder coating RAP aggregates. Research indicates that mechanical blending affects only a small portion of RAP asphalt (Huang et al., 2005). Therefore, it is reasonable to assume the blending process between

RAP and virgin asphalt during mixing as a diffusion process, during which virgin and aged asphalt molecules move and penetrate into each other, trying to achieve an ultimate uniform mix of the two. Although a number of methods have been introduced for the study of asphalt blending, there is still a lack of method to directly observe the concentration changes during diffusion process. Fluorescence microscopy has been introduced in the study of asphalt blending because of its capability of distinguishing virgin and aged asphalt (Navaro et al., 2012). In this study, fluorescence microscopy combined with Fick's second law and molecular simulation were used to quantify the diffusion process of virgin and aged asphalt. The diffusion coefficient was back-calculated to determine the diffusion rate.

1.1.4 Current Challenges for the Utilization of RAS

The use of RAS in HMA is expected to provide significant benefits to the asphalt industry and highway agencies by reducing the amount of virgin asphalt binder added to the mixture. In spite of the potential benefits of the use of RAS in asphalt mixtures, many states are still cautious in the use of high RAS content in asphalt mixtures because of construction and durability concerns. One concern is that air-blown asphalt is typically used in the manufacturing of asphalt shingles; this type of asphalt binder has a greater viscosity than the regular asphalt binder used in HMA. Another major concern with RAS relates to the variability in the properties of the recycled materials originating from different sources. The objective of this study is to introduce a new approach to recycling asphalt shingles in asphalt construction in which RAS binder is separated into soft and hard fraction through a dissolve and extraction process according to the polarity. In the proposed process, the viscosity of the soft fraction can be controlled by the types and composition of solvent and used as common asphalt or rejuvenator. The proposed process offers the potential to increase the percentage of asphalt shingles used in the mixture and may allow for a better control of the properties of binder blend.

1.2 Literature Review

Two critical questions regarding better utilization RAP/RAS, based on aforementioned discussion, have been brought into the attention of the asphalt industry. One is the understanding of the blending process between the recycled old binder and the new binder; another is the utilization of recycled asphalt shingle. The latest literature review related to these two topics is organized as follows:

1.2.1 Quantitively Evaluation of the Blending Efficiency of Plant Asphalt Mixture

There are three possible blending situations for recycled asphalt mixtures. The first one is that RAP binder can be fully blended with virgin binder to coat both virgin and RAP aggregates. Several state transportation agencies have adopted this approach and assumed that RAP binder is 100% reusable in their mix design, and then establish virgin binder content once the design binder content is determined (Johnson et al., 2010, Shirodkar et al., 2011, Zaumanis and Mallick, 2015).

The second scenario is the “Black rock” theory. “Black rock” theory is based on the premise that RAP may actually perform as nothing more than an aggregate (McDaniel et al., 2000). While in this case RAP is still used as recycled aggregate, the major economic savings coming from use of RAP binder vanish. In addition, if the stiff, highly oxidized binder does not truly blend with virgin binder in the mixture, the use of the blending charts commonly adopted for RAP recycling is unnecessary (Huang et al., 2005, McDaniel et al., 2000). In order to refute the “black rock” theory, Soleymani et al (Soleymani et al., 2000) simulated a “black rock” condition. The researchers made three mixtures, denoted Cases A, B, and C. The black rock scenario, Case A, was created by extracting the binder from a

RAP and adding only the recovered aggregate to a new mixture of virgin aggregate and virgin binder. Case B was considered a “true” mixture, where RAP was added directly to the mixture with virgin aggregate and binder. The “total blend”, Case C, was created by mechanically blending virgin binder and recovered RAP binder and adding it to the virgin and RAP aggregate to make the mixture. This study concluded that RAP does not behave as a black rock. At a high RAP content (40%), the mixture performed similarly to that of a 100% blend. The researchers also concluded that at least partial blending occurs in almost all the cases.

The third scenario is that partial blending happens between RAP and virgin binders, which is supported by many researchers (Zhao et al., 2013a, Zhao et al., 2013b, Bowers et al., 2014, Shu et al., 2008, Huang et al., 2010, Huang et al., 2005, Soleymani et al., 2000). McDaniel et al. (McDaniel et al., 2000) addressed this scenario in the NCHRP Project 9-12 and concluded that partial blending does occur to a significant extent. Soleymani et al. (Soleymani et al., 2000) conducted a similar study and found that 50% of the actual mixtures do not perform similarly to either black rock or total blending mixtures, indicating that insufficient blending affected the performance of mixtures containing high RAP.

The blending efficiency can be quantified by mobilization rate, which means the percentage of aged binder that can participate in the formation of homogeneous asphalt binder film. Analytical methods such as Gel Permeation Chromatography (GPC), Fourier Transform Infrared Spectroscopy (FTIR), atomic force microscopy (AFM), environmental scanning electron microscopy (ESEM), X-ray computer tomography (CT), dynamic shear rheometer (DSR) and bending beam rheometer (BBR) have been used to investigate the blending efficiency of virgin and aged binder (Shirodkar et al., 2011, Zhao et al., 2015b, Bowers et al., 2014, Booshehrian et al., 2012, Bennert and Dongré, 2010, Rinaldini et al., 2014, Huang et al., 2005, Zearley, 1979, Carpenter and Wolosick, 1980, Zhao et al., 2015a, Nahar et al., 2013a, Zhao et al., 2014, Druta et al., 2009, Copeland, 2011, Bonaquist, 2005, Mogawer et al., 2013, Hajj et al., 2012, Swiertz et al., 2011, Swiertz and Bahia, 2011). The test methods can be classified as optical method, dissolve method and mechanical method based on the test procedure.

The dissolve method is widely used to investigate the blending process of aged binder. It involves lixiviating binder blend using a solvent, the resulting solute being collected gradually and characterized in terms of mass fractions of virgin and aged binder. This experimental technique is able to assess the extent to which the aged binder participates in binder blend based on the parameters in the production process, such as processing temperature and mixing time (Huang et al., 2005, Zearley, 1979, Carpenter and Wolosick, 1980, Zhao et al., 2015a, Bowers et al., 2014).

In order to avoid the influence of dissolve process, a method has been developed to assess the blending efficiency by comparing the measured dynamic modulus of the mixtures with predicted dynamic modulus from binder testing of as-recovered binders (Copeland, 2011, Booshehrian et al., 2012). The degree of blending between the RAP, RAS, and virgin binders also can be evaluated by comparing the dynamic modulus of mixtures to a dynamic modulus predicted using the complex modulus of the recovered binders and the Hirsch model (Bonaquist, 2005, Mogawer et al., 2013, Bennert and Dongré, 2010, Hajj et al., 2012). A new developed testing mortars also is used to evaluate the blending efficiency by modifying the analysis procedure for estimating the low-temperature properties of RAP binder and binder blend (Swiertz et al., 2011, Swiertz and Bahia, 2011).

Optical methods have been proven to be effective in distinguishing between virgin and aged binders directly (Nahar et al., 2013a, Zhao et al., 2014, Druta et al., 2009). AFM is used to probe the change of microstructural properties from a RAP (Nahar et al., 2013a)/ recycle asphalt shingle (RAS) (Zhao et al., 2015b) binder and virgin bitumen to the blending zone of these two. With this visualization technique, virgin binder could be differentiated from aged binder qualitatively using levels of grey using X-ray CT scanner, and research indicates that RAP binder has a certain ability to be remobilized and to blend with virgin binder(Druta et al., 2009).

These methods expend the understanding on the blending process of recycled asphalt materials. However, there is still not a commonly accepted method to determine the blending efficiency, and it is desirable to find a convenient method for determining the blending efficiency of RAP or RAS. A new visual observation tool without the tedious binder extraction process should be much needed for distinguishing virgin from aged binders so that it would be much easier and more practical to quantify the blending efficiency of recycled asphalt binder in an asphalt mixture.

Navaro et al. (Navaro et al., 2012) utilized fluorescence microscopy to investigate the degree of blending between virgin and aged binders. In the fluorescence photograph, the aged binder could be distinguished from the virgin binder, as the latter is fluorescent. The advance of this method is that the blending of virgin and age can be observed directly. However, the fluorescent intensity of binders was controlled by multiple factor such as chemical compositions and experimental conditions. In addition, the research of Navaro et al. does not give the conclusion about how much of aged binder can be used in each condition. Therefore, to efficiently use this method in the study of asphalt blending, the fluorescent characteristics of virgin and aged binders need to be further examined, and the quantitative relationship between fluorescent intensity and aged binder content also need to be investigated.

1.2.2 Quantitively Evaluation of the Diffuse Process of Virgin and Aged Asphalt

Early studies on diffusion process between virgin and RAP asphalts were motivated by the use of asphalt rejuvenators. Oliver studied the penetration of rejuvenating oils into existing road surface by measuring the penetrating rate. The diffusion coefficient is found to follow the Arrhenius laws(Oliver, 1975). Carpenter and Wolosick adopted a staged extraction method to study the effect of a rejuvenator on asphalt mixture. Asphalt binder coating aggregate was divided into two layers by a chemical solvent during the two-stage dissolution process. The properties of asphalt layers were tested and compared to investigate the diffusion process of rejuvenators (Carpenter and Wolosick, 1980).

Karlsson and Isacsson conducted a comprehensive study on the diffusion of rejuvenators into asphalt binders using Fourier transform infrared spectroscopy (FTIR-ATR) (Karlsson and Isacsson, 2003) and dynamic shear rhymester (DSR) (Karlsson et al., 2007). In the FTIR method, thin layers of asphalt and rejuvenator were placed on a zinc plate and diffusion was monitored by absorbing the infrared spectra. The diffusion coefficient was calculated by fitting the experimental data to the mathematical solution of Fick's law (Karlsson and Isacsson, 2003). In the DSR method, two thin layers of a rejuvenator and an aged binder, respectively, were brought into contact using DSR parallel plates. The specimen was further divided to 20 sub-layers to calculate the concentration of the rejuvenator. A pre-assumed diffusion coefficient was used to obtain concentration distribution file. Then the concentration file was transferred into a theoretical viscosity and complex modulus to fit the experimental data. A single diffusion coefficient was determined by using fitting curves (Karlsson et al., 2007). The DSR method was verified by other researchers later (Rad, 2013b, Kriz et al., 2014). Mechanical testing was also applied in the study of rejuvenator-asphalt diffusion and results suggested that a certain degree of blending has been achieved in the mixes (Navaro et al., 2012, Kooij and Verburg, 1996, Coffey et al., 2013).

Although a number of methods have been introduced for the study of asphalt blending, there is still a lack of method to directly observe the concentration changes during diffusion process. Fluorescence microscopy has been introduced in the study of asphalt blending because of its capability of distinguishing virgin and aged asphalt (Navaro et al., 2012). In this study, fluorescence microscopy combined with Fick's second law was used to quantify the diffusion process of virgin and aged asphalt. The diffusion coefficient was back-calculated to determine the diffusion rate.

1.2.3 Utilization of RAS into Pavement

The use of RAS in hot-mix asphalt is expected to provide significant benefits to the asphalt industry and highway agencies by reducing the amount of virgin asphalt binder that is added to the mixture. The fibrous shingle base also contains valuable fibers that may enhance the performance of asphalt mixtures (Elseifi et al., 2012). Since the early 1990s, a number of research studies evaluated the use of RAS in HMA and its influence on the mix mechanical behavior. Two strategies may be adopted in the recycling and processing of tear-off asphalt shingles.

In the first strategy, the practices consist of dry blending RAS with the aggregates before the asphalt binder is added to the batch, similar to RAP. The use of RAS resulted in a decrease in the required virgin binder content and improved the mixture resistance to permanent deformation. However, mixture resistance to low temperature cracking appears to decrease when asphalt shingles are used (Grzybowski, 1993). Button et al. evaluated the influence of adding 5–10% of asphalt shingles on the mechanical properties of asphalt mixtures as compared with untreated mixes. The use of RAS resulted in a decreased tensile strength and creep stiffness of the mixture but it improved the mix resistance to moisture damage (Button et al., 1996).

In the second strategy, RAS is ground to ultrafine particle sizes and blended with asphalt binder through a wet process. In the wet process, the ground recycled material is blended with the binder at a high temperature prior to mixing with the aggregates. Based on the results of the experimental program, the use of RAS modification through the wet process would generally improve or not influence the high temperature grade of the binder, but it also reduces the low temperature grade of the binder. Results of high-pressure gel permeation chromatography (HP-GPC) showed that the proposed wet method of modification produced a slight increase in the high molecular weight (HMW) (>3000 daltons) content in the prepared blends at higher RAS contents, suggesting that a fraction of the RAS binder contributes to the blend properties (Elseifi et al., 2012).

Based on the literature above, the use of asphalt shingles improved the rutting resistance of the mixture but the mix had lower fatigue and low temperature cracking resistance. This concern may be addressed by using the proposed process in this study.

1.3 Research Problems

Although previous studies, as shown above, have proposed methods to evaluate the blending efficiency of recycled asphalt mixtures, there still exists a need to extend and modified these methods for the demand of plant-produced asphalt mixtures.

In addition to the blending efficiency, the diffuse process between virgin and aged asphalt also needs to be further addressed. The literature review shows that some methods were adopted to evaluate the diffusion process, but the evaluated factors that affect the blending efficiency were limited to mixing temperature and mixing time, and none of the previous research correlate the diffusion process to the properties of asphalt. These limitations hinder the further development and full implementation of a highly sustainable pavement system.

Furthermore, it was found that the containing of high percentages of RAS significantly affect the performance of the asphalt mixtures. Accordingly, a different but valuable perspective to utilize RAS in pavement without affect the performance of asphalt mixture need to be developed.

1.4 Research Objectives and Significance

Figure 1.1 presents the research flow chart of this study. The systematic evaluation of the blending efficiency of plant-produced mixture containing high-RAP will offer comprehensive knowledge on diffusion process and detailed guidance in handling certain type of recycled technology in specific structure layers. The fulfillment of the diffusion study will provide a deep insight of the blending mechanisms between the aged and new binders, fundamentally help with the mix design process with consideration of recycled materials and promote the efficient and effective use of asphalt recycling technologies. Furthermore, the mobilization rate evaluation will be able to validate the prediction of diffusion process using property parameters. All these ultimately contribute to a better utilization of recycling asphalt material and a new method to utilizing asphalt shingle is proposed.

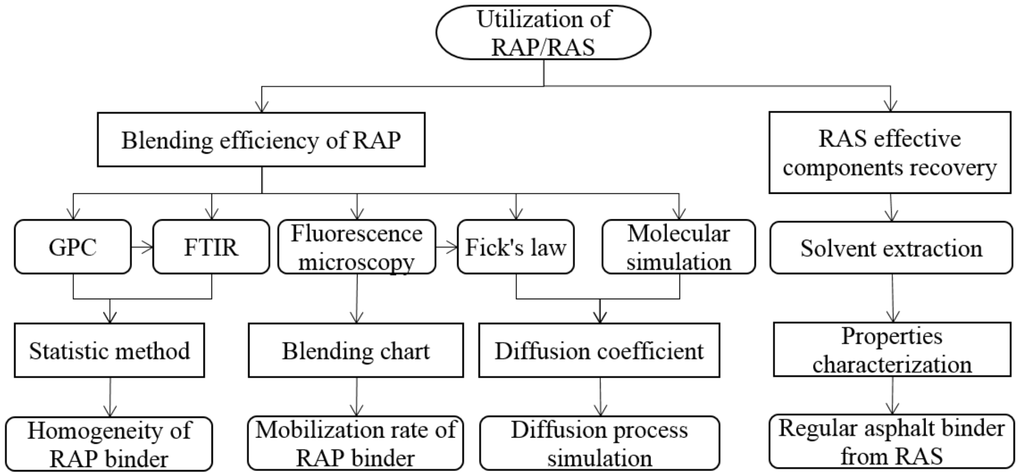

Figure 1.1 Flow chart of the proposed research

1.5 Structure of Dissertation

The dissertation is divided into eight chapters. Chapter 1 provides background and literature support for the studies presented herein. Chapter 2 presents a method of using variation of aging index to evaluate the blending efficiency of RAP. Chapter 3 develops a new method of using fluorescence microscopy to investigate the blending efficiency of RAP. Chapter 4 presents a study of using fluorescent method to evaluate the blending efficiency of three mixtures with different mixing method. Chapter 5 investigates the diffusion process between virgin and aged asphalt using molecular simulation method. Chapter 6 develops a method of testing diffusion coefficient of virgin and aged asphalt using fluorescence microscopy. Chapter 7 presents a study of using solvent extraction method to recover common asphalt binder from RAS. Chapter 8 presents an outline of the conclusions as well as the recommendations for future research.

Chapter II Characterizing Blending Efficiency of Plant Produced Asphalt Paving Mixtures Containing High RAP

A version of this chapter was originally published by Yongjie Ding, Baoshan Huang, and Xiang Shu.

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Yongjie Ding was the principle researcher and author of "Characterizing blending efficiency of plant produced asphalt paving mixtures containing high RAP". Yongjie Ding's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang and Dr. Xiang Shu provided guidance throughout the research process as well as editorial assistance.

2.1 Abstract

The incorporation of high percentage (> 30%) recycled asphalt pavement (RAP) into asphalt mixtures has become more popular. Various methods have been proposed to determine how much of RAP binder can be effectively blended into virgin binder. However, few methods can be used to test the blending efficiency of plant-produced asphalt mixtures. This study proposed a method of measuring the blending efficiency of plant-produced mixtures using Fourier Transform Infrared Spectroscopy (FTIR). Three types of asphalt mixtures, including one warm mix, two hot mixes with or without rejuvenator, were used to validate the proposed method. Results indicate that RAP particles varied in oxidation, but mixing RAP binder with virgin binder could reduce this heterogeneity. Among the three mixtures, warm mix showed the highest blending efficiency, while adding rejuvenator had a limited effect on the blending efficiency. The proposed method was further verified using Gel Permeation Chromatography (GPC).

2.2 Introduction

With the ever-increasing cost of aggregate and asphalt binder, the incorporation of high percentage (> 30%) of recycled asphalt pavement (RAP) into asphalt mixtures has become more and more popular (Huang et al., 2010, Shu et al., 2008, Zhao et al., 2012, Zhao et al., 2013a). The use of RAP can produce significantly economic and environmental benefits. However, with more RAP recycled into asphalt mixtures, some associated concerns also emerge. A major concern is whether or not the aged RAP binder can truly blend with virgin binder and is available to coat aggregates. RAP binder has experienced a service life of aging and become stiff and brittle. When RAP is added into new aggregate and binder, it can negatively impact the performance of asphalt mixtures if the aged binder is not fully blended with virgin binder.

The blending efficiency of aged binders has been studied by many researchers in the laboratory. Researchers usually used particular virgin aggregates to mix with RAP and virgin binder to make mixtures (Zhao et al., 2013a, Zhao et al., 2013b), then visually detected and separated them from RAP aggregates and tested the amount of aged binder that was mobilized and transferred from RAP to virgin aggregates during mixing. The feasibility of this approach depends on the fact that virgin and RAP aggregates could be separated after the mixing process. However, for plant-produced mixtures, it is almost impossible to visually detect and separate virgin aggregates from RAP particles when both are similar in size and shape. Therefore, a new approach needs to be developed to determine the blending efficiency of plant-produced RAP mixtures when virgin and RAP aggregates cannot be separated from each other.

The main objective of this study was to utilize Fourier Transform Infrared Spectroscopy (FTIR) as a tool to determine the blending efficiency of plant-produced recycled asphalt mixtures. Some parameters based on FTIR were employed to evaluate the blending efficiency of recycled mixtures when virgin and RAP aggregates could not be separated. Gel Permeation Chromatography (GPC) was also utilized to verify the results from FTIR.

2.3 Laboratory Experiment

2.3.1 Materials

Three plant-produced mixtures were selected in this study including one warm mixture produced using foaming technology, one hot mixture with rejuvenator, and one hot mixture without rejuvenator. One performance grade asphalt binder PG 64-22, commonly used Tennessee, USA, was used in all three mixtures. All three mixtures followed the same gradation. The virgin aggregates consisted of # 5, # 7 and # 10 stones and natural sands. The RAP was processed and then sieved as RAP processed 3/4 and 5/16. The asphalt content of RAP was 4.61%. The RAP content was 50% for all three mixtures. Table 2.1 presents the properties for each batch of materials, including the percentage and gradation of virgin aggregates, RAP and total mixtures. The Marshall mix design procedure was employed to design mixture because it is the standard mix design method adopted by the Tennessee Department of Transportation (TDOT). The optimum asphalt content was 4.5% for all three mixtures.

Table 2.1 Properties of the materials used in the mixtures

Sieve Size	Percentage Passing						
	# 5	# 7	# 10	Natural Sand	RAP Processed		Total
					Passing 3/4	Passing 5/16	
1.25"	100	100	100	100	100	100	100
3/4"	56	100	100	100	100	100	91
3/8"	8	54	100	100	68	100	71
No.4	2	5	86	95	35	95	56
No.8	1	3	56	82	22	72	40
No.30	0	0	23	50	14	37	21
No.50	0	0	16	28	10	27	14
No.100	0	0	12	12.7	6	20	9.6
No.200	0	0	9.5	4.6	4	13.5	6.3
Total	20	5	15	10	25	25	100

Both WMA and HMA mixtures were sampled during production at the plant. The mixing temperature for WMA and HMA mixtures were 130 °C and 165 °C, respectively. The content of rejuvenator was 0.4 % by weight of asphalt binder. The rejuvenator was first added into virgin binder and then mixed with the aggregates.

2.3.2 Procedure for Characterizing Blending Efficiency

20 samples including 5 large aggregate particles, 10 medium aggregate particles, and 5 fine aggregate particles were selected from each batch. The target of this research was the spread of aged binder on the whole mixture involving different aggregate sizes. Therefore, one aggregate particle can be used as a sample which is assumed to be coated with a film of homogeneous binder. The choice of 20 samples was determined based on two factors: 1). To make sure that all aggregate types (aggregate size, virgin or RAP) were chosen in one batch of samples. For example, 5 small aggregate particles were chosen, and the chances for virgin aggregates being selected in small aggregates was 42%. The probability

of small virgin aggregates not being included in one batch of materials was $0.58^5=0.06$, which was an event with little chance. 2). It takes about one hour to prepare and test one sample and about 20 hours to finish one batch of 20 samples, which is an amount of time can be accepted in laboratory.

Table 2.2 presents the properties for each batch of materials, including size distribution and aggregate source. Some of virgin aggregate particles could be identified in this study because the particles larger than 3/4 inch sieve were all virgin aggregates. All the RAP aggregate particles could not be identified because both virgin and RAP aggregates were the same limestone of similar size. However, the aggregate source could be determined based on the gradations of different aggregates and RAP as well as their contents in the mixture. For example, for small aggregates which passing No. 4 Sieve, the percent of two types of RAP passing No. 4 size was 0.35 and 0.95 respectively, and 0.56 for the total mixture. The content of the two types of RAP in total mixture was both 0.25. Therefore, the chance for a small aggregate particle being from RAP was [(0.35 * 0.25) + (0.95 * 0.25)] / 0.56 = 0.58.

Table 2.2 Properties of the materials used in the blending study

Materials	Size Distribution	Aggregate Source
Small Aggregate Particles	Passing No. 4 Sieve	42% Virgin + 58% RAP
Medium Aggregate Particles	Passing 3/4 inch Sieve and retained on No. 4 Sieve	50% Virgin + 50% RAP
Large Aggregate Particles	Retained on 3/4 inch Sieve	100% Virgin

The binder coated on the aggregate particles was dissolved by trichloroethylene (TCE) and used to make FTIR samples. FTIR samples were made by drop-casting asphalt solution into films on potassium bromide (KBr) salt plates with toluene. The films were then placed in a vacuum oven for a minimum of 2 hours at 100 °C to ensure the evaporation of the toluene (Bowers, 2013). The films were then tested using a Nicolet 6700 FTIR. Data were processed using the OMNIC software that is standard with the equipment.

2.4 Development of FTIR Parameters for Blending Efficiency

In asphalt chemistry, the major functional group of asphalt binder commonly used to monitor oxidation is the carbonyl (C=O) band that can be found at the wavelength of 1695 cm^{-1}. The growth in carbonyl is due to the oxidation process – the chemical reaction between asphalt binder and oxygen in the atmosphere (Liu et al., 1998).

Figure 2.1 compares the FTIR chromatograms of one virgin binder (PG 64-22) and one RAP binder used in this study. It can be seen that the area of C=O peak of RAP binder was significantly larger than that of the virgin binder. The significant difference in C=O area between virgin and RAP binders provides the basis for using FTIR in blending efficiency study.

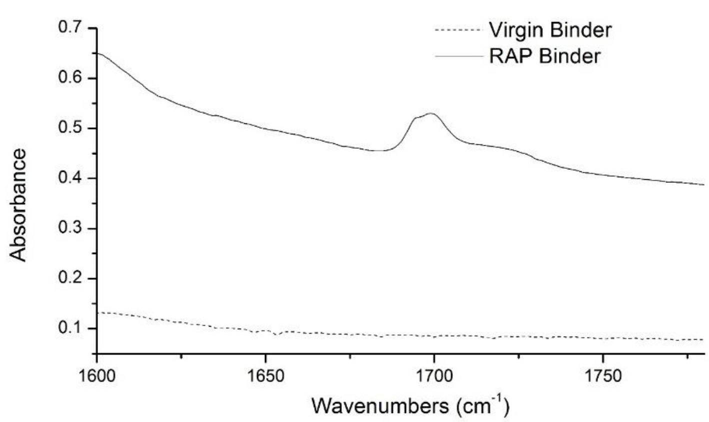

Figure 2.1 Peaks of FTIR curves at carbonyls (c=o) for virgin and RAP binders

Researchers have also found that the saturated C-C vibration band at approximately 1455 cm^{-1} remains relatively constant before and after aging for asphalt binders of the same source and PG grade (Shirodkar et al., 2011, Bowers et al., 2014). This allows for an aging index (AI) to be defined for asphalt binder by using Equation (1). An increase in AI indicates an increase in the content of aged binder such as in RAP or RAS.

$$Aging\ index(AI) = \frac{Area\ of\ carbonyl\ (c{=}o)\ band\ at\ {\sim}1695cm^{-1}}{Area\ of\ satutated\ C{-}C\ stretch\ band\ at\ {\sim}1455cm^{-1}} \qquad (2.1)$$

In the study, the question of interest is how much RAP binder can be blended with the virgin binder other than behave as “black stone”? The blending efficiency, therefore, is defined as how much of RAP binder can be mobilized and blended with virgin binder during the mixing process. As mentioned before, in some cases, the virgin aggregates cannot be separated from RAP aggregates if their size and material sources are similar. In this study, one parameter was proposed for characterization of blending efficiency if virgin aggregates cannot be distinguished from RAP aggregates. The proposed parameter was the coefficient of variability (CV) (Equation 2.2) of AI of a number of representative samples from a batch of material.

$$CV = \frac{Standard\ divation\ of\ AI}{Mean\ of\ AI} \qquad (2.2)$$

In this study, 20 representative samples were selected for one batch, including 5 large aggregate particles, 10 medium particles, and 5 fine particles. Because RAP binder is significantly different from virgin binder in aging, AI would vary highly from particle to particle if no blending existed between RAP and virgin binders, resulting in a large CV. CV is expected to decrease with the increased degree of blending between RAP and virgin binders.

Because RAP did not contain aggregate particles larger than 3/4 inch in all three mixtures, all the selected aggregate particles larger than 3/4 inch were virgin aggregate. Since virgin aggregates could be visually detected and separated from RAP aggregates, a new parameter, the mean value of AI of the binder from virgin aggregates, was proposed for characterizing blending efficiency. A higher AI value indicates a higher carbonyl content in the binder. For a blend of two specific virgin and RAP binders, a higher AI of the binder from virgin aggregates means that a larger portion of RAP binder was transferred from RAP aggregates onto virgin aggregates. Therefore, the AI obtained from larger aggregates is expected to increase with the increase in blending efficiency. In addition, the differences in AI value between the binder from large aggregates and the binder from the whole batch aggregates can also be used as an index for blending efficiency. The difference is expected to decrease with the increase in blending efficiency.

These proposed parameters are able to be used to compare the degree of blending, but cannot be used to determine whether the blended binder is homogeneous or not. Virgin binder can be treated as a homogeneous mix. Therefore, the binder from HMA produced in the laboratory without RAP was used as a homogeneous baseline material. To make the baseline material, aggregates were heated to 175 °C, 10 °C higher than the target mixing temperature of 165 °C for more than 2 h before mixing. The virgin binder was heated up to 165 °C and then mixed with aggregates for 2 min. The newly blended mixture was heated at 160 °C for 2 h to simulate the short term aging process. Then 20 aggregate particles with the same size distribution as before were picked out and the binder on them was extracted and subjected to FTIR test. The variability of AI of these 20 aggregates was used as the homogeneity baseline. Table 2.3 presents the amount of raw materials used for one batch of the baseline mix.

Table 2.3 Amount of raw materials used for the homogeneous baseline mix

Material	Amounts Used/(g)
Aggregate #5	764
Aggregate #7	191
Aggregate #10	573
Natural Sand	382
Virgin Binder	90
Total	2000

2.5 Validation by GPC

GPC is a size exclusion chemistry technique that yields molecular weight distribution of the analytes on the basis of molecular size (Bowers, 2013) It has been successfully used in RAP blending study because it is capable of differentiating aged binder from virgin binder due to the fact that aged binder has a higher portion of large molecules than virgin binder (Bowers et al., 2014, Zhao, 2014).

In order to obtain quantifiable parameters, the GPC chromatogram was divided into two fractions based on molecular weight distribution: large molecular fraction and small molecular fraction. The large molecule threshold was set on 3000 Dalton following the suggestion by Zhao et al. (Zhao, 2014). LMS% is defined as the percentage of large molecular fraction over the total area of the chromatogram generated by GPC. A large LMS% indicates higher a larger molecular fraction in the binder. For a blend of two specific virgin and RAP binders, a higher LMS% means a higher RAP concentration in the blend (Zhao et al., 2013a).

As in the FTIR method, 20 samples including 5 large aggregate particles, 10 medium particles and 5 fine particles were selected from each batch. Each aggregate was eluted with trichloroethylene (TCE) for a complete extraction, then recovered in a 20 ml vial with a water bath of 70 °C in less than 15 min until the solvent was no longer transparent. The recovered binder was used to make standardized samples and subjected to GPC testing. The CV of LMS% was compared with that of FTIR to validate the results from the FTIR method.

2.6 Results and Discussion

2.6.1 Validation by GPC

Figure 2.2 shows the CVs of one RAP and one hot mixture without rejuvenator generated by GPC and FTIR. It can be seen that, for both GPC and FTIR, the CV of RAP was larger than that of the hot mixture without rejuvenator. A more careful comparison of the GPC and FTIR results shows both GPC and FTIR gave a CV of RAP that was approximately 2-3 times of that of the hot mixture without rejuvenator. FTIR yielded a higher CV than GPC. This indicates that both FTIR and GPC can be effective for identifying aged binder in a binder blend. Because FTIR test is easier and more convenient to perform than GPC test, FTIR was selected in this study to evaluate the blending efficiency of plant-produced asphalt mixtures.

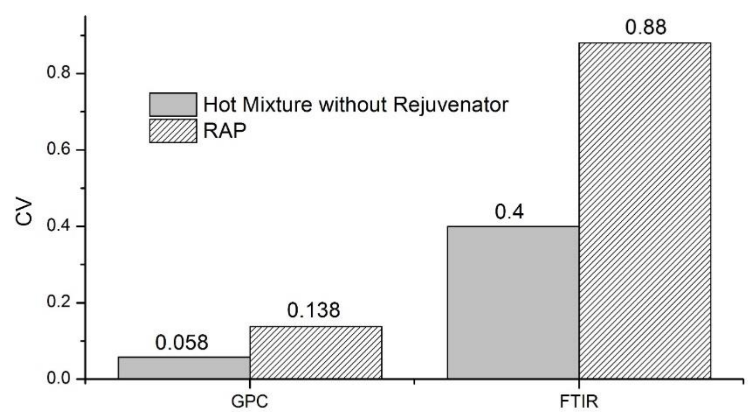

Figure 2.2 CVs of RAP and hot mix without rejuvenator from GPC and FTIR

2.6.2 Coefficient of Variability

Figure 2.3 presents the CVs of AI of the mixtures used in this study. It was found that the CV of RAP was much higher than that of other mixtures, indicating that the degree of oxidation was highly variable among the aged binder in RAP particles and mixing RAP binder with virgin binder could reduce the heterogeneity of RAP binders. It is also found that the CVs of all three mixes were higher than that of the homogeneity baseline, which indicates that RAP binder could partially blend with virgin binder in all three mixes. The CV of warm mix was the closest to that of the homogeneity baseline and thus the most homogeneous situation may have occurred to warm mix. The CV of hot mix without rejuvenator was larger than that of the mix with rejuvenator, indicating that addition of rejuvenator had an effect on blending efficiency because rejuvenators can soften virgin, thus improving the blending and diffusion between virgin and RAP binders.

The reduced heterogeneity of binders could also be contributed to the mixed "scrape-offs" effect caused by direct contact with virgin aggregates or the blending effect that happened between RAP and virgin binders. In order to determine which effect was dominant, RAP aggregates were heated to 165 °C and then mixed with virgin aggregates with no virgin binder added. The CV of RAP aggregates after mixing process was 0.87 and showed an insignificant difference from that before mixing. This indicates that the reduced heterogeneity of RAP binders was mainly due to the blending effect between RAP and virgin binders.

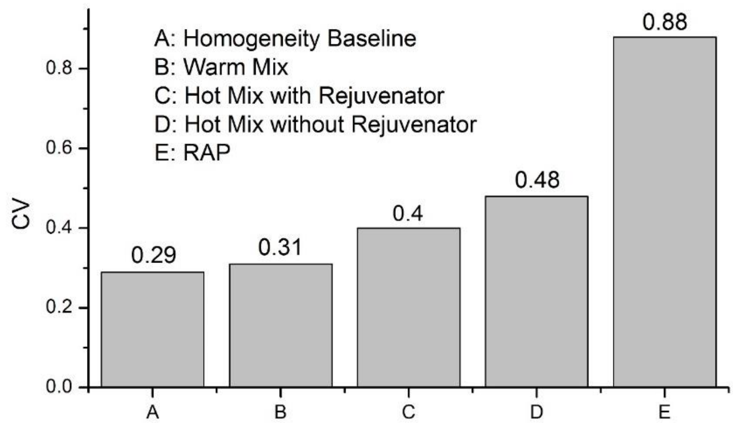

Figure 2.3 CVs of three mixes and baseline

2.6.3 Mean Values of AI for Binders on Large Virgin Aggregates

Figure 2.4 presents the mean AI values for binders extracted from large virgin aggregates and those from all the aggregates. Except for the virgin aggregates of hot mix without rejuvenator, the AI means of virgin aggregates and total aggregates were all between the range of virgin and RAP binders (0.20-0.71). The lower AI of virgin aggregates of hot mix without rejuvenator is probably caused by experiment error.

The AIs of virgin aggregates were closest to that of the total mixtures in warm mix, which suggests that warm mix had the highest blending efficiency among three mixes. These are consistent with the results from the CV method. It should be noticed that the AI values of the hot mix with rejuvenator was higher than other two mixes in both virgin aggregates and total mixtures. This should be caused by the addition of rejuvenator which has an obvious peak around 1750 cm^{-1} (shown in Figure 2.5). For the hot mixes without and with rejuvenator, the AI ratios of virgin aggregates and total mixture were 1.88 and 1.39, respectively, which indicates that adding rejuvenator benefited blending efficiency.

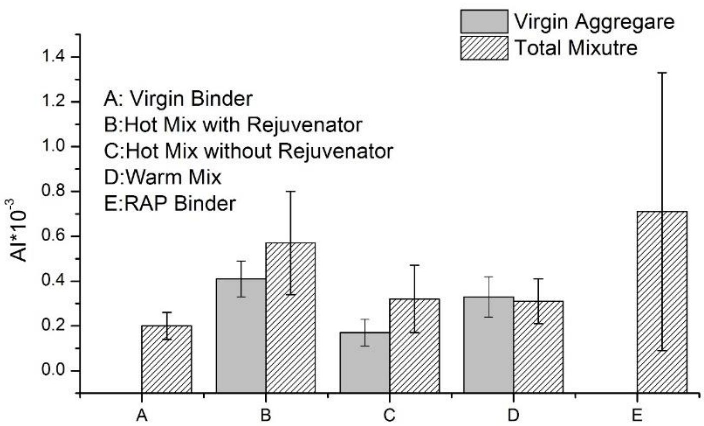

Figure 2.4 Contrast of Means of AI of the binders on large virgin aggregates and all aggregates

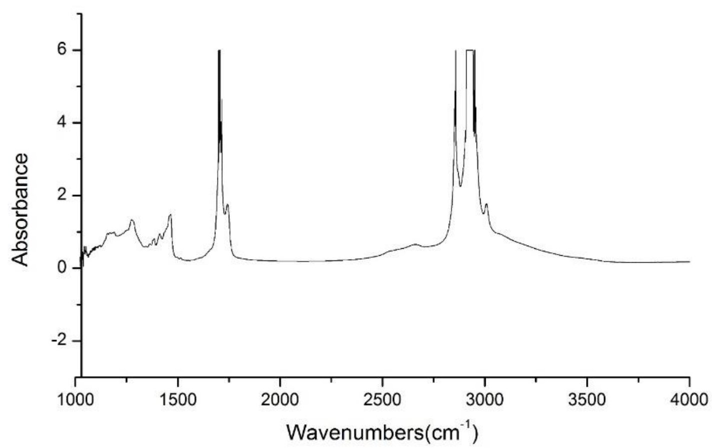

Figure 2.5 FTIR spectrum of rejuvenator

2.6.4 Analysis of the Similarity in Variation among Mixtures

As mentioned above, RAP particles varied in the degree of oxidation, and mixing RAP binder with virgin binders could reduce the variation. Therefore, the difference between the AI variability of mixtures and RAP is expected to increase with increasing blending efficiency.

In this study, the similarity in AI variability was analyzed using the Levene method. In the Levene method, a small Significance coefficient indicates a higher variability difference. For a comparison between two mixtures, a lower Significance coefficient means that a higher variability difference in the degree of binder oxidation existed between the two mixtures. Figure 2.6 shows the results from the comparison of homogeneity baseline, RAP, and three mixes. For all three mixes, the Significance coefficients with homogeneity baseline were all larger than that with RAP, which indicates that the degree of oxidation of all three mixes were closer to the homogeneity situation than to RAP. The results also indicate that blending efficiency of warm mix was the highest because it had the largest Significance coefficient with homogeneity baseline and smallest one with RAP. The Significance coefficient of hot mixes with and without rejuvenator had a slight variation with each other, which suggests that the difference in binder oxidation between these two mixes was not as significant as with warm mix.

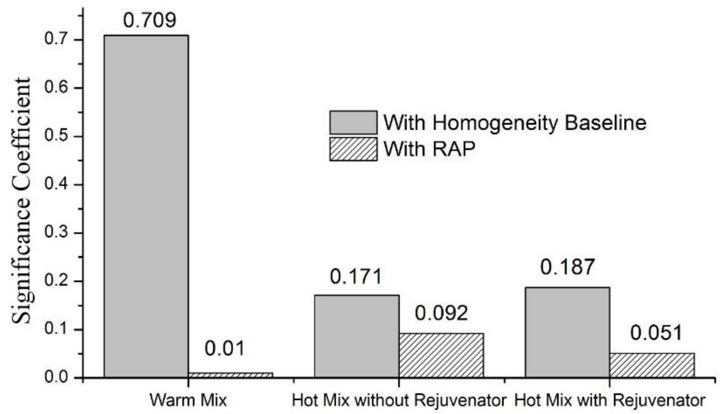

Figure 2.6 Significance coefficients of variability contrast between mix methods and baseline

Figure 2.7 compares the variability among three mixes. It can be seen that the Significance coefficient between hot mixes with and without rejuvenator was the highest, and these two mixes had similar Significance coefficients with warm mix, which also demonstrates that there was no significant variability difference between hot mixes with and without rejuvenator. It also can be found that that the variability of warm mix had obvious difference with the other two mixes. These results indicate that, among three mixes, warm mix showed the highest blending efficiency of the recycled asphalt mixture, whereas addition of rejuvenator only showed a slight improvement in blending efficiency compared to the mix without rejuvenator.

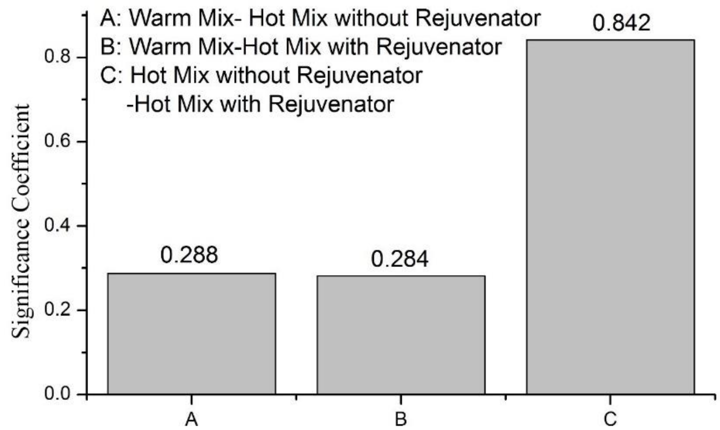

Figure 2.7 Significant coefficient of variability contrast among three mix methods

2.7 Conclusions

One new approach was proposed for evaluating the blending efficiency of plant-produced recycled asphalt mixtures when virgin and RAP aggregates cannot be separated from each other. The blending efficiency of three mixes including one warm mix, two hot mixes with or without rejuvenator, were used to validate the method. Such parameters as CV, AI means of virgin aggregates, and similarity in variation were used to evaluate the blending efficiency. The following conclusions were drawn:

(1) FTIR was an effective technique for differentiating between virgin and RAP binder. The CV of AI was found to decrease with the increasing degree of blending between RAP and virgin binders, which provides the basis for characterizing the blending efficiency of recycled mixtures containing RAP. The binder of HMA produced in the laboratory without RAP could be used as the fully-blended baseline in this method.

(2) RAP particles varied in the degree of oxidation of RAP binder. Mixing RAP binder with virgin binder could reduce the heterogeneity.

(3) Among three mixes, warm mix showed the highest blending efficiency.

(4) Addition of rejuvenator showed a slight improvement in blending efficiency of recycled mixtures. However, the mixtures with and without rejuvenator showed only a slight difference in the degree of oxidation. Therefore, compared with warm mix, adding rejuvenator had a limited effect on blending efficiency.

Chapter III Utilizing Fluorescence Microscopy for Quantifying Mobilization Rate of Aged Asphalt Binder

A version of this chapter was originally published by Yongjie Ding, Baoshan Huang, and Xiang Shu.

Yongjie Ding, Baoshan Huang, and Xiang Shu. Utilizing fluorescence microscopy for quantifying mobilization rate of aged asphalt binder. Journal of Materials in Civil Engineering, 2017

Yongjie Ding was the principle researcher and author of "Utilizing fluorescence microscopy for quantifying mobilization rate of aged asphalt binder". Yongjie Ding's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang and Dr. Xiang Shu provided guidance throughout the research process as well as editorial assistance.

3.1 Abstract

The asphalt paving industry has been increasing the use of recycled asphalt pavement (RAP). However, there is a concern over the percentage of the aged asphalt binder in RAP that can actually be blended into the virgin binder and thus become available to coat aggregate. In this study, a laboratory procedure was proposed for quantifying the mobilization rate of the aged binder using fluorescence microscopy. A new parameter, mean grey value (MGV), was derived from the fluorescence image and used to differentiate between recycled and virgin binders as well as their blends. A blending chart was generated in terms of MGV for the virgin-aged asphalt blends containing 0-100% RAP binder and used as a baseline for the quantification. It was found that there existed a linear relationship between MGV and RAP binder content. A laboratory experiment was conducted to validate the proposed method. Glass cullets were added as a special type of aggregate so that they could be retrieved after mixing and tested by fluorescence microscopy. Results show that the mobilization rate of RAP binder from fluorescent method was improved with an

extended mixing time and an elevated temperature.

3.2 Introduction

There is a demand for incorporating more reclaimed asphalt pavement (RAP) in the asphalt paving industry due to social, economic and environmental benefits. During the production of asphalt paving mixtures, aged asphalt binder in RAP is heated and blended with hot virgin binder to coat aggregates. However, there is a concern whether the aged asphalt can be 100% blended with the virgin binder and made available for reuse in asphalt mixtures. Previous studies have shown that partial blending may occur when RAP is mixed with virgin binder and aggregates (Ding et al., 2016a, Huang et al., 2005, Shirodkar et al., 2011, Zhao et al., 2015b, Zofka et al., 2004). Therefore, the assumption of 100% blending may result in insufficient asphalt content in asphalt paving mixtures, thus leading to poor pavement performance or a shorter pavement service life.

Blending efficiency can be quantified using a term mobilization rate, which is defined as the percentage of aged binder that can be mobilized and blended into virgin binder to coat aggregate particles. Analytical methods have been used to investigate the blending efficiency of virgin and aged binder, including Gel Permeation Chromatography (GPC), Fourier Transform Infrared Spectroscopy (FTIR), atomic force microscopy (AFM), environmental scanning electron microscopy (ESEM), X-ray computer tomography (CT), dynamic shear rheometer (DSR) and bending beam rheometer (BBR) (Bennert and Dongré, 2010, D'Angelo and Dongré, 2009, Bonaquist, 2005, Booshehrian et al., 2012, Bowers et al., 2014, Carpenter and Wolosick, 1980, Copeland, 2011, Druta et al., 2009, Hajj et al., 2012). The test methods can be classified into optical microscopy method, chemical dissolution method and mechanical property method according to the tests used.

The chemical dissolution method is widely used to investigate the blending process of aged binder. It involves lixiviating binder blend using a chemical solvent, the resulting solute being collected gradually and used to determine the mass fractions of virgin and aged binder. This experimental technique is able to assess the extent to which the aged binder is blended into virgin binder in the production process as well as the effects of different factors on blending, including processing temperature and mixing time (Bowers et al., 2014, Carpenter and Wolosick, 1980, Huang et al., 2005, Zearley, 1979).

In order to avoid the chemical dissolution process, a method has been developed to assess the blending efficiency by comparing the measured dynamic modulus of recycled mixtures with that predicted from binder testing of as-recovered binders (Booshehrian et al., 2012, Copeland, 2011). The degree of blending between RAP, RAS, and virgin binder can also be evaluated by comparing the dynamic modulus of mixtures to a dynamic modulus predicted using the complex modulus of the recovered binders and the Hirsch model (Bennert and Dongré, 2010, Mogawer et al., 2013). A method is developed to evaluate the blending efficiency by modifying the analysis procedure for estimating the low-temperature properties of RAP binder and binder blend (Swiertz et al., 2011, Swiertz and Bahia, 2011).

Optical microscopy methods have been proven to be effective in directly distinguishing between virgin and aged binders (Druta et al., 2009, Nahar et al., 2013a). AFM is used to probe the change of microstructural properties from a RAP (Nahar et al., 2013a)/ recycle asphalt shingle (RAS) (Zhao et al., 2015b) binder and virgin bitumen to the blending zone of these two. With this visualization technique, virgin binder could be differentiated from aged binder qualitatively using grey level. Research indicates that RAP binder shows a certain ability to be remobilized and to be blended with virgin binder (Druta et al., 2009).

These studies improved the understanding of the blending process of recycled asphalt materials. However, there are still no commonly accepted methods available to determine the blending efficiency. It is desired to develop a convenient method for determining the blending efficiency of RAP. A new visual observation tool without the tedious binder extraction process is desirable for distinguishing virgin from aged binders so that it would be much easier and more practical to quantify the blending efficiency of recycled asphalt binder in an asphalt mixture.

Navaro et al. (Navaro et al., 2012) utilizes fluorescence microscopy to investigate the degree of blending between virgin and aged binders. In the fluorescence photograph, the aged binder could be distinguished from the virgin binder due to their difference in fluorescence, which provides the basis for determining blending efficiency of RAP with fluorescence microscopy. However, the fluorescent intensity of binders is controlled by multiple factors such as chemical composition and experimental condition. Therefore, to efficiently use this method in asphalt blending, the fluorescent characteristics of virgin and aged binders need to be further examined, and the quantitative relationship between fluorescent intensity and aged binder content also needs to be investigated.

3.3 Fluorescence of Asphalt

Fluorescence is a phenomenon that ultraviolet or visible light is absorbed by an organic molecule, thus causing excitation of an electron from an initially occupied, low-energy orbital to a high-energy, previously unoccupied orbital (Khorasani 1987). Fluorescence in asphalt molecules is essentially related to electronic excitation of the conjugated π-systems (aromatic components) and of C=O groups (Khorasani, 1987, Mills and White, 2012, Zhang et al., 2013). Research indicates that extractable C=O groups exhibit a weak fluorescence; while the aromatic hydrocarbon fractions show a moderate fluorescence.

Highly condensed systems, such as those present in asphaltenes, are virtually non-fluorescent because many energy exchanges are possible through large conjugated π-systems, thus giving rise to nonradiative de-excitation (Khorasani, 1987, Mills and White, 2012, Zhang et al., 2013).

Saturate fractions are expected to exhibit no fluorescence. Therefore, dilution in a saturated hydrocarbon matrix is the most favorable case for aromatics to emit fluorescence. The molecular environment, such as proportion of saturates to aromatics, polarity, intermolecular interactions, have a decisive effect on the fluorescence intensity of asphalt. The fluorescence intensity of asphalt is thus primarily controlled by the type and concentration of aromatic molecules relative to the concentration of saturates compounds (Dennis et al., 2012, Stasiuk and Snowdon, 1997).

The fluorescence microscopy is an optical microscopy that uses the emission of fluorescence to study the properties of organic or inorganic substances (Petryayeva et al., 2013). Fluorescence microscopy has been used to visualize voids and cracking of asphalt mixtures (Eriksen and Wegan, 1993), and to observe the state of asphalt binders when they are modified with polymers (Buisine et al., 1993, Daly et al., 1993). The polymer-rich phase that is swelled by the oily aromatic part of asphalt appears to be yellow colored while the asphaltene phase is dark (Brûlé et al., 1988, D'Angelo and Dongré, 2009, Lu and Isacsson, 1999).

For asphaltenes and maltenes fractions, the asphaltenes produce little to no fluorescence, but the maltenes exhibit strong fluorescence in the observed spectral region (Handle et al., 2016). For SARA fractions, the aromatics and resin phases are the only components capable of sufficiently intense fluorescent emission (Handle et al., 2016). Research also indicates that as bitumen ages, its fluorescence emission intensity decreases

(Grossegger et al., 2017). Therefore, fluorescent intensity can be used to distinguish virgin from aged binders.

The objectives of this study were the to develop a parameter based on fluorescence effect that is suitable for the study of virgin and RAP binder blending and use the new fluorescent parameter to build a blending chart between virgin and RAP binders to develop a new method to determine the RAP binder mobilization rate, and to apply the method to laboratory produced asphalt mixtures with varied mixing conditioning.

3.4 Material and Methodology

3.4.1 Material

To investigate if fluorescence intensity can be used to distinguish virgin and aged binders, four SHRP asphalts including AAD-1, AAG-1, AAK-1, AAM-1 were used in this study. The SHRP asphalts were aged by rolling thin-film oven (RTFO) (ASTM, 2010b) and pressurized aging vessel (PAV) methods (ASTM, 2010a). The virgin binder used to build blending chart was a typical PG 64-22 binder commonly used in the Tennessee, USA. The RAP binder was extracted from one RAP with asphalt content of RAP was 4.6 % following ASTM D 6847–02 standard (ASTM, 2010c). To investigate the influence of aging degree on the fluorescent property of binder blend, one highly aged binder from tear-offs RAS with asphalt content of 21% was used in this study.

3.4.2 Asphalt Mixture

The blending efficiencies of a series of asphalt mixtures containing RAP were evaluated to verify the proposed method. Mixing time and temperature were considered as two key factors that affect the binder blending efficiency in that previous research indicates that the blending efficiency of aged binder would increase with the increase in mixing time and temperature (Zhao et al., 2014).

Figure 1 shows a detailed schematic for asphalt mixture producing and testing procedure. To observe the binder using a fluorescence microscope, a glass cullet (Figure 3.1(a)) was used as a special aggregate and added into the mixture because it has two parallel planes and can be tested directly under a fluorescence microscope (Figure 1(f). This study used a mixture containing 50 % RAP content and 2.19 % virgin asphalt binder content. Figure 3.2 shows the particle size distribution of the mixture. A mixture of 2,000 g was produced for each batch, covering 10 g of glass cullet. The aggregates were heated to 10 °C higher than target mixing temperature for more than 2 h before mixing. RAP samples were heated to 110 °C for 2 h to avoid further aging. Virgin binder was heated to the target mixing temperature for 2 h. The aggregates were pre-blended with RAP samples for 10 seconds and then mixed with the virgin binder for a predetermined mixing time. Two mixing temperatures, 130 °C and 160 °C were selected to represent hot and warm mixing scenarios and three mixing times were used: 0.5 mins, 3 mins and 6 mins. Glass cullet were separated from the mixture after mixing and then tested under a fluorescence microscope (Figure 3.1(f)). For each batch of material, 10 samples were tested and the mean value of 10 samples was used as the result of the batch.

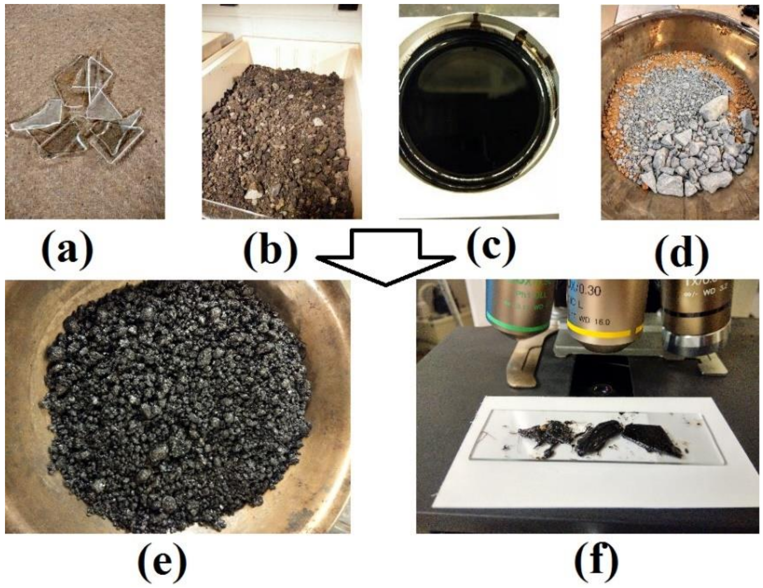

Figure 3.1 Asphalt mixture producing and test process (a) Glass cullet; (b) RAP; (c) Virgin asphalt; (d) Virgin aggregate; (e) Asphalt mixture; (f) Glass cullet tested by fluorescence microscopy

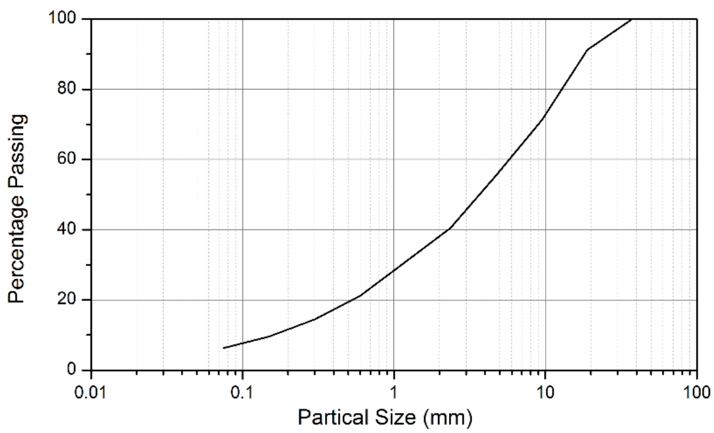

Figure 3.2 Particle size distribution curve of aggregate

3.4.2 Methodology

3.4.2.1 Fluorescence Intensity Measurement

The fluorescence intensity was measured by a Nikon Y-IDP fluorescence microscope in this study. The specimen was illuminated with light of a specific wavelength, causing a light of longer wavelengths. The illumination light was separated from the much weaker emitted fluorescence using a spectral emission filter. The filters were chosen to match the spectral excitation and emission characteristics of the fluorophore used to label the specimen. The distribution of a single fluorophore was imaged by digital camera.

The charge coupled device (CCD) technology was used to produce quantitative digital images by fluorescence microscopy. The input light incident on the CCD creating output electronic charge is an intrinsically linear process. Each pixel is an independent linear photometer. The grey value of the pixel can be used to measure the brightness of the image which is linearly dependent on the input fluorescent intensity. In this study, mean grey value (MGV) of the image was developed to characterize the fluorescence intensity of a material. MGV was defined as the mean of the grey value of a set area of the fluorescence image and can be easily obtained through post-processing of the image. Virgin binder exhibited high grey value than aged binder as shown in Figure 3.3, so that the MGV of binder blend would decrease with the increasing of aged binder content. It can be expected that the MGV of one image would be affected by experimental conditions and material properties. Therefore, the variations of MGV with the factors such as exposure time, material properties were investigated in this study. The digital image collection process followed the procedure of ASTM F2998 (ASTM, 2014).

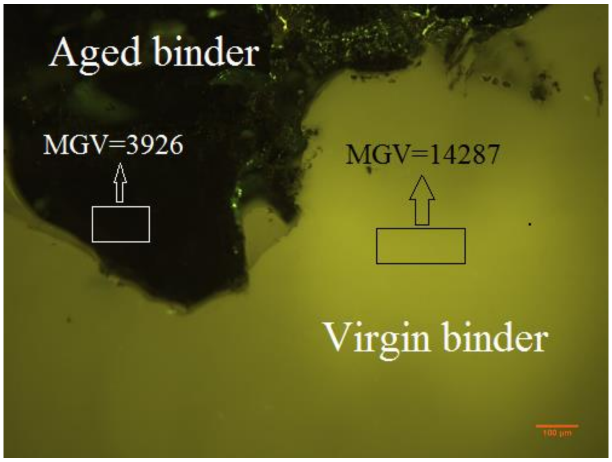

Figure 3.3 Fluorescence images of virgin and aged asphalt samples

3.4.2.2 Determination of RAP Binder Blending Efficiency

The blending process of virgin and aged binder is illustrated in Figures. 3.4 and 3.5. In Figure 3.4, the dark section is aged binder, and the yellow background is virgin binder. The binder blend was stirred at 150 °C for 30 seconds, 2 mins and 5 mins and observed under a fluorescence microscope. The results indicate that the aged binder was mobilized and blended into virgin asphalt to form a homogeneous binder blend by stirring at 150 °C for 5 mins.

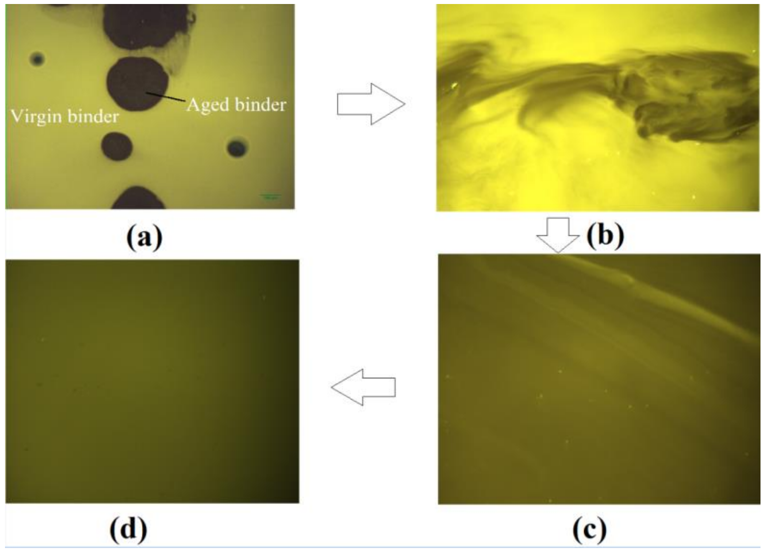

Figure 3.4 Blending process between virgin and aged binder (a) aged asphalt on the top of virgin asphalt; (b) binder blend stirred for 30 s; (c) binder blend stirred for 2 mins; (d) binder blend stirred for 5 mins

Figure 3.5 illustrates the partial blending scenario that may occur in a recycled asphalt mixture. Part of the aged binder film around RAP aggregate (outmost layer) is mobilized and blended into virgin binder to form a binder blend during the mixing process. The inner layer of RAP binder is not mobilized and does not contribute to binder blend. The mobilized RAP binder may also interact with the virgin binder, yielding a homogeneous binder blend that coats both virgin and RAP aggregates. If the RAP binder content can be determined in a binder blend, then the percentage of mobilized RAP binder can be calculated based on the proportions of total virgin and RAP binder. If a particular property or parameter of asphalt blended is a function of RAP binder content and can be measured in the laboratory, then RAP binder content in the blend can be quantitatively determined.

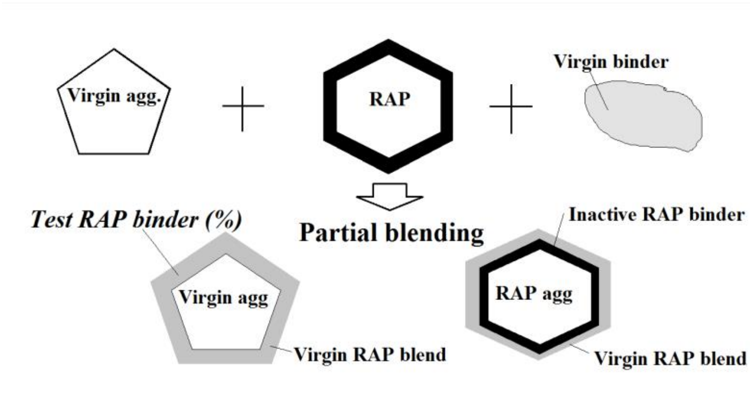

Figure 3.5 Partial blending scenario

In this study, a series of equation was proposed to calculate the mobilization rate of RAP binder on this basis of the research of Zhao et al. (Zhao et al., 2015a). The RAP binder content of binder blend is defined as active RAP binder divided by total binder blend, which can be expressed by the weight (W) of active RAP binder and virgin binder as shown in Equation (3.1).

$$\text{RAP binder (\%)} = \frac{W_{active\ RAP\ binder}}{W_{active\ RAP\ binder} + W_{virgin\ binder}} \tag{3.1}$$

Where, the percentage of RAP binder in binder blend is denoted as RAP binder (%).

Then the weight of active RAP binder can be express by the RAP binder (%) as Equation (3.2).

$$W_{active\ RAP\ binder} = \frac{\text{RAP binder (\%)} \times W_{virgin\ binder}}{1 - \text{RAP binder (\%)}} \tag{3.2}$$

Finally, the mobilization rate can be expressed as the active RAP binder divided by total RAP binder as shown in Equation (3.3).

$$Mobilziartion\ rate = \frac{W_{active\ RAP\ binder}}{W_{total\ RAP\ binder}} = \frac{\text{RAP binder (\%)} \times W_{virgin\ binder}}{(1 - \text{RAP binder (\%)}) \times W_{total\ RAP\ binder}} \tag{3.3}$$

Table 3.1 presents an example of the calculation of mobilization rate for an actual case. Assuming RAP binder (%) is determined in the laboratory as 30%, the weight (W) of RAP and virgin binder expressed as the percentage of total mixture. The mobilization rate can be calculated based on the weight of RAP and virgin binder and RAP binder (%). In the case in Table 3.1, mobilization rate is calculated as 45%, which means 45% of the RAP binder can be mobilized during mixing and contribute to coating the aggregates.

Table 3.1 Example of mobilization rate calculation

Parameter	Description	Value
RAP binder (%)	RAP binder percentage by binder blend	30%
$W_{total\ RAP\ binder}$	RAP binder percentage by total mixture	2.2%
$W_{virgin\ binder}$	Virgin binder percentage by total mixture	2.3%
$W_{active\ RAP\ binder}$	Active RAP binder percentage by total mixture	0.99%
$Blending\ rate$	Active RAP binder percentage by total RAP binder	45%

In this case, the key point in the calculation of mobilization rate is the determination of the RAP binder (%). A straightforward method to determine RAP binder (%) is to build a blending chart with one certain parameter and interpolating the laboratory-testing result of the sample. This study developed a blending chart for blending research using MGV derived from the fluorescence intensity of binder blend.

3.4.2.3 Building a Blending Chart in Terms of MGV

If all the MGVs of a binder blend have a linear relationship with the aged binder content, the construction process of a blending chart only needs to test MGVs of virgin and aged binder and will be significantly simplified. To verify this assumption, one RAP binder and one highly-aged asphalt binder from a recycled asphalt shingle (RAS) were used to build blending chart in this study. To build a blending chart, samples with RAP/RAS binder content ranging from 0 to 100% in a 10% increment were tested for their MGV. The mixtures of virgin binder and recovered RAP/RAS binder were first heated to 170 °C (for RAP) and 190 °C (for RAS) and stirred for 30 minutes, then placed into a vacuum oven (170 °C for RAP and 190 °C for RAS) for another 2 hours. Finally, the mixed binder was spread on a microscope slide and tested.

3.5 Results and Discussion

3.5.1 Influence of Test Conditions on MGV

It is expected that MGV of an image is affected by experimental conditions. Figure 3.6 shows the MGVs of virgin and aged asphalts binder as a function of exposure time and wavelengths of excited light. It can be seen that the MGVs increased with an extended exposure time. In the low MGV range (<50000), there was a linear relationship between MGV and exposure time, but the trend became quadratic gradually in high MGV region (>50000). The MGVs also varied under different excited lights. Therefore, same excited light and exposure time are required to keep the MGVs of binder being comparable.

It is also noticed that the MGVs of virgin and aged binder were almost the same under excited wavelength of 330-380 nm, which indicates that the aged binder could not be distinguished from virgin binder under this test condition. To differentiate between virgin and aged binders as well as binder blends with varying aged binder content, it is desirable that MGV is sensitive to the aged binder ratio, which means virgin and aged binder have a large MGV difference. Therefore, a differentiating factor (DF), which is defined as the ratio of the MGV of aged binder to that of the virgin binder (Equation (3.4)), was used to measure the sensitivity of MGV to the binders in this study. A lower DF means a large MGV difference between virgin and aged asphalt binders, indicating that MGV is more sensitive to the aged binder content in binder blend.

$$\text{Differentiation Factor} = \frac{MGV_{aged\ binder}}{MGV_{virgin\ binder}} \tag{3.4}$$

Figure 3.7 shows the variations of DF with exposure time and wavelength of input light. It indicates that DF decreased first and then increased with exposure time. The exposure time range of 0.5-1.5 s showed a relatively lower DF, thus making DF more sensitive to aged binder content. Among three wavelengths of input lights, 450-490 nm showed the lowest MGV ratios for the exposure time between 0.5 s and 1.5 s and thus was selected as input light in this study.

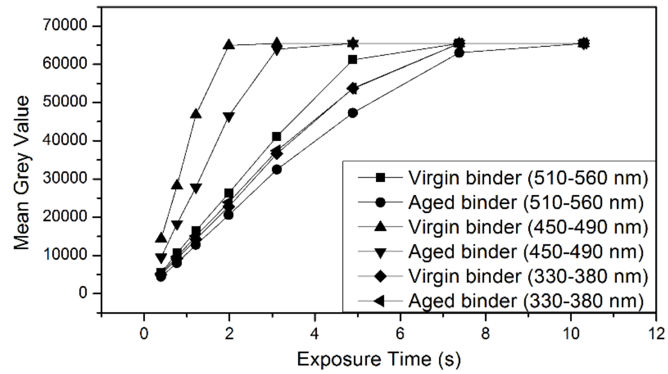

Figure 3.6 MGVs of virgin and aged asphalt as a function of exposure time

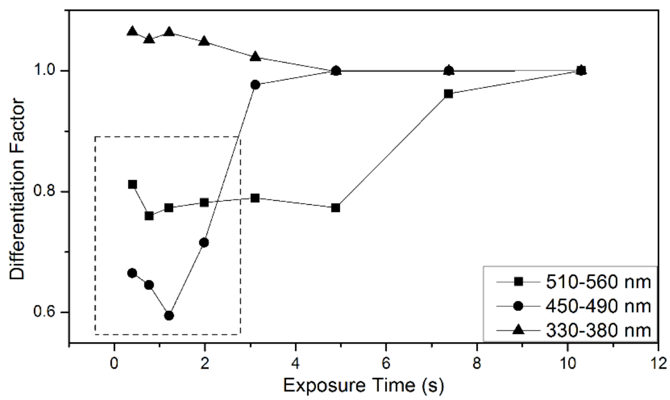

Figure 3.7 MGV ratios of aged and virgin binder at different conditions

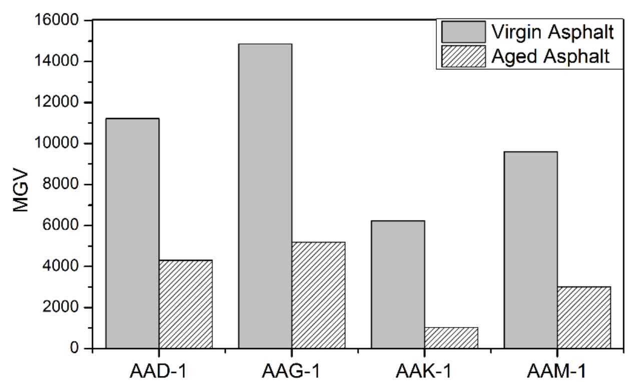

Figure 3.8 MGV of virgin and aged SHRP asphalt

3.5.2 MGV of Virgin and Aged Asphalt

Figure 3.8 shows the MGVs of four SHRP asphalts before and after aging process (RTFO+PAV). The aged asphalts all exhibited lower MGV than virgin asphalt, which indicates that the MGV method proposed in this study can differentiate between virgin and aged asphalts. It is also noticed that MGV of virgin asphalts is different for asphalts from diverse sources, one such example is that MGV of virgin binder AAK-1 was much lower than that of AAG-1.

3.5.3 Blending Chart

The "blending chart" generated by blending one typical PG 64-22 binder with a RAP binder is presented in Figure 3.9. Linear correlations between RAP binder content and MGVs were revealed for virgin-RAP blend high R^2 values (0.976). Accordingly, a linear regressive equation (Equation (5)) was obtained and can be used later to determine RAP binder once the blended binder is tested for MGV. It should be noted that Equation (5) was derived from the asphalt used in this study. For other asphalt, the complete process of building blending chart needs to be repeated because the MGV of asphalt varies with its chemical composition.

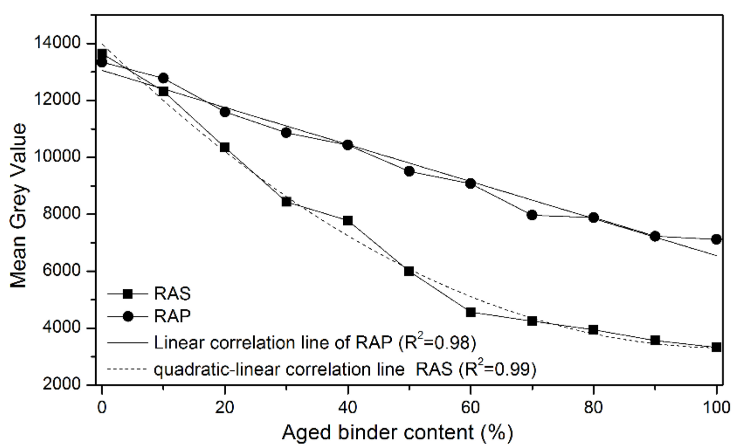

Figure 3.9 Blending chart generated with MGV

The MGV of the binder blend showed a poor linear relationship (R^2=0.91) but a good quadratic (R^2=0.992) relationship with the RAS binder content. Therefore, the relationship between MGVs and aged binder content should not be simplified as linear and the construction of blending chart should include as many data points of a binder blend as one can get.

$$\text{RAP binder (\%)} = \frac{13056 - MGV_{binder\ blend}}{6508} \tag{3.5}$$

3.5.4 Determination of RAP Binder Blending Efficiency

Figure 10 shows the MGVs and RAP binder (%) of binder blend, and the mobilization rates of RAP binder. The RAP binder (%) was calculated based on the MGVs shown in Figure 10 (a) and Equation (3.5). As stated before, the virgin asphalt content was 2.19 %, the RAP binder content was 4.6% × 50% = 2.3 % for total mixture. Then the mobilization rate can be calculated by Equation (2) and (3). The MGVs (Figure 3.10 (a)) showed a downward trend with the increase in both mixing temperature and mixing time. The decrease of MGVs of the binders can be attributed to the increase of RAP binder (%) (Figure 3.10 (b)), indicating that more RAP binder was mobilized onto glass cullet with the increase in mixing time and temperature.

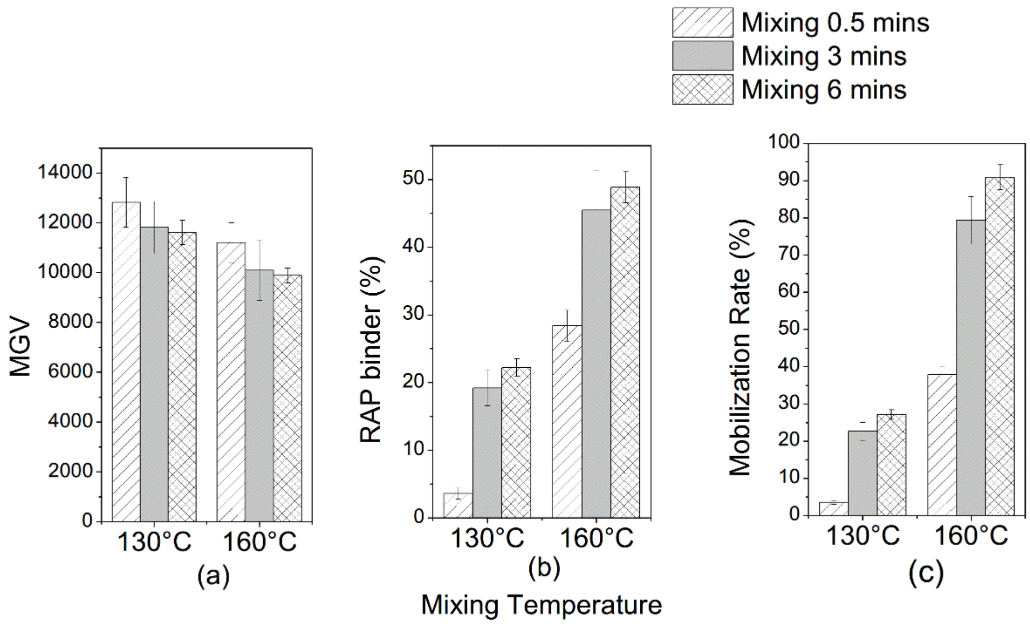

Figure 3.10 Test results of binder blends (a) Mean grey value (b) RAP binder content (c)Mobilization rate

As expected, the mobilization rate of RAP binder (Figure 10 (c)) increased with the increase in mixing time and temperature, and agreed with previous results from numerous researchers (Kriz et al., 2014, Nahar et al., 2013a, Navaro et al., 2012, Bowers et al., 2014), which suggests that the method proposed in this study can evaluate the blending process of aged binder accurately.

3.6 Conclusions

In this study, a new procedure was developed using fluorescence microscopy to differentiate between RAP and virgin binders as well as their blends. A new parameter, MGV based on fluorescence image, was utilized to quantitatively determine the mobilization rates of aged asphalt binder in RAP. A "Blending Chart" was generated, showing the change of MGV with RAP binder content. Ultimately, a new method was proposed to quantitatively determine the mobilization rate of aged binder in RAP by directly measuring the MGV of the binder blend. The test procedure is summarized as follows:

(1) Test the MGV of virgin and RAP binder as well as binder blend with varying RAP binder contents to generate a “blending chart” in terms of MGV;

(2) Test the binder blend on the surface of aggregate for its MGV;

(3) Determine the RAP binder content of the binder blend; and

(4) Calculate the mobilization rate.

The sensitivity of MGV to aged binder content was affected by test conditions. One index, Differentiation Factor, was used to measure the sensitivity of MGV to aged binder content. Results indicate that the MGV measured at the wavelength of 450-490 nm and the exposure time of 0.5-1.5 s was most sensitive to aged binder content.

For construction of a blending chart, it was found that there existed a linear relationship between MGV of a binder blend and its RAP binder content, and a quadratic relationship between MGV of a binder blend and its RAS binder content. Therefore, the relationship between MGV and aged binder content of a binder blend could be different for asphalt from diverse sources.

Glass cullet was selected as a special aggregate and added into the mixtures because it has two parallel planes and can be tested by a fluorescence microscope directly. The results indicate that the mobilization rate increased with the increase of mixing time and temperature. It should be noted that the glass cullet used as tracking aggregates may not be able to fully represent the mixing scenario. The shape, size, absorption, surface texture, and other characteristics of aggregates could affect the mobilization rate of aged binder.

Further research is needed to investigate the effects of these factors and to find more suitable tracking materials.

Chapter IV Blending Efficiency Evaluation of Plant Asphalt Mixtures Using Fluorescence Microscopy

A version of this chapter was originally published by Yongjie Ding, Baoshan Huang, and Xiang Shu.

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Yongjie Ding was the principle researcher and author of "Blending efficiency evaluation of plant asphalt mixtures using fluorescence microscopy". Yongjie Ding's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang and Dr. Xiang Shu provided guidance throughout the research process as well as editorial assistance.

4.1 Abstract

With the use of high percentage recycled asphalt pavement (RAP), there is an increasing concern over how much of the aged binder in RAP that can be blended into virgin binder. In this study, a laboratory procedure was proposed based on fluorescence microscopy for quantifying the mobilization rate of aged binder in plant-produced RAP mixtures. This procedure was derived from the mean gray value of an asphalt-coated aggregate particle. A linear blending chart was developed and used to relate aged binder content to the mean gray value of binder blend. The mobilization rate of aged binder was calculated on the basis of surface area proportion of aggregates with different size. Three types of asphalt mixtures, including one warm mix with foaming technology, two hot mixes with or without rejuvenator, were used to validate the proposed method. Results indicated that the mobilization rate varied by aggregate type (virgin or RAP). The mobilization rate of three mixtures show no obvious difference.

4.2 Introduction

With the ever-increasing cost of aggregate and asphalt binder, the incorporation of recycled asphalt pavement (RAP) into asphalt mixtures has become more and more popular (Huang et al., 2010, Shu et al., 2008, Zhao et al., 2012, Zhao et al., 2013a). The use of RAP can produce significantly economic and environmental benefits. RAP has gone through a service life of aging and its binder has become highly stiff and brittle. In the production process, RAP is heated by hot aggregate instead of directly by fire to avoid further ageing. Therefore, the stiff binder on RAP may not be able to flow freely. Lack of a clear understanding of blending efficiency of recycled asphalt has been a major concern in determining the effective asphalt binder in asphalt mixtures containing RAP. The blending efficiency is defined as the percentage of the aged asphalt binder in RAP that can be blended into virgin asphalt binder and thus become available to coat aggregate. If RAP binder is not 100% blended with virgin binder, the effective asphalt content in a mixture would be lower than its design asphalt content and the mixture performance be compromised.

Previous studies (Bowers et al., 2014, Huang et al., 2005, Zhao et al., 2015a, Ding et al., 2016b) have shown that partial blending happened during the mix process of RAP. This conclusion indicates that only part of the aged binder can be utilized to coat the aggregate. Under this situation, the assumption of 100% blending efficiency may result in two problems. First, the coating of virgin aggregate will be too thin to reach the target film thickness. Second, the binder on RAP aggregate will be stiffer than expected, lowering resistance to fatigue and low temperature cracking. Therefore, it is critical to accurately determine blending efficiency of RAP mixtures.

The methods for determining blending efficiency are based on two major categories of asphalt properties: chemical properties and mechanical properties. Mechanical property method involves measuring dynamic modulus (Al-Qadi et al., 2009), binder content (Shirodkar et al., 2011, Bennert and Dongré, 2010), and so on. Chemical property methods use such chemical testing techniques as gel permeation chromatography (GPC) (Zhao et al., 2015a, Bowers et al., 2014, Zhao et al., 2013a, Zhao et al., 2014, Zhao et al., 2015b), Fourier transform infrared (FTIR) (Bowers et al., 2014) and fluorescence microscopy (Navaro et al., 2012) to determine the RAP binder content in a blend of virgin and RAP binders. Among the above-mentioned chemical techniques, GPC and FTIR methods need to extract asphalt binder from aggregate particles to make samples for further testing. Therefore, the heterogeneity of binder on aggregate cannot be determined. In addition, the process of using chemical a chemical solvent to dissolve asphalt binder makes the test time-consuming and complicated. The extraction and recovery process may also affect the accuracy of the test result. Therefore, a new method without tedious binder extraction and recovery is more desirable for determining the blending efficiency of RAP binder. Fluorescence microscopy has the potential to be one of these methods.

The fluorescence microscopy is an optical microscopy that uses the emission of fluorescence to study properties of organic or inorganic substances (Hagemann and Hollerbach, 1986, Khorasani, 1987, Rost, 1995). Fluorescence microscopy has been used for the analysis of oil and petroleum products since the 1980s (Spadafora et al., 1985). Navaro et al. (Navaro et al., 2012) first utilized fluorescence microscopy to investigate the degree of blending between virgin and aged binders. They analyzed fluorescence microscope images using a pair of photographs, taken under white light (WL) and ultraviolet light (UVL) of the same position of a section of compacted recycled asphalt mixtures sample. They then utilized an image processing software to quantify the degree of blending between the virgin and RAP binders. To eliminate the influence of aggregate two masks were used to hide the aggregate from the binder in an image. In the UVL photograph, the aged binder can be distinguished from the virgin binder, as the latter is fluorescent. However, the threshold value to distinguish between mastic and aggregate can only be chosen by experience. There is not a quantified index available to determine whether all the aggregate have been hidden. In addition, the test procedure proposed by Navaro et al. (Navaro et al., 2012) seems too complex to be used in the field.

In this study, a new term, mean gray value, was derived from the image of fluorescence microscopy. Results show that there existed a linear relationship between mean gray value and RAP binder content for binder blends. Aggregate particles coated with asphalt binder can be directly tested by fluorescence microscopy to estimate binder content. There is no need to cut asphalt mixture samples and hide the aggregate like Navaro et al. did (Navaro et al., 2012). Therefore, fluorescence microscopy is potentially a simple, effective and efficient method for determining RAP blending efficiency.

4.3 Objective and Scope

The primary objective of this study was to examine the potential of using fluorescence microscopy to determine the blending efficiency of asphalt mixtures containing RAP. The proposed method directly used mixtures collected from asphalt plant without cutting or dissolving them. A blending chart was first developed to show the relationship between the mean gray value of a mixture sample and the content of aged binder and then employed as a baseline to determine RAP binder content. On the basis of the blending chart, a new method was adopted to determine the RAP binder mobilization rate of a mixture, which considered the proportion of the surface area aggregates with different size. The proposed method was validated with three asphalt mixtures, including one warm mix with foaming technology, two hot mixes with or without rejuvenator.

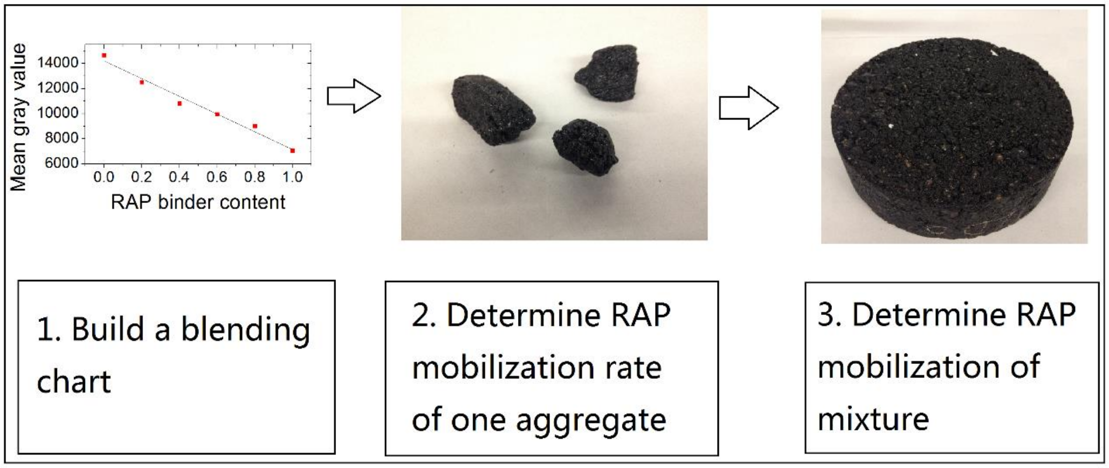


Figure 4.1 The main steps of the test method

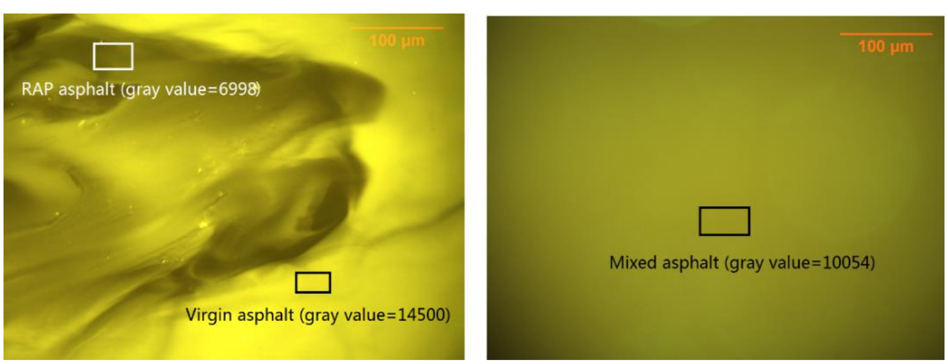
4.4 Methodology

The proposed fluorescence microscopy method for determining blending efficiency of RAP mixtures is based on the differences in fluorescence between virgin and RAP binders. The procedure of this method includes three steps as shown in Figure 4.1.

4.4.1 Building A Blending Chart in Terms of Mean Gray Value

Since the fluorescent effect of a material is inherently related to its chemical composition and structure, the different components of asphalt show different fluorescence, especially for virgin and aged binders (Khorasani, 1987). Fluorescence in asphalt molecules is essentially related to electronic excitation of the conjugated π-systems (aromatic components) and of C=O groups (Khorasani, 1987, Zhang et al., 2013, Mills and White, 2012, Stasiuk and Snowdon, 1997, Dennis et al., 2012). For the two-component asphalt system (asphaltenes and maltenes), asphaltenes produce little to no emissions, but maltenes exhibit strong fluorescence in the observed spectral region (Handle et al., 2016). For the four-component asphalt system (saturates, aromatics, resins and asphaltenes, i.e., SARA), aromatics and resins are the only components capable of sufficiently intense fluorescent emission (Handle et al., 2016). Research also indicates that as asphalt binder ages, its fluorescence emission intensity decreases (Grossegger et al., 2017). It is generally believed that the decrease in fluorescence emission during aging is due to the conversion of resins into asphaltenes. Therefore, fluorescence intensity can be used to distinguish between virgin and aged asphalt binders.

Figure 4.2 shows the blending process between virgin and RAP binders in fluorescence images. RAP binder was extracted and recovered according to AASHTO T 319 Method (AASHTO, 2010b). The fluorescence pictures were taken immediately and 5 minutes after RAP binder was placed on a virgin asphalt at 150 ℃ under a fluorescence microscope. It can be seen that virgin binder showed a higher fluorescence strength than RAP binder. It is noted that the gray value of the mixed binder was in the middle of the virgin and RAP binder, indicating that gray value can be used to quantify the blending between virgin and RAP binders.



Before mixing (b) After heating 5 mins

Figure 4.2 RAP and virgin binders under fluorescence microscopy

Because virgin and RAP binders showed different fluorescence strength, the fluorescence strength of an asphalt mixture, depending on its asphalt blend of both virgin and aged binders, would vary with the percentage of aged RAP binder content in the asphalt blend. Since RAP binder showed a lower fluorescence strength than virgin binder, it is expected that the fluorescence of an asphalt blend would decrease with the increase in RAP content. To determine the blending efficiency of a RAP mixture, a blending chart has to be first built to showing the relationship between fluorescence of asphalt blend and RAP binder content. In this study, an index, mean gray value, which represents the average fluorescence strength of a fluorescence image (0.5 mm × 0.6 mm) and was derived from image processing, was used to distinguish between asphalt blends with RAP binder contents. The fluorescent strength of asphalt blends with varying RAP binder content (0~100%) was measured and used to build the blending chart (shown in the first step of Figure 1). With the blending chart, the RAP binder content of an asphalt blend could be determined according to its fluorescent strength, i.e., mean gray value.

4.4.2 Determination of RAP Binder Mobilization Rate of One Aggregate

The mobilization rate of RAP binder can be calculated based on the RAP binder content from the first step. A series of equations have been derived by Zhao et al. (Zhao et al., 2015a) to quantitatively determine the mobilization rate of RAP binder through the RAP binder content in the blend. The mobilization rate of RAP binder was defined as the percentage of RAP binder that can be mobilized, peeled off RAP aggregate and blended with virgin aggregate as shown in Equation 4.1 (Zhao et al., 2015a). The mobilization of RAP binder is due to the mechanical mixing of RAP with virgin aggregate and the dissolving effect of virgin asphalt.

$$W_{(mobilized\ RAP\ binder)} = P_{(b,RAP)} * Mobilization\ rate \tag{4.1}$$

The RAP binder content RAP binder $(\%)_{blend}$ can be expressed as the mobilization rate as shown in Equation 4.2.

$$\text{RAP binder } (\%)_{blend} = \frac{W_{(mobilized\ RAP\ binder)}}{W_{(mobilized\ RAP\ binder)} + W_{(virgin\ biner)}} = \frac{P_{(b,RAP)} * Mobilization\ rate}{P_{(b,RAP)} * Mobilization\ rate + P_{(b,virgin)}} \tag{4.2}$$

where, W = the weight of binder, $P_{(b,\ RAP)}$ = the percentage of RAP binder by total mixture, and $P_{(b,\ virgin)}$ = the percentage of virgin binder by total mixture.

Then the mobilization rate of RAP binder can be derived from Equation 4.2 and shown in Equation 4.3.

$$\text{Mobilizaation rate} = \frac{P_{(b,virgin)} * RAP\ binder\ (\%)_{blend}}{P_{(b,RAP)} * (1 - RAP\ binder\ (\%)_{blend})} \tag{4.3}$$

The determination of RAP binder $(\%)_{blend}$ is a key step to obtain the mobilization rate. However, it should be noted that, RAP binder $(\%)_{blend}$ used in this method was only the value of one aggregate by testing its fluorescence strength. The fluorescence of aggregate here means the fluorescence of asphalt coating this aggregate. The fluorescence was only from asphalt, so the fluorescence of aggregate was not included in this study. It is expected that the value of RAP binder $(\%)_{blend}$ would not be a constant number for difference aggregate sizes, especially for RAP and virgin aggregates. As shown in Figure 4.3, a RAP aggregate particle would show a higher RAP binder content than a virgin aggregate if not all the aged RAP binder is mobilized and peeled off RAP aggregate. Therefore, the mobilization rate would be higher for RAP and lower for virgin aggregate. A method is needed to determine the RAP binder mobilization rate of a mixture consisting of different aggregates.

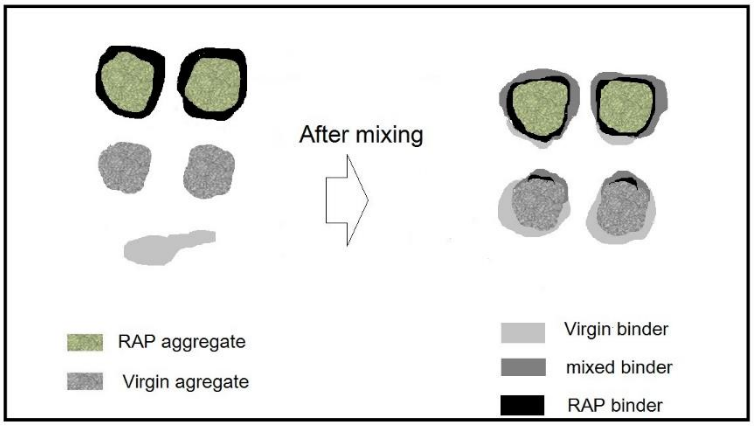


Figure 4.3 The instance of partial asphalt blending in mixture containing RAP

4.4.3 RAP Binder Mobilization of A Mixture

In order to obtain an accurate overall blending efficiency for a RAP mixture, different aggregate sizes need to be taken into account. In this study, the overall mobilization rate of a mixture could be obtained based on the surface area proportions of aggregates with different sizes, such as large and small aggregates. The use of aggregate surface area instead of aggregate weight was due to the fact that surface area is directly related to the asphalt film around aggregate particles. The mobilization rate of large and small aggregates was measured separately first, then the overall mobilization rate of a mixture could be calculated according to Equation 4.4.

$$Mobilization\ rate = Mobilization\ rate_{large\ aggregate} \times Surface\ area\ percentage_{large\ aggregate} + Mobilization\ rate_{small\ aggregate} \times Surface\ area\ percentage_{small\ aggregate} \quad (4.4)$$

4.5 Experimental Program

4.5.1 Material

4.5.1.1 Asphalt Mixtures

The mixtures were produced in an asphalt plant in three different ways, including hot mix with rejuvenator, hot mix without rejuvenator, and warm mix with foaming technology. The rejuvenator content was 0.4 % by weight of asphalt binder. During the production process, the rejuvenator was first added into virgin binder and then mixed with aggregates. The mixing temperatures for warm mix and hot mix were 145 °C and 155 °C, respectively. After production, the mixtures were stocked in a silo for another two hours.

One performance grade asphalt binder PG 64-22 was used in all three mixtures. The Marshall mix design procedure was employed to design mixture. The asphalt content was 4.5% for all three mixtures, with 2.19% coming from virgin binder and 2.31% from RAP binder.

4.5.1.2 Aggregate Gradation

The same aggregate gradation was used for all three mixtures and is presented in Table 4.1. The virgin aggregates consisted of # 5, # 7 and # 10 stones and natural sands. RAP was processed and then sieved as RAP passing ¾" and 5/16". RAP content was 50% for all three mixtures and its asphalt content was 4.61%.

Table 4.1 Gradation of the aggregates used in the mixtures

Sieve Size	Percentage Passing						
	# 5	# 7	# 10	Natural Sand	RAP Processed		Total
					Passing 3/4	Passing 5/16	
1.25"	100	100	100	100	100	100	100
3/4"	56	100	100	100	100	100	91
3/8"	8	54	100	100	68	100	71
No.4	2	5	86	95	35	95	56
No.8	1	3	56	82	22	72	40
No.30	0	0	23	50	14	37	21
No.50	0	0	16	28	10	27	14
No.100	0	0	12	12.7	6	20	9.6
No.200	0	0	9.5	4.6	4	13.5	6.3
Total	20	5	15	10	25	25	100

For the calculation of mobilization rate, the aggregate of the mixture could be divided into two aggregate sizes as shown in Figure 4.4. The large aggregate was the portion of aggregate retained on ¾" sieve, and the rest was small aggregate. The mobilization rate of virgin aggregate could be determined from large aggregate because large aggregate was 100% virgin aggregate (Figure 4.4). The surface area was be 28.4 ft^2/lb for small aggregate /lb and 2 ft^2/lb for large aggregate (Ishai and Craus, 1977). The surface area proportions were 0.006 and 0.994 for large and small aggregates, respectively.

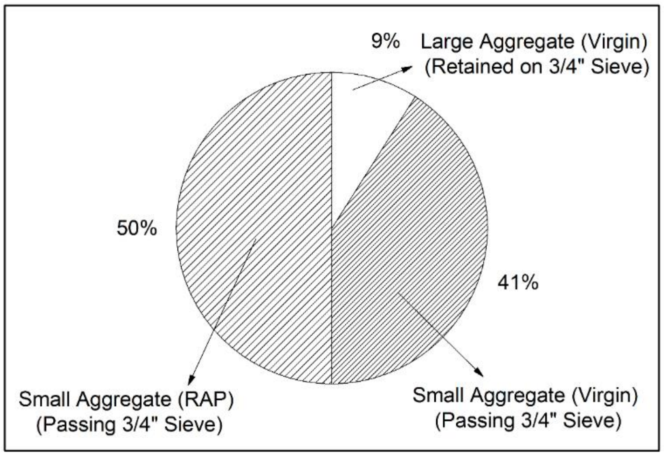


Figure 4.4 Proportions of large and small aggregates by mass

4.5.2 Procedure for Determining Blending Efficiency

4.5.2.1 Preparation of Blending Chart

RAP was first dissolved in trichloroethylene (TCE) and recovered according to the AASHTO T 319 method (AASHTO, 2010b). The recovered RAP binder was then mixed with a virgin binder at different RAP contents. The blend of virgin and RAP binder was heated to 155 °C and stirred for 5 minutes, then kept in oven (155 °C) for another 2 hours to simulate the plant production process and also to make a homogeneous blend. The asphalt blend was spread on a microscope slide and tested with a fluorescence microscope.

4.5.2.2 Aggregate Selection

Individual asphalt-coated aggregate particle was used as a test sample in the study. It is assumed that the particle is coated with a film of homogeneous asphalt binder. Two aggregate sizes were considered: large aggregate (aggregate retained on the ¾” sieve) large aggregate) and small aggregate (those passing the ¾” sieve). For each aggregate size, 20 aggregate particles were randomly selected as test samples.

4.5.2.3 Test by Fluorescence Microscopy

Aggregate particles were placed under a fluorescence microscope and observed directly as shown in Figure 4.5. In order to test the fluorescence strength of the samples under the same condition, the samples need to have a relatively flat surface that is larger than 1 mm^2 and can be placed at a constant distance parallel to the camera lens. In this study, a distance of 2 mm was used. The test was performed with a Nikon Y-IDP 9 fluorescence microscope at 20 times magnification. The wavelength of excitation light was 450-490 nm. The mean gray value was obtained by post-processing of the fluorescence images. One example of the determination of the gray value is shown in Figure 4.2. An area of the image was selected and then the mean gray value of the area can be calculated using software ImageJ.

One concern about fluorescence microscopy test is that the rough surface of aggregate causes negative effects to the measurements of mean gray value. To eliminate this concern, two batches of samples, glass cullet and common aggregate coated with the same binder, were tested by fluorescence microscopy under the same condition. The results are shown in Figure 4.6. A one-way ANOVA test was performed on the data and a significant coefficient of 0.525 was obtained with a confidence interval of 0.95, meaning that no significant difference was found between the samples of glass cullet and common aggregate. Therefore, aggregate samples could be observed directly under a fluorescence microscope to obtain reasonable gray value.

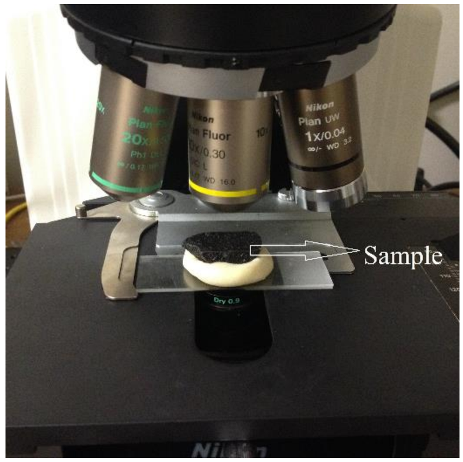


Figure 4.5 Aggregate tested by fluorescence microscopy

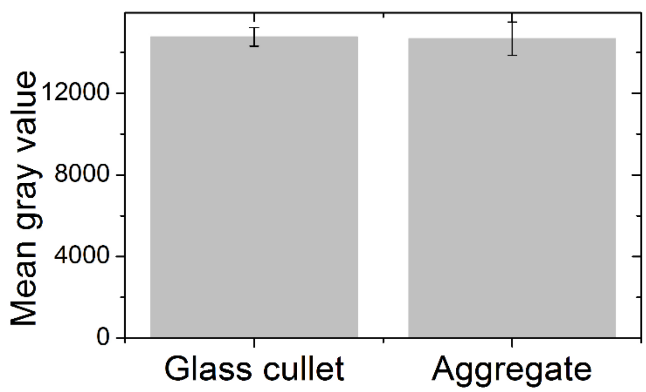


Figure 4.6 Mean gray values of asphalt samples on glass cullet and aggregate

4.6 Results and Discussion

4.6.1 Blending Chart in Terms of Mean Gray Value

A blending chart was first developed in terms of mean gray value of asphalt samples to show the relationship between mean gray value of asphalt samples and RAP content and used as a baseline for determining the blending efficiency of an asphalt mixture. To build this blending chart, asphalt samples with RAP contents ranging from 0 to 100% with an increment of 20% were tested for their mean gray values.

Figure 4.7 shows the blending chart of virgin-RAP blend. It can be seen that the mean gray value of asphalt decreased with the increasing RAP content and a linear regression equation, Equation 4.5, could be used to fit the relationship very well (R^2=0.97). Therefore, Equation 5 could be used to calculate RAP Binder $(\%)_{Blend}$ if the mean gray value was obtained for an asphalt sample with an unknown RAP content. Then the mobilization rate can be expressed by mean gray value as shown in Equation 4.6.

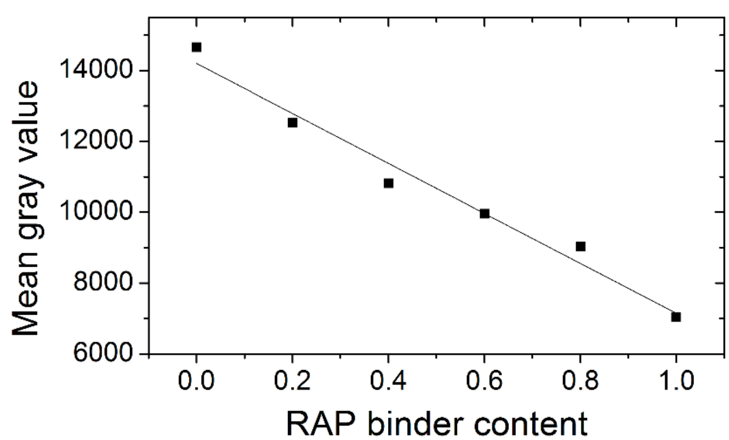


Figure 4.7 blending chart generated with mean gray value

$$\text{Mean Grey Value} = -7058 * \text{RAP Binder}(\%)_{\text{Blend}} + 14198 \quad (4.5)$$

$$\alpha_M = \frac{P_{(b,virgin)} * (14198 - Mean\ Gray\ Value)}{P_{(b,RAP)} * (Mean\ Gray\ Value - 7140)} \quad (4.6)$$

4.6.2 Blending Efficiency Results

Figure 4.8 and 4.9 show the mean gray value and the mobilization rates of single aggregate in different asphalt mixtures. As expected, the ranking of the mobilization rate is consistent with that of mean gray value for the mixtures. The mobilization rate of three mixtures show no obvious differences. At the same time, it is noted that large and small aggregates showed different mobilization rates with large aggregates. The reason for the different mobilization rate is because of the high RAP aggregate content of small aggregate. It can be predicted that the mobilization rate of RAP aggregate was higher than virgin aggregate in this research, because the mobilization rate of virgin aggregate could be determined from large aggregate and the higher mobilization rate of small aggregate was the combination of virgin and RAP aggregate.

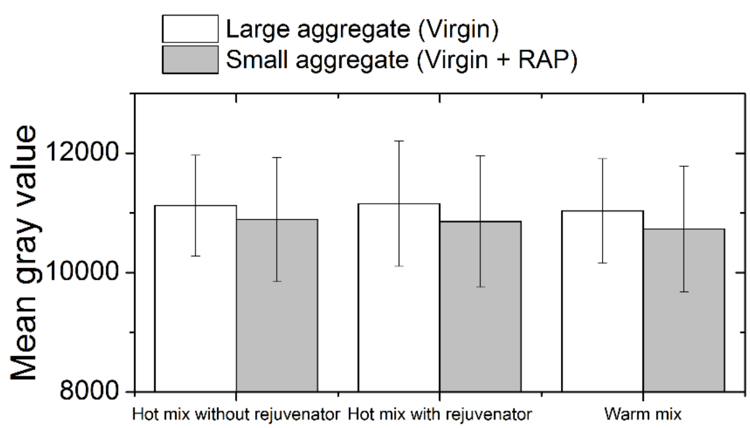


Figure 4.8 Mean gray values for different mixing conditions

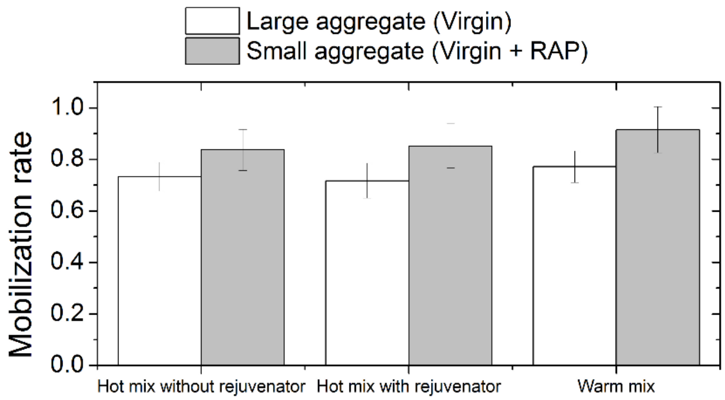


Figure 4.9 Mobilization Rate for different mixing conditions

The overall mobilization rate of a mixture could be obtained based on the surface area proportion of large and small aggregate. The surface area proportion calculated according to Equation 4.7 was 0.006: 0.994, so the overall mobilization rate of a mixture could be calculated according to Equation 4.8. Figure 4.10 shows the overall mobilization rates of the mixtures. It can be seen that the overall mobilization rate of a mixture determined according to this method was close to small aggregates because of low proportion of large aggregate.

$$Surface\ area\ proportion_{large\ aggregate} = \frac{Weight\ proportion_{large\ aggregate} \times Surface\ area_{large\ aggregate}}{Surface\ area_{total\ mixture}} \tag{4.7}$$

$$Mobilization\ rate = Mobilization\ rate_{large\ aggregate} \times 0.006 + Mobilization\ rate_{small\ aggregate} \times 0.994 \tag{4.8}$$

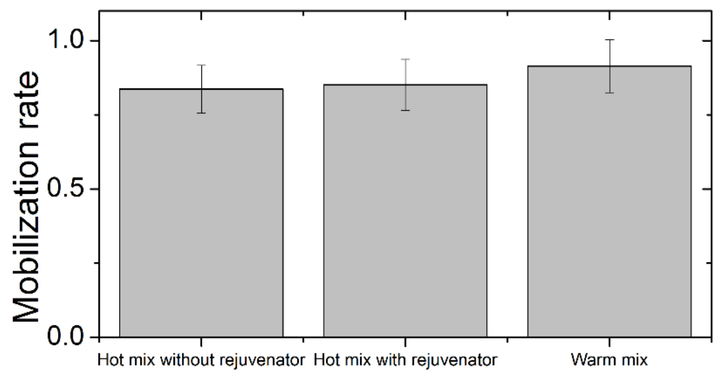


Figure 4.10 Overall mobilization rates of the mixtures

4.7 Conclusions

A method was proposed to determine the mobilization rate of RAP asphalt mixtures using fluorescence microscopy. The mobilization rate was defined as the proportion of RAP binder that can be mobilized to the surface of aggregate. This method was based on the difference in fluorescence strength of virgin and RAP binders under fluorescence microscopy. A blending chart was developed to show the relationship between mean gray value of fluorescence image and RAP content and used as a baseline against which blending efficiency can be determined. To validate the proposed method, three plant-produced asphalt mixtures were tested for their blending efficiency, which included a hot mix with rejuvenator, a hot mix without rejuvenator, and a warm mix with foaming technology. Based on the study, the following conclusions can be drawn:

(1) A method was developed and validated to be effective for determining blending efficiency of RAP asphalt mixtures using fluorescence microscopy.

(2) The mean gray value of fluorescence image could be used to determine the mobilization rate of RAP mixtures. There existed a linear relationship between mean gray value of asphalt blend and RAP content.

(3) The mobilization rates were different for large and small aggregates because of different RAP contents. The overall mobilization rate of a mixture could be determined by considering the surface area of large and small aggregate.

(4) The mobilization rate of three mixtures show no obvious difference.

Chapter V Use of Molecular Dynamics to Investigate Diffusion Between Virgin and Aged Asphalt Binders

A version of this chapter was originally published by Yongjie Ding, Baoshan Huang, Xiang Shu and Mark Woods:

Yongjie Ding, Baoshan Huang, Xiang Shu and Mark Woods. Use of molecular dynamics to investigate diffusion between virgin and aged asphalt binders. Fuel, 2016

Yongjie Ding was the principle researcher and author of "Use of molecular dynamics to investigate diffusion between virgin and aged asphalt binders". Yongjie Ding's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang, Dr. Xiang Shu and Mark Woods provided guidance throughout the research process as well as editorial assistance.

5.1 Abstract

The incorporation of recycled (aged) binder into virgin asphalt has become more popular in asphalt paving industry nowadays. However, the exact mechanism of the diffusion process between virgin and aged binders is still largely unclear. This paper presents a study in which molecular dynamics (MD) simulation was employed to investigate the diffusion between virgin and aged binders. Two asphaltic models with three components including asphaltenes, resin, and oil were built with different components ratio. The model of aged binder was constructed by increasing the asphaltenes ratio on the basis of virgin binder. The results of simulation was verified by GPC and both show that the diffusion of large molecules in asphalt was a critical factor for the diffusion of binders in that it was more susceptible to the changes of temperature. In an inter-diffusion model of virgin and aged binders, the diffusion coefficients of binders were not only determined by the diffusion ability itself, but also influenced by the properties of the diffusion acceptor. Based on this finding, the effect of different sequence of adding rejuvenator during recycling of asphalt mixtures was investigated. The result shows that adding rejuvenator into aged binder first

could accelerate the inter-diffusion rate between virgin and aged binder in maximum level, thus increased the efficiency of recycling.

5.2 Introduction

Asphalt binders act as thermoplastic adhesives for the aggregates in pavement structures. Historically people have been treating the binder as a homogeneous "glue" within the binder-aggregate composite. Recently, the use of aged binders including recycled asphalt pavement (RAP) and recycled asphalt shingles (RAS) has become more and more popular, due to environmental and economic concerns. The incorporation of aged or highly aged (such as binder from RAS) asphalt binder into asphalt paving mixtures has raised main questions. There have been concerns over the overall mixture performance with the inclusion of recycled asphalt (Daniel and Lachance, 2005, Huang et al., 2005, Shu et al., 2008, Zhao et al., 2012, Huang et al., 2006) as well as the blending efficiency between virgin and aged binders (Zhao, 2014, Bowers, 2013). When RAP/RAS is recycled into asphalt mixtures, one key question is how much of the aged binder in RAP/RAS can be blended into virgin binder. There are three assumptions about the blending situation between virgin and aged binders. The first one is that the aged binder is expected to attain enough workability to blend with virgin binder so as to coat both the virgin and recycled aggregates as a homogeneous film. The second assumption is the "Black rock" theory that is based on the premise that the RAP/RAS may actually perform as nothing more than an aggregate. The third assumption is that partial blending happening between virgin and aged binders. This assumption was supported by many researchers and studies show that most of mixing samples belong to this category (Huang et al., 2005, Bowers, 2013, Bowers et al., 2014, Zhao, 2014, Zhao et al., 2013a, Zhao et al., 2012). A further analysis into the blending between the aged and virgin binder reveals that even though the binders may be "blended" together, they may still retain their original microstructures and behave as heterogeneous composite, rather than a homogeneous new binder. Nahar et al. (Nahar et al., 2013b) and Zhao et al. (Zhao et al., 2015c) investigated the microstructures between aged binder from RAP (Nahar et al., 2013b) and RAS (Zhao et al., 2015c) and the virgin asphalt and concluded that there existed a "blending" zone in which the aged and virgin binders started to co-mingle and formed a homogeneous new binder. However, the governing mechanism(s) of blending at the molecular level has not been well instigated.

The blending between virgin and aged binders can be defined as an inter-diffusion process, in which virgin and aged binder diffuse into each other and become homogeneous at molecular level (shown in Figure 5.1). The diffusion rate of binders varies under different mixing conditions and thus results in diverse degrees of blending at molecular level. Due to the complicated chemical structures of binders and the influencing factors, the mechanism of the diffusion process is difficult to quantify. Therefore, it is still difficult to design an optimized procedure that can maximize the true blending with the proper mixing conditions and addition of additives (such as rejuvenating agents). A better understanding of the asphalt binder diffusion process and correctly quantify the influencing factors will help better utilizing the recycled asphalt materials without compromising the performance of asphalt pavements.

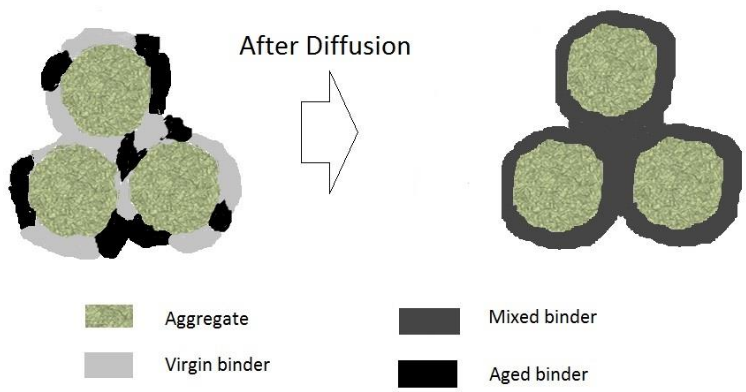


Figure 5.1 Diffusion process between virgin and aged binders

The main objective of this study was to use molecular dynamics (MD) simulation as a tool to simulate the diffusion of virgin and aged binders and investigate the approaches that can accelerate the diffusion rate. Gel permeation chromatography (GPC) was considered to validate the MD model constructed in this study. Utilizing the validated MD model, the molecular diffusion between virgin and aged binder was quantified and the effects on the sequence of adding rejuvenator during asphalt recycling was investigated.

5.3 Molecular Diffusion of Asphalt Binders

The diffusion process investigated in this study refers to the binder homogenization after virgin and aged binders have contacted to each other. The earlier studies of asphalt diffusion were conducted to evaluate the penetration of rejuvenators into the asphalt (Oliver, 1974, Carpenter and Wolosick, 1980, Noureldin and Wood, 1987, Karlsson and Isacsson, 2003). The virgin-aged binder diffusion was brought to the attention of researchers in recent years due to the increased use of recycled materials (Karlsson et al., 2007, Rad, 2013a, Kriz et al., 2014). Karlsson et al. (Karlsson et al., 2007) used dynamic shear rheometer (DSR) with parallel plates to monitor the diffusion of a soft bitumen (rejuvenator) into a stiff one at 60, 80 and 100 ºC. The diffusion coefficients determined were compared with the corresponding diffusion coefficients obtained from FTIR-ATR. The comparison showed that the rate of diffusion detected by the DSR are of the same magnitude, but somewhat higher than the ones detected by FTIR-ATR. Zhao et al. (Zhao et al., 2014) conducted an analysis of diffusion for RAP and RAS mixtures through staged extraction method. The extracted binder was subjected to GPC to obtain large molecule size percentage (LMS %) for further analysis. The results indicate that a relatively complete diffusion process could be achieved at 155ºC within 15 minutes and 125ºC within an hour in RAP mix. The RAS-virgin binder diffusion is found to be in a very slow rate. The finding suggested that the binder homogeneity caused by molecular diffusion could potentially be an issue for RAS mixtures.

5.4 MD Simulation

5.4.1. Background on Molecular Simulation

MD simulation means using statistical mechanics-based theoretical methods and computational techniques to model or mimic the behavior of molecules under different conditions (Allen and Tildesley, 1989, Frenkel and Smit, 2001). In MD simulation, a model is constructed to represent a molecule and then the atoms within the molecule are assigned a force field that is consistent with. The function of force field is to determine the potential energy of the molecules. The properties of molecular models can be simulated by using a system of coupled nonlinear partial differential equations that are based on Newtonian mechanics. The interactions among molecules are determined by the force field used. In MD simulation, the properties of molecular model such as energy density and diffusion coefficient can be determined at any given point in time.

MD simulation has been commonly used to model the diffusion behavior in polymer molecules. Torres (Torres et al., 2000) applied molecular simulation to investigate the properties of ultrathin polymeric films near the glass transition and showed that the diffusion coefficient of ultrathin polymeric films depends on the dimensions of the system. Charati (Charati and Stern, 1998) calculated the diffusion coefficients of He, O_2, N_2, CO_2, and CH_4 at 300 K in four silicone polymers by MD simulations. The estimated diffusion coefficients are found decreasing with the increasing size of the polymer side chains and of the penetrant molecules. Krishna Pant carried out a simulation of diffusion of a small-molecule penetrant in an amorphous polymer matrix for the examples of methane in polyethylene (PE) and methane in polyisobutylene (PIB). The results are in accord with the available experimental data (Pant and Boyd, 1993).

The use of molecular simulation to understand the behavior of asphalt binders is still limited. Zhang (Zhang and Greenfield, 2007a, Zhang and Greenfield, 2007b) used MD simulation to calculate rotational relaxation time, diffusion coefficient, and zero-shear viscosity for a model asphalt system over a temperature range of 298–443 K. Two three-component systems are taken as simple computational models of asphalt. In a follow-up work, Zhang (Zhang and Greenfield, 2008) investigated the physical properties and microstructures of computational model asphalts using MD simulations in an all-atom framework. A new asphalt model was proposed that is targeted toward asphalt AAA-1 of the Strategic Highway Research Program (SHRP) based on elemental composition and speciation. The density and thermal expansion coefficient matches better with experimental data than the predictions using earlier model asphalts. Bhasin et al. (Bhasin et al., 2010) employed MD simulation to investigate the correlation of chain length and chain branching to self-diffusivity of binder molecules. The findings based on molecular simulations are consistent with the experimental data. The results demonstrate a good correlation between the chain length and branching to the healing characteristics of different asphalt binders.

5.4.2 MD Simulation Methodology

One commercial software Material Studio was used for simulation in this research. The first step of conducting molecular simulations is to build molecular model. An ensemble of three different types of molecules, each representing one component of asphalt binders (asphaltenes, resin, and oil) was used as asphalt model. This approach followed the method used by Zhang (Zhang and Greenfield, 2007a, Zhang and Greenfield, 2007b, Zhang and Greenfield, 2008). A structure for the asphaltenes molecule that was originally proposed by Groenzin and Mullins (Groenzin and Mullins, 2000) was adopted in this research. The n-C_{22} and 1, 7-dimethylnapthalene molecules were used to represent resin and oil separately. The chemical structures of three components is shown in Figure 2. The weight proportion of asphaltenes, resin, and oil for virgin and aged binder was selected as approximately 20-20-60 and 40-20-40, respectively. The concentrations of n-C22 and 1, 7-dimethylnapthalene were chosen based on the alkane: aromatic carbon ratio (72.2:27.8) reported by storm et al. (Storm et al., 1994) for the oil components, thus treating 1, 7-dimethylnapthalene as combing aspects of oil and resin categories. This led to mixtures with 60wt% n-C_{22} and 20wt% 1, 7-dimethylnapthalene. According to dispersed polar fluid model, the cause of mechanical properties difference between virgin and aged binders is the increased of polar components led to more intramolecular structure and the molecular size. Therefore, the strategy of building aged binder model is to increase the content of polar and large molecular components which is asphaltenes in this research. The numbers of molecules in the asphalt model were shown in Table1.

One of strategy of designing rejuvenator is to improve the balance of chemical fractions of aged binders (Boyer and Engineer, 2000). In this research, the chemical difference between virgin and aged binders included the molecular size and the ratio of aromatic carbon. Ethyltetralin (shown in Figure 5.2) was chosen as rejuvenator because of its low molecular size and medium aromatic carbon ratio that in the middle of n-C_{22} and 1, 7-dimethylnapthalene. The low molecular size could increase the diffusion ability of asphalt model; and the medium aromatic ratio could make ethyltetralin be easily dissolved into asphalt binder. Rejuvenator was added into asphalt in two different sequences: adding into virgin binder first and adding into aged binder first. In order to magnify the effect of rejuvenator, the rejuvenator content was chosen as 10% of binder weight which was higher than in actual situation. The increase of diffusion coefficient of asphalt model caused by the adding of rejuvenator was calculated and the influence of different application sequence was investigated.

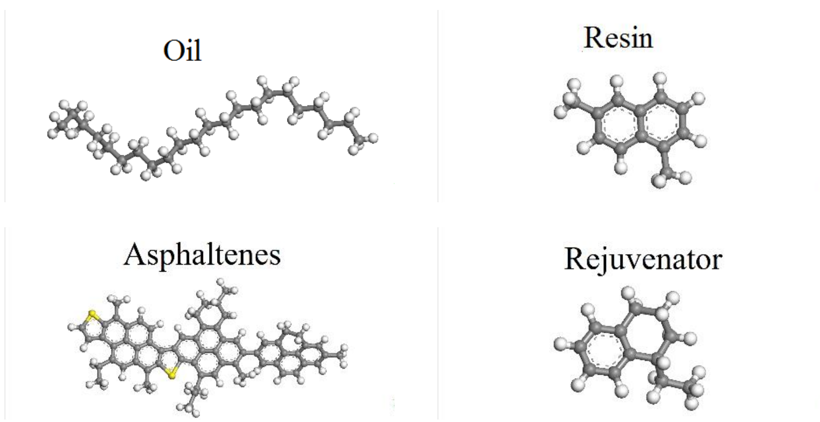


Figure 5.2 Molecular structure of asphaltic components and rejuvenator

Table 5.1 Number of molecules and target density of models

Models	Number of molecules				Target density
	Asphaltenes	Resin	Oil	Rejuvenators	
Virgin binder	3	18	24	0	0.85
Aged binder	6	18	18	0	0.95
Virgin binder + Rejuvenator	3	18	24	18	0.83
Aged binder + Rejuvenator	6	18	18	18	0.91

The second step of the simulation was to determine the target density. The asphalt model was constructed on the basis of the assumed weight proportions of each constituent with a target total molecular weight of 13000 Dalton per cell. The MD simulation with NPT (constant temperature, constant pressure) ensemble was used for 100 ps and then run an anneal with 300K-500 K for 5 cycles. Then this configuration was further refined by using MD simulation for another 100 ps with NPT ensemble. The density of the last frame was chosen as the target density which is shown in Table 5.1.

The models of virgin and aged binder were built with target density using amorphous cell tool. All the models were built with the same width and length for the convenience of layer model construction. The model ran a MD simulation with NVT (constant temperature, constant volume) ensemble for 100 ps and then an anneal with 300-500 K for 5 cycles. Then the model was run another MD simulation with NVT ensemble for 100 ps. The mean square displacement of last 100 ps was chosen to calculate the diffusion coefficient.

The single models of virgin and aged asphalt were assembled together in z axis to form a layer model (shown in Figure 5.3) that could simulate the inter-diffusion behavior between virgin and aged binders. If one part of the layer is taken as the subject of the inter-molecular, the other part on the opposite side can be addressed as the acceptor. It should be noted that, there was a thin vacuum between virgin and aged binders. Therefore, the diffusion process of the binder in layer model was separated into two stages based on diffusion time: Layer model stages I (0-100 ps) and Layer model stage II (100-200 ps). The molecules diffused across the vacuum in Layer model stage I; and the inter-diffusion process mainly existed in Layer model stage II.

An explicit atom representation of each molecule was used in the simulations. The COMPASS force field was selected. Periodic boundary conditions were used in all simulations. The time step equaled to 0.5 fs. With the time step of 0.5 fs, the standard deviation of total energy was much lower than potential energy and kinetic energy, which means the time step was smaller enough. In addition, one simulation with time step of 0.5 fs can be finished in our workstation (Thinkpad W530) within the tolerance time which is several hours. Therefore, time step of 0.5 fs was chosen in this research. The nose method was used to maintain a constant temperature. The cut-off distance for interaction was always 1.2 nm.

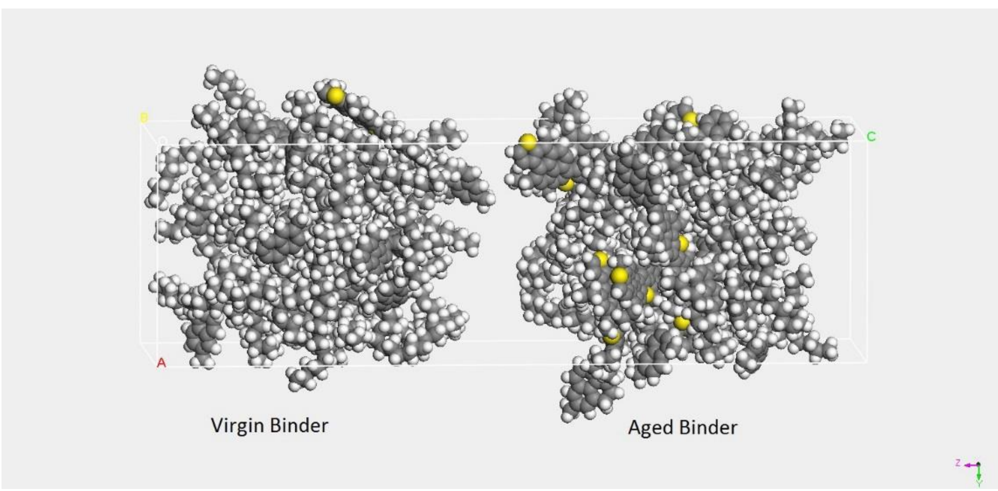


Figure 5.3 Layer model of virgin and aged binder

5.5 Results of Simulation and Validation By GPC

5.5.1 Results of Simulation

In order to verify the model, two parameters were calculated using MD simulation and then compared with the GPC results. The first one was the variation of diffusion rate with molecular weight in single model (shown in Figure 5.4) which indicates that an increase in the molecular weight resulted in an increase in the diffusion coefficient. The second parameter was the influence of temperature on the diffusion of different components in layer model. The timescale for molecular simulation is ps (1ps=10^{-12} s) and is far smaller than the real mixing process. Besides, virgin and aged binder can only contact on one side in the layer model and the difference of aged binder ratio cannot affect the diffusion process. Due to these limitations, only the influence of temperature on the diffusion can be compared with the mixing progress in reality and therefore was investigated in this research.

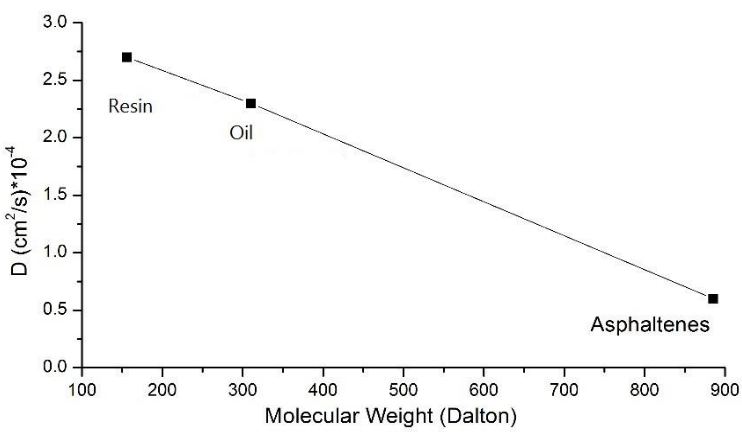


Figure 5.4 Relation between molecular weight and diffusion coefficient at 170 ºC

The diffusion rate of one molecule includes Brownian motion and the unilateral movement caused by concentration gradient. In order to compare with the data of GPC, only the unilateral movement in the layer model were collected using density method. The density distribution (shown in Figure 5.5) of components in z axis at the ending time was collected to calculate the concentration at virgin binder region using Equation 5.1.

$$Components\ percentages = \frac{\left(\frac{A_v}{A_W}\right) \times M_c}{M_v} \tag{5.1}$$

Where, A_v -Area of density curve at virgin binder region (0-50 Angstrom), A_w-Area of the whole density curve. M_c-whole molecular weight of components, M_{v}-molecular weight at virgin binder region (0-50 Angstrom).

Then the density of particular area at the ending of the diffusion process was collected. Figure 5.5 presents the density distribution of components. CV was utilized to measure the variation of components percentage with the mixing conditions. A large CV means that the molecules in this molecular size intervals were more susceptible to the changes of mixing conditions. The changes of components' percentages with temperatures in virgin binder area (shown in Figure 5.6) indicate that the CV of large molecules was obvious higher than the others, which suggests that the diffusion of asphaltenes was more sensitive to temperature.

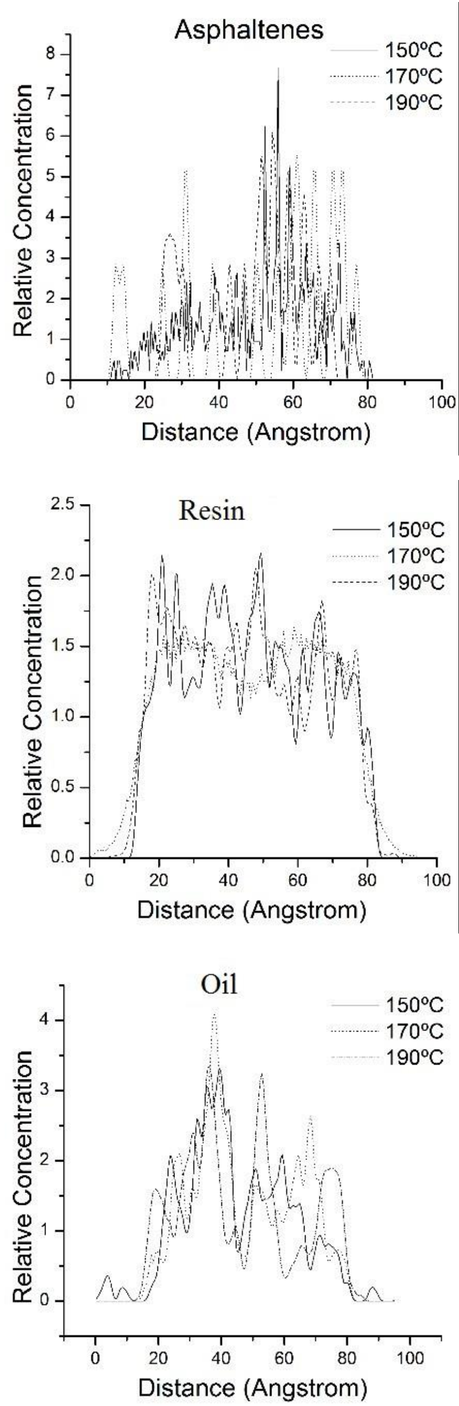


Figure 5.5 Components concentration distribution along z axis

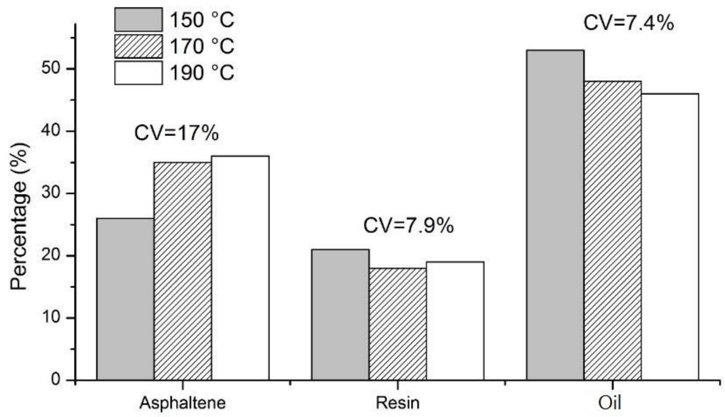


Figure 5.6 Relation between mixing temperature and percentage of different component

5.5.2 Validation by GPC Test

Asphalt binders are composed of molecules with different molecular shape and size. Therefore, the diffusion rates of molecules can be indirectly collected by the molecular size distribution (MSD) of the binders before and after diffusion process. GPC as a test method is mainly used to determine the molecular size distribution (MSD) of materials. Usually, the GPC curves were divided into three parts, including large molecular size (LMS), medium molecular size (MMS) and small molecular size (SMS) (Terrenzio et al., 1997).

The GPC data used in this research are quoted form the study conducted by Zhao et al (Zhao et al., 2013a). In this research, aggregates of three different sizes (large, medium and small) were designed to be mixed with RAS and virgin binder to make mixtures. The small aggregates were pre-blended with RAS as mixing carriers. The three different types of aggregates were separated after mixing was complete, and the binders on the aggregates were tested by GPC. RAS content and mixing time and temperature were considered as three parameters that affect the binder blending efficiency. The detail of the mixing process, mixing time and RAS content variation can be find in the published paper by Zhao et al. (Zhao et al., 2013a). The mixing temperatures used in this research were 150 ºC, 170 ºC and 190 ºC, separately.

The GPC data of binders from medium aggregates was selected for analysis. The GPC curves of binders were separated into three parts based on molecular weight distribution (shown in Table 5.2 (Daly et al., 2013)). The simulation results show that the diffusion rates are different for molecules with various molecular sizes. Figure 5.7 presents the GPC results of mixed binders under conditions with and without diffusion effect. The binder without diffusion effect was produced by simply mixing RAS and virgin binders together and dissolved to be homogeneous; and the sample with diffusion effect was dissolved from one of the medium aggregates of the mixtures in the blending efficiency study mentioned above and with the same LMS% as the binder without diffusion effect. It can be seen that the MMS% and SMS% were different between two binders even though they had the same LMS%, which indicates that the diffusion rates were different for molecules with various molecular size and agreed with the simulation results.

Table 5.2 Molecular size threshold (Daly et al., 2013)

Name	Molecular Weight Intervals (Daltons)	Elution Time (Minutes)
LMS	>3000	7.02-9.928
MMS	1000-3000	9.928-10.56
SMS	200-1000	10.56-11.275

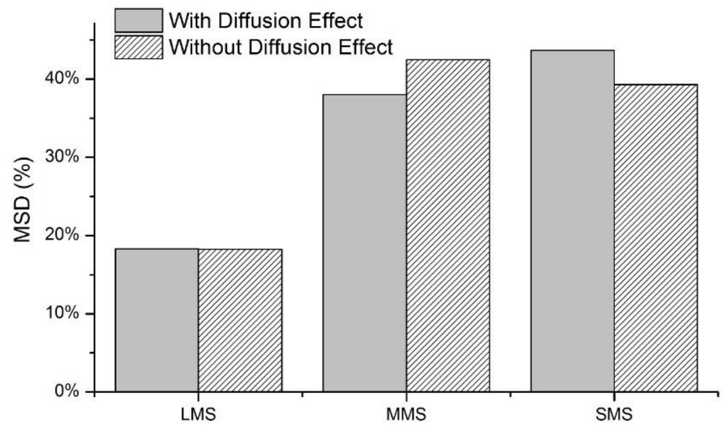


Figure 5.7 Comparison of percentage MSD due to diffusion effect

One can imagine if the diffusion of molecules with one particular molecular weight interval is susceptible to the changes of mixing conditions, the variation of the percentage of these molecules under different mixing conditions should be higher. Therefore, the coefficient of variability (CV) can be used to determine the sensitivity to mixing conditions of particular set of molecules. The variations of MSD% of binders on medium aggregates with temperature were presented in Figure 5.8. It can be seen that the CV of LMS was obviously larger than MMS and SMS, which suggests that the influence of mixing conditions on diffusion process mainly functioned on large molecular part. In this case, the direction of large molecular diffusion was from RAS to virgin binders because the large molecular ratio of RAS binders was higher than virgin binders. Therefore, the diffusion of large molecules from RAS to virgin binders should be the critical step that controlled the inter-diffusion rate of the whole structures. These results are consistent with the conclusion of simulation which shows that the diffusion of asphaltenes was more sensitive to temperature. It also suggests that, despite these limitations, MD simulation model used in this research showed the same diffusion law with the real situations, thus can be applied for the investigation of asphalt binder diffusion.

It should also be noticed that the trend of MSD changes with temperature was not as regular as the simulation results. For example, in simulation results, the values of asphaltenes percentage increased with the increasing of temperature, but the LMS (%) of 190 ºC was lower than which in 170 ºC. These results indicate that the diffusion of asphalt molecules in reality is a complicated process and might be influenced by more factors other than molecular size, such as the intermolecular interaction between molecules.

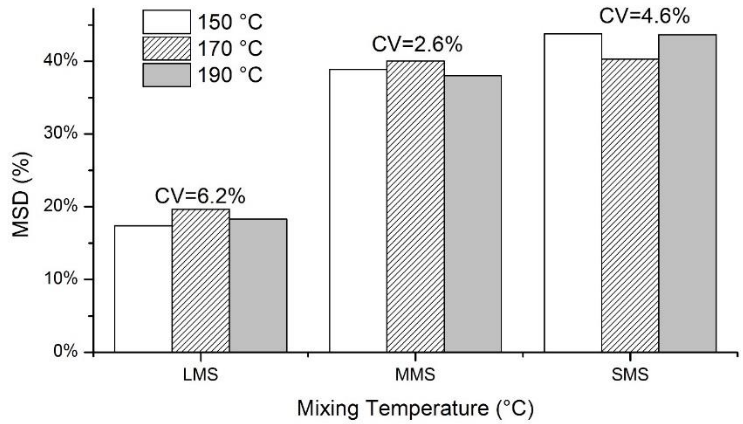


Figure 5.8 Relation between mixing temperature and percentage of MSD

5.6 Quantification of Diffusion of Binders

As previously stated, the diffusion coefficient can be derived from the mean square displacement of all atoms in the model. The diffusion behavior of binders should be different in single and layer model in that the surrounding environment has changed. Figure 9 compares the diffusion coefficients of virgin and aged binder in single and layer systems. As previously stated, the molecules diffused across the vacuum between two layers in Layer model stage I and then into acceptor on the opposite side in Layer model stage II. Results in Figure 5.9 indicate that the diffusion coefficient of virgin binder was larger than aged binder while the molecules diffuse in vacuum (the diffusion in single system can be viewed as in vacuum). However, in inter-diffusion process, the diffusion coefficient of virgin and aged binder has no much differences.

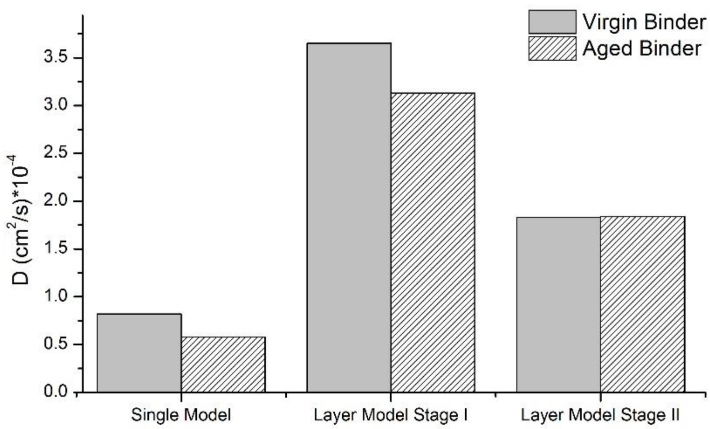
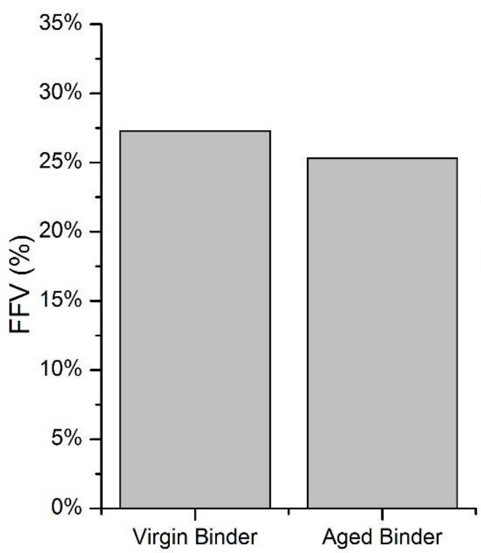
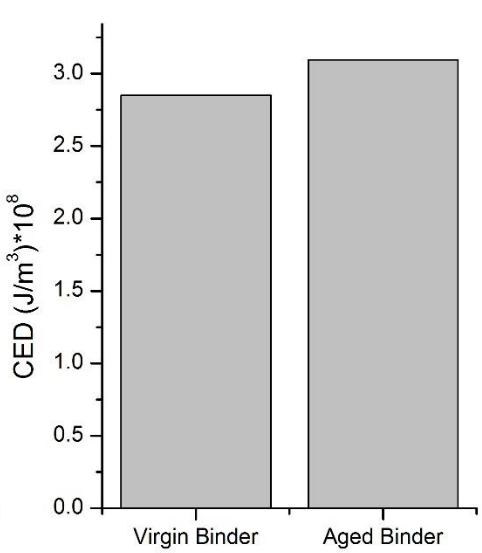


Figure 5.9 Diffusion coefficient of asphalt molecules in single and layer model

The fraction of free volume (FFV) is a parameter that evaluates the volume that has not been occupied by the molecules in a model. The value of FFV determines the amount of volume available for the molecules to diffuse. Cohesive energy density (CED) is the energy that is needed to remove a given molecule from its nearest neighbors. It can evaluate the inter-molecular bonding strength. The CED of one material increase with the increasing of molecular weight; on the opposite, the FFV of one material has an inverse relationship with molecular weight. The reason for aged binder with higher CED and lower FFV (shown in Figure 5.10) was because the molecular size of aged binder was larger than virgin binder. The CED was also correlated with the intermolecular interaction. The polarity of asphaltenes was higher than other components thus behave stronger intermolecular interaction. There were more asphaltenes in aged binders, so the intermolecular interaction of aged binders was stronger and led to higher CED. For the model of virgin and aged asphalt, high CED not just means that the diffusion ability of molecules in this model is weak, but also suggests that molecules from outside is difficult to diffuse into this model. Results in Figure 5.10 demonstrate that although the diffusion coefficient of aged binder was lower than that of virgin binder in single model, the virgin binder was still hardly diffused into aged binders because aged binder with higher CED and lower FFV. On the contrary, the diffusion of aged binder into virgin binder was much easier because there were less obstructs for diffusion inside virgin binder. Therefore, all these factors led to that aged binder diffused as the same rate as virgin binder in a layer model stage II.





(a) Fraction of free volume (b) Cohesive energy density

Figure 5.10 Properties of virgin and aged binder model

5.7 Effects of Rejuvenator Application Sequence

Applying rejuvenator into mixture is one common procedure to improve the blending efficiency of virgin and aged binders. The addition of rejuvenator can soften the binder and accelerate the molecular diffusion. However, the amount of rejuvenator addition is usually less than five percent of the binder weight and cannot be in contact with all the binders. If the rejuvenator was mixed with virgin binder first, the diffusion rate of virgin binder will be accelerated, but its influence on the properties of aged binders should be weaken. The opposite situation will be happened if the rejuvenator was mixed with aged binder first. Therefore, the application procedure of rejuvenator can influence the diffusion rate of the whole structure. The results in Figure 11 suggest that adding rejuvenator into aged binder first can more efficiently accelerate the diffusion of the whole structure. On the opposite, adding rejuvenator into virgin binder first has no obvious influence on the inter-diffusion rate of virgin and aged binder.

Result in Figure 5.11 indicates that adding rejuvenator into aged binder first can significantly improve the diffusion coefficient of asphaltenes molecules. Combining the conclusion mentioned before that the diffusion of large molecules is critical for the whole diffusion. The diffusion rate increasing of asphaltenes (large molecules) might be the reason that adding rejuvenator into aged binder can efficiently accelerate the diffusion of the whole structure.

Asphalt binder is one kind of colloid structure material and the large molecules bind together by intermolecular forces and form a network structure. The network structure might be the principle barrier for the diffusion of asphalt molecules. The addition of rejuvenator could break the network structure and accelerate the molecular diffusion. The content of large molecules of aged binder was higher, therefore, adding rejuvenator into aged binder first was more efficiently in accelerate the inter-molecular diffusion of virgin and aged binders.

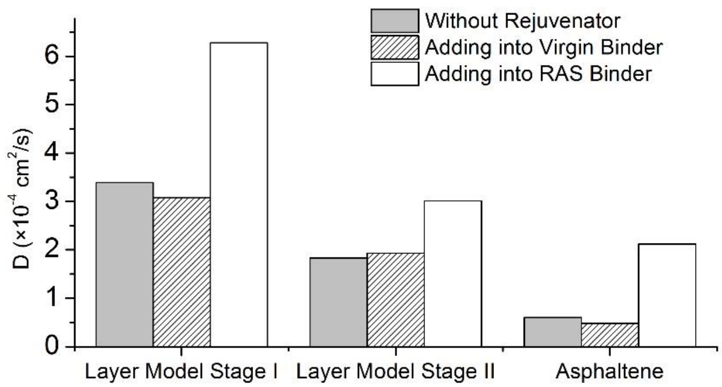


Figure 5.11 Relation between diffusion coefficient and the sequence of adding rejuvenator

5.8 Conclusion

A study has been conducted to investigate the diffusion process of virgin and aged binders using MD simulations. Based on the results, the following can be concluded:

(1) The results of simulation indicate that the diffusion rate of asphaltic molecules increase with the rising molecular weight. The influence of temperature on the diffusion of asphaltenes was obvious larger than resin and oil, which suggests that the diffusion of large molecules was the critical step that controlled the diffusion rate of the whole structure. The results of MD simulation were in agreement with the GPC conclusions, and thus can be applied to investigate the diffusion between virgin and aged binders.

(2) In the single model, the diffusion coefficient of virgin binder was higher than aged binder; whereas, the diffusion coefficient of virgin binder has the same diffusion rate with aged binder in layer model stage II. This result indicates that, in an inter-diffusion process of binders, the diffusion coefficient was not only determined by the diffusion ability itself, but also influenced by properties of the acceptor on the opposite side.

(3) The simulation results show that applying rejuvenator into virgin binder first had no obvious benefit for increasing the diffusibility of the whole layer; whereas, adding rejuvenator into aged binder first could significant accelerate the diffusion of the whole model.

Chapter VI Fluorescence Microscopy for Determining Diffusion Coefficient between Virgin and Aged Asphalt Binders

A version of this chapter was originally published by Yongjie Ding, Baoshan Huang, Xiang Shu and Xingyi Zhu:

Yongjie Ding, Baoshan Huang, Xiang Shu and Xingyi Zhu. Fluorescence microscopy for determining diffusion coefficient between virgin and aged asphalt binders, Association of Asphalt Paving Technologists Annual Meeting (AAPT), 2018

Yongjie Ding was the principle researcher and author of "Use of molecular dynamics to investigate diffusion between virgin and aged asphalt binders". Yongjie Ding's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang, Dr. Xiang Shu and Dr. Xingyi Zhu provided guidance throughout the research process as well as editorial assistance.

6.1 Abstract

Diffusion between virgin and aged asphalt plays a critical role in ensuring a final uniform asphalt binder in mixtures containing recycled asphalt pavement (RAP). Understanding the diffusion phenomenon and determining the diffusion coefficient have a significant effect on asphalt mix design and asphalt mixture performance. In this study, a new method was proposed to utilize fluorescence microscopy to determine the diffusion coefficient of aged RAP binder in recycled mixtures. First, Fick's second law was applied to quantify the diffusion process in a two-layered virgin-aged binder model and to obtain the analytical solution to the distribution of virgin and aged binders. Then, fluorescence microscopy was used in the laboratory to differentiate between virgin and aged binders and to back-calculate their concentrations from fluorescence image. The diffusion coefficient was determined by fitting the analytical solution to the laboratory concentration measurements. Comparison of the diffusion coefficient by the proposed method and that using the dynamic shear rheometer (DSR) method from the literature shows that the diffusion coefficient

determined by fluorescence microscopy was of the same magnitude to, but slightly lower than that by DSR method. The diffusion coefficient was also predicted using another theoretical method – free volume theory. Parameters describing the asphaltic model in the free volume theory were determined from analysis of the chemical structure of asphalt, viscoelastic relaxation properties, and glass transition temperature of asphalt as well as from the diffusion coefficient measured from laboratory experiments. Diffusion coefficient predicted by the free volume theory shows that diffusion coefficients of asphalt were closely dependent on temperature and asphalt type.

6.2 Introduction

Lack of a clear understanding of blending and diffusion between virgin and recycled asphalt has been a major concern in determining the effective asphalt binder in asphalt mixtures containing recycled asphalt pavement (RAP) and the uniformity of asphalt binder in the recycled mixtures. Although the degree of blending between virgin and RAP asphalt is dependent on such factors as mixing conditions and constituent asphalt chemistry, complete or nearly complete blending is often assumed to achieve the maximum cost savings potential. However, the poor performance of some high-RAP mixtures has prompted the study on the degree of blending that actually occurs in high-RAP mixtures (Ding et al., 2016a, Ding et al., 2016b, Kriz et al., 2014).

In reality, aged asphalt in RAP asphalt is a thin film of binder coating RAP aggregates. Research indicates that mechanical blending affects only a small portion of RAP asphalt (Huang et al., 2005). Therefore, it is reasonable to assume the blending process between RAP and virgin asphalt during mixing as a diffusion process, during which virgin and aged asphalt molecules move and penetrate into each other, trying to achieve an ultimate uniform mix of the two.

The Brownian motion of molecules causes mass transfer between virgin and aged asphalt in the diffusion process. To initiate this transfer, asphaltic molecules should gain enough energy to move through the medium. The diffusion process of asphaltic molecules is affected by many factors, including shape and size of asphaltic molecules, temperature, forces between molecules (Crowder and Cussler, 1997). The diffusion rate is closely related to diffusion coefficient, which reflects the mobility of molecules due to diffusion. Fick's second law is commonly used for the mathematical description of diffusion, which is expressed as follows (Crank, 1975):

$$\frac{dc}{dt} = D\frac{d^2c}{dx^2} \tag{6.1}$$

where, c is the concentration, t is time, D is the diffusion coefficient, x is the position.

Fick's law assumes constant pressure and temperature throughout the sample. Fick's law can be solved to obtain a mathematical or numerical expression of the concentration in terms of time, position, and the diffusion coefficient based on material type and boundary conditions to interpret the experimental data. Diffusion coefficient is obtained by fitting the mathematical expression to the experimental data.

6.3 Objectives and Scope

The objectives of this study were to develop a laboratory test method for determining diffusion coefficient between virgin and aged asphalt binders and to quantify the diffusion process in recycled asphalt mixtures. First, Fick's second law was applied to obtain the theoretical distribution of virgin and aged binders in a two-layered model. Then, fluorescence microscopy was utilized in the laboratory to differentiate between virgin and aged binders and to characterize their distribution in the two-layered specimen. Diffusion coefficient was determined by fitting the theoretical solution to the laboratory measurements. The diffusion coefficient also was predicted using the free volume theory.

6.4 Theoretical Solution of Diffusion between Virgin and Aged Binder

A two-layered virgin-aged binder model was used in this study for determination of asphalt diffusion coefficient. Figure 6.1 shows the model and its initial conditions. Virgin and aged asphalt samples were placed together to form a two-layered model. In the aged asphalt layer, the initial concentration of virgin asphalt is 0, and in the virgin asphalt layer, the concentration is 1. For aged asphalt, the initial concentration of aged asphalt layer and virgin asphalt layer is 1 and 0, respectively. The two layers have a total thickness of L, and the thickness of each layer is aL and bL (a+b=1), respectively (Karlsson and Isacsson, 2003).

The boundary conditions of the model are given in Equation 6.2.

$$\left.\frac{dc_{virgin\ asphalt}}{dx}\right|_{x=0} = 0 \qquad \left.\frac{dc_{virgin\ asphalt}}{dx}\right|_{x=L} = 0 \tag{6.2}$$

The diffusion between virgin and aged binders in the two-layered model can be simplified as a one-dimensional diffusion process. Given the initial and boundary conditions, the concentration of virgin asphalt at position x and time t, c(x,t), at position x and time t, is given as follows (Karlsson and Isacsson, 2003):

$$c(x,t) = (1-a) - \frac{2}{\pi}\sum_{n=1}^{\infty}\frac{\sin(n\pi a)}{n}\cos\left(\frac{n\pi x}{L}\right)exp\left\{-\left(\frac{n\pi}{L}\right)^2 Dt\right\} \tag{6.3}$$

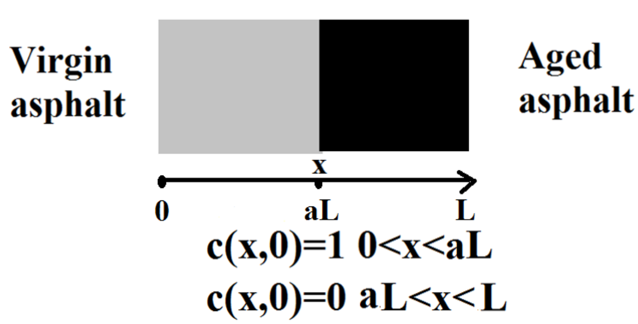


Figure 6.1 A two-layered virgin-aged asphalt model

6.5 Laboratory Test Method and Analysis Procedure

In the laboratory test, fluorescence microscopy was utilized to determine the concentration distribution of asphalt along the sample thickness. Fluorescence microscopy is capable of differentiating aged from virgin binders because of their difference in fluorescence (Ding et al., 2018). Ding et al. showed that the mean grey value (MGV) of a fluorescence image of an asphalt blend is directly related to the contents of virgin and aged binder. Therefore, by measuring the MGV at a small area on a two-layered sample, the concentrations of virgin and aged binders at that point can be determined. The following section gives a detailed description of the laboratory test and analysis procedure.

6.5.1 Materials

Virgin and aged SHRP asphalts were used in the laboratory test. The asphalts selected in the study included virgin AAD-1, aged AAD-1, virgin AAK-1, and aged AAK-1. The SHRP asphalts were aged by rolling thin-film oven (RTFO) (ASTM, 2010b) and pressurized aging vessel (PAV) methods (ASTM, 2010a).

6.5.2 Use of Fluorescence Microscopy

Fluorescence is a phenomenon that ultraviolet or visible light is absorbed by an organic molecule, thus causing excitation of an electron from an initially occupied, low-energy orbital to a high-energy orbital (Khorasani, 1987). Fluorescence in asphalt molecules is essentially related to the electronic excitation of the conjugated π-systems (aromatic components) and of C=O groups (Zhang et al., 2013).

The fluorescence intensity of asphalt is primarily controlled by the type and concentration of aromatic molecules relative to the concentration of saturates compounds (Dennis et al., 2012, Stasiuk and Snowdon, 1997). For SARA fractions, the aromatics and resin phases are the only components capable of sufficiently intense fluorescent emission

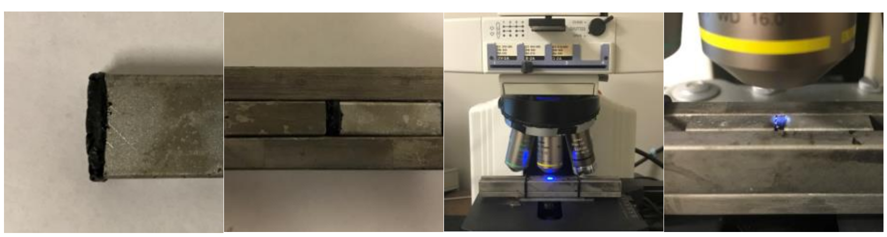
(Handle et al., 2016). Research also indicates that as bitumen ages, its fluorescence emission intensity decreases (Grossegger et al., 2017). Therefore, fluorescent intensity can be used to distinguish virgin from aged binders.

Fluorescence microscopy is an optical microscopy that uses the emission of fluorescence to study the properties of organic or inorganic substances (Petryayeva et al., 2013). A parameter, mean grey value (MGV), was derived from the fluorescence image and used to differentiate between virgin and aged binders as well as their blends (Ding et al., 2017). MGV was defined as the mean of the grey value of a set area of the fluorescence image and can be obtained through post-processing of the image. Virgin binder exhibits a high grey value than an aged binder. Therefore, MGV of a binder blend decreases with the increase in aged binder content.

6.5.3 Sample Preparation and Testing

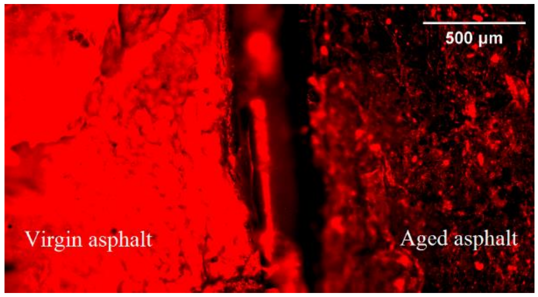
The BBR mold was used to make the two-layered virgin-aged asphalt samples. Thin layers (1 mm thick) of virgin and aged asphalt were obtained by applying asphalt on the end pieces of BBR mold with an area of 6.35 mm × 12.7 mm (Figure 6.2 (a)). The samples were prepared by weighing pre-determined amount of virgin and aged asphalt (0.08 g), which was equivalent to the 1-mm thickness. Then, thin layers were formed by carefully heating the binders to allow them to spread out on top of an end piece. To avoid aging from heating, the heating temperature was controlled within the range of 60-80 °C. Asphalt layers were heated in a sample holder at 60 °C for 3 min to ensure a true contact with end piece. Another end piece was pressed at the top of thin layer to form a smooth plane.

The 1-mm layers of virgin and aged asphalt were brought into contact to form a two-layered sample (Figure 6.2 (b)) for fluorescence microscopy testing. The samples were conditioned at a test temperature in a heating oven. The fluorescent images of a sample were taken during the diffusion/conditioning process (Figure 6.2 (c, d)). The images were taken with a resolution of 10× every 1 or 5 minutes. For the digital image collection process, the procedure of ASTM F2998 (ASTM, 2014) was followed. Samples were imaged on a fluorescence microscopy fitted at with a CCD camera and filter cubes for fluorophore visualization. Once the images are collected, they were analyzed with image analysis tool ImageJ. Figure 6.3 (a) shows an example of the fluorescent image of the virgin-aged asphalt layers. It can be seen that the border of virgin and aged asphalt is not clear. A post-possessing process was adopted to improve the contrast between virgin and aged asphalt using of ImageJ. First, the objective lens of microscopy was lifted 2 mm to collect the image as shown in Figure 6.3 (b). Then then contrast of the image was increased to maximum to generate a clear border between virgin and aged asphalt as shown in Figure 6.3 (c). It should be noted that all the images should be processed by the same procedure to ensure the MGV generated from the image is comparable.



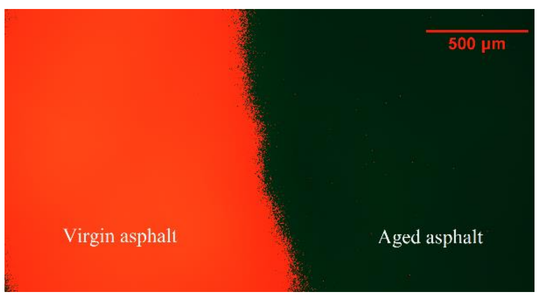
(a) (b) (c) (d)

Figure 6.2 Sample preparation and test process for fluorescence microscopy test ((a) single asphalt layer; (b) in-contact asphalt layers (c, d) asphalt layers tested in fluorescence microscopy)



(a) Before post-possessing

(b) Image collected by lifting objective lens 2 mm



(c) Image with improving contrast

Figure 6.3 Fluorescence image of the virgin-aged asphalt specimen

6.5.4 Fluorescence Image Processing

Each fluorescence image was divided into four slices (Figure 6.5 t (1)) and the MGV of each slice was obtained through image processing (Ding et al., 2018). The grey value of selected slice was collected using ImageJ to generate MGV. In a previous study of the authors, the MGV of a fluorescence image was found to be directly related to the contents of virgin and aged binders (Ding et al., forthcoming). To back-calculate concentrations of virgin and aged asphalt from the MGV of fluorescence image, the relationship between MGV and concentration of virgin (or aged) binder has to be established for a specific pair of virgin and aged binders as a base line. To achieve this goal, samples of asphalt blends with aged (or virgin) binder content ranging from 0 to 100% at a 10% increment were tested for their MGV (Ding et al., forthcoming).

Figure 6.4 shows the plot of MGV vs. virgin asphalt content for one SHRP binder, AAK-1. Clearly, it reveals a linear relationship between MGV and virgin asphalt content with a R^2 value of 0.99. Therefore, a linear regressive equation (Equation 5) was obtained and used to back-calculate concentration of virgin asphalt from MGV. It should be noted that different relationships have to be established for different combinations of virgin and aged asphalt binders for this purpose.

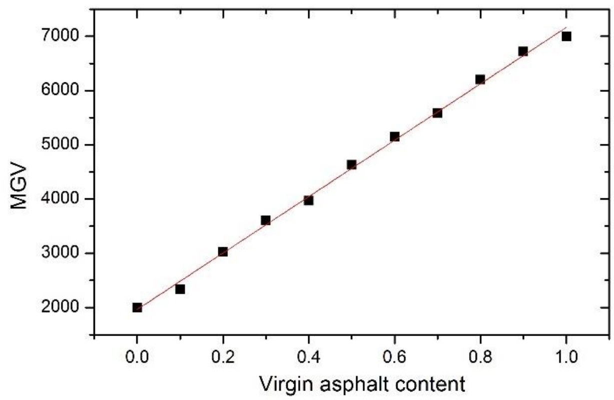


Figure 6.4 Plot of MGV vs. virgin asphalt content for AAK-1

$$\mathrm{MGV} = 5201.3 \times \text{virgin asphalt content} + 1965.8 \tag{6.4}$$

6.5.5 Procedure for Determining Diffusion Coefficient

The diffusion coefficient of asphalt was determined by fitting the theoretical solution from Fick's second law to the laboratory concentration measurements from fluorescence microscopy (Figure 6.5). The procedure is summarized as follows.

(1) The diffusion coefficient was treated as a constant. The concentration of virgin asphalt c (x, t) was obtained from Equation 6.1 as a function of position x and time t, as shown in P (1) in Figure 6.5.

(2) The 3-D plot of c vs. x and t can be further converted to 2-D plot of c vs. t (see P (2) in Figure 6.5) or plot of c vs. x (see P (3) in Figure 6.5).

(3) The concentration of asphalt was measured in the laboratory using the two-layered sample and the fluorescence microscopy technique for the four slices in a sample. The average asphalt concentration of each slice was used as the concentration at the middle of the slice.

(4) The theoretical concentration curve was adjusted by gradually changing the diffusion coefficient in such a way that the calculated curve fitted the experimental data in an optimal way. A nonlinear regression was used to fit the theoretical solution to the laboratory concentration measurements to minimize the deviation. One example of fitting predicted concentrations to experimental results is shown in Figure 6.5. It can be seen that the predicted concentration curve with a diffusion coefficient of 5×10^{-13} m^2/s fit well the laboratory measurements. Therefore, the diffusion coefficient was determined to be 5×10^{-13} m^2/s.

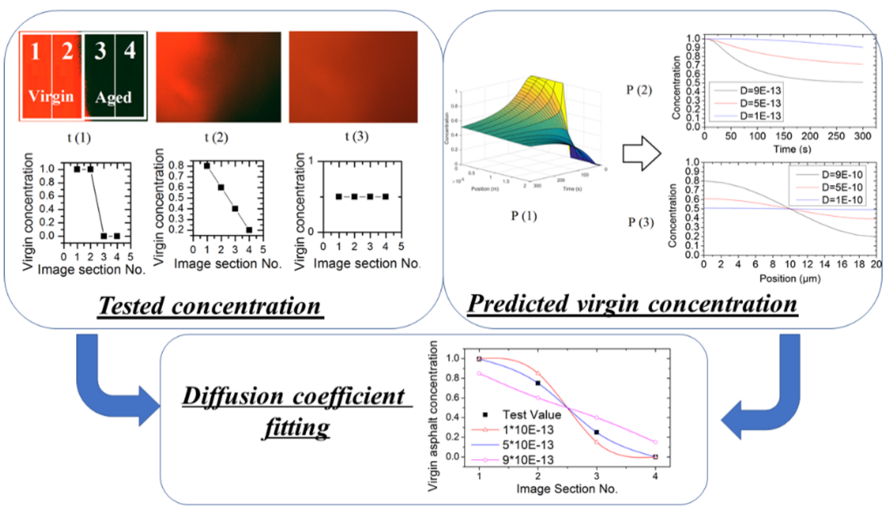


Figure 6.5 Process of diffusion coefficient fitting (Measured concentrations: fluorescence image if virgin and aged asphalt layer system, t (1) before diffusion, t (2) during diffusion, t (3) after complete diffusion, the image has been strengthened by ImageJ to increase the contrast; Calculated virgin concentration curves: P (1) Simulation of concentration profile change, combined effect of time and distance, P (2) Concentration-Time profile, P (3) Concentration-Position profile)

6.6 Diffusion Coefficient Prediction Using Free Volume Theory

Diffusion in asphalt is complicated due to the complex chemistry of asphalt. Despite a lack of the chemical structure of asphalt, it is still highly desirable to obtain diffusion coefficients from its readily available properties. One way to predict diffusion coefficient of asphalt is through free volume theory.

6.6.1 Free Volume Theory

Free volume theory has been used in the prediction and correlation of viscosities and self-diffusion coefficients of polymeric materials (Duda et al., 1982, Vrentas et al., 1985a, Vrentas et al., 1985b). The free volume, V_f, is defined as the space in a solid or liquid that is not occupied by the molecules i.e. the empty space. According to the free-volume theory, the diffusion rate of material is primarily dependent upon the average fractional free volume of the system.

In one-component liquid systems. It is assumed that the interstitial free volume is distributed uniformly among the molecules. Following Cohen and Turnbull (Cohen and Turnbull, 1959), the diffusion coefficient of a one-component system can be written as:

$$D_1 = D_{01}\exp(-\frac{\gamma\hat{V}_1^*}{\hat{V}_{FH}}) \qquad (6.5)$$

Here, D_1 is the diffusion coefficient of material, $\hat{V}_{FH}$ is the average hole free volume per molecule in the liquid; $\hat{V}_1^*$is the critical local hole free volume required for a molecule of species one to jump to a new position; γ is an overlap factor (which should be between 0.5 and 1) which is introduced because the same free volume is available to more than one molecule.

Equation 6.5 reflects the dependence of the diffusion process on the probability that a molecule will obtain sufficient energy to overcome attractive forces and on the probability that a fluctuation in the local density will produce a hole of sufficient size so that the diffusing molecule can jump.

6.6.2 Diffusion Coefficient Prediction of Virgin and Aged Asphalt

In this study, Equation 6.5 was applied on the virgin-aged asphalt system for the diffusion coefficient prediction. The system was composed of both virgin and aged asphalt, so the critical local hole volume was calculated by both layers. One approach for the calculation of diffusion coefficient of solvent-polymer system was adopted in this study (Duda et al., 1982, Kim et al., 1994). In the virgin-asphalt layer system, the self-diffusion coefficient of virgin asphalt, D_1, was expressed by the following equation (Duda et al., 1982, Kim et al., 1994):

$$D_1 = D_{01}\exp\left(-\frac{\omega_1\hat{V}_1^* + \omega_2\xi\hat{V}_2^*}{\hat{V}_{FH}/\gamma}\right) \tag{6.6}$$

Here, $\hat{V}_1^*$ is the specific critical hole free volume of virgin asphalt, $\hat{V}_2^*$ is the specific critical hole free volume of aged asphalt, $\hat{V}_{FH}$ is the average hole free volume per gram of the system, ω_i is the mass fraction of component i, γ is an overlap fraction.

The quantity, ξ, can be determined from Equation 6.7 (Duda et al., 1982, Kim et al., 1994):

$$\xi = \tilde{V}_1^*/\tilde{V}_2^* = \hat{V}_1^* M_1/\hat{V}_2^* M_2 \tag{6.7}$$

Here, $\tilde{V}_1^*$ is the critical molar volume of virgin asphalt; $\tilde{V}_2^*$ is the critical molar volume of aged asphalt; M_1 is the average molecular weight of virgin asphalt; and M_2 is the average molecular weight of aged asphalt.

The average hole free volume of virgin and aged asphalt, $\hat{V}_{FH}$,is given by Equation 6.8 (Duda et al., 1982, Kim et al., 1994):

$$\frac{\hat{V}_{FH}}{\gamma} = \left(\frac{K_{11}}{\gamma}\right)\omega_1\left(K_{21} + T - T_{G_1}\right) + \left(\frac{K_{12}}{\gamma}\right)\omega_2\left(K_{22} + T - T_{G_2}\right) \tag{6.8}$$

Here, K_{11} and K_{12} are the virgin asphalt free-volume parameters, and K_{21} and K_{22} are the aged asphalt free-volume parameters.

These parameters were determined for the virgin and aged asphalt system by following the procedures previously suggested by Vrentas et a1. (Vrentas et al., 1985a, Vrentas et al., 1985b).

The critical hole free volumes, $\hat{V}_i^*$, were replaced with the specific volumes at 0 K, $\hat{V}_i^*(0)$, which were estimated by group contribution theory (Duda, Vrentas, et al., 1982). The average molecular model for SHRP asphalt was used here (Jennings et al., 1993). The resulting values of $\hat{V}_1^*$ and $\hat{V}_2^*$ were 0.91 and 0.93 cm^3/g, respectively.

Values were determined using the viscosity data of virgin asphalt. The resulting values of, respectively.

Values of K_{11}/γ and $K_{21} - T_{G1}$, K_{12}/γ and $K_{22} - T_{G2}$ were determined using the shift parameters of the WLF equation, $C_1 = 19$ and $C_2 = 92$, representing the viscoelastic behavior of asphalt (Anderson et al., 1994). The value of T_{G_1}as determined based on the report of Marasteanu, et al. (Marasteanu et al., 2007). The resulting values were:

$\frac{K_{11}}{\gamma} = 2.26 \times 10^{-4}$, $K_{21} - T_{G_1} = -166.45$, $\frac{K_{12}}{\gamma} = 2.31\times10^{-4}$ and $K_{22} - T_{G_2} = -171.95$.

In general, the pre-exponential factor D_{01} should be expressed as Equation 6.9 (Vrentas and Duda, 1979). This result accounts for the energy per mole that a molecule needs to overcome attractive forces which hold it to its neighbors. In the previous version of the theory, it was argued that the temperature variation of D_{01} is not important. The assumption of negligible energy effects (E=0) is often acceptable in the predictive version of the theory (Kim et al., 1994) and adopted in this study.

$$D_{01} = D_0 \exp\left(-\frac{E}{RT}\right) \tag{6.9}$$

The parameters for the free volume theory can be obtained from density, viscosity, and chemical structure of asphalt except for D_{01}. The value of D_{01} can be evaluated using one diffusivity data collected from experiment. The values of D_{01} was determined to be 5.1^{-4} m^2/s, using the self-diffusion coefficient data of the virgin and aged AAK-1 asphalt system. Combine Equations 6.6 through 6.8, The equation for the diffusion coefficient of the virgin-aged asphalt system can be derived as follows.

$$D_1 = 5.1^{-4}\exp\left(-\frac{\omega_1\hat{V}_1^* + \omega_2\xi\hat{V}_2^*}{\frac{\omega_1\hat{V}_1^*}{4025.6}\times(92 - T_{d1} + T) + \frac{\omega_2\hat{V}_2^*}{4025.6}\times(92 - T_{d2} + T)}\right) \qquad (10)$$

The parameter D_{01} was from the test results of AAK-1. It can be expected that the predicted diffusion coefficient is consistent with the test results of AAK-1. A question is raised: Can this equation be applied to other asphalt? To answer this question, the properties of SHRP AAD-1 was introduced into Equation 10 and the diffusion coefficient was calculated as a function of temperature and then compared to the experimentally measured diffusion coefficient.

6.7 Results and Discussion

6.7.1 Verification of the Proposed Fluorescence Microscopy Method

In order to verify the proposed fluorescence microscopy method for determining diffusion coefficient of asphalt, the same SHRP asphalt binders, AAD-1 and AAK-1, were tested for their diffusion coefficients using the DSR method developed by Karlsson, et al. (Karlsson et al., 2007), Rad, et al. (Rad et al., 2014), and Kriz, et al. (Kriz et al., 2014). Figure 6.6 compares the diffusion coefficients of virgin asphalt into aged asphalt determined by fluorescence microscopy and those by DSR method. It can be seen that the diffusion coefficients obtained from these two methods were of the same order of magnitude, but the coefficients from fluorescence microscopy were slightly lower than those from DSR method. Figure 6.6 also show a relatively linear relationship between diffusion coefficient and temperature in the log plot within the temperature range of 80–160 °C. This indicates that the proposed fluorescence microscopy was capable of determining diffusion coefficient of asphalt with a two-layered virgin-aged asphalt model.

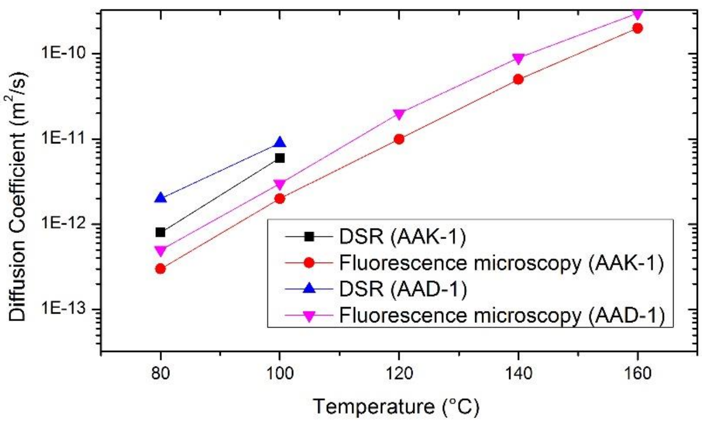


Figure 6.6 Comparison of diffusion coefficients by fluorescence microscopy and DSR method

6.7.2 Effects of Temperature and Test Condition

To investigate the influence of temperature and test conditions on diffusion coefficient, a series of tests were performed using virgin and aged asphalt. It is expected that MGV of an image is affected by test conditions such as exposure time and wavelengths of excited light. In photography, exposure time refers to the amount of light per unit area, so the MGV increases with an extended exposure time. MGV also varies under different excited lights.

During the experimental study, it was found that the MGV of asphalt decreased with heating time at a certain rate due to asphalt oxidation and evaporation. The decreasing rate of MGV was also related to heating temperature.

6.7.2.1 Effect of Test Condition

Figure 7 shows the diffusion coefficients under seven exposure time (0.1-2.55 s) and three excited light conditions. The results show that diffusion coefficient first increased and then decreased with the increase in exposure time. A statistical analysis shows that excited light condition did not have significant influence on diffusion coefficient. However, as indicated in Figure 6.7 the diffusion coefficients between 1.02-2.55 s of exposure time showed a minor difference among three excited lights, which implies that the excited light had a minor, but detectable, effect on the diffusion coefficient. Therefore, same excited light and exposure time are required to keep the MGVs of asphalt samples comparable.

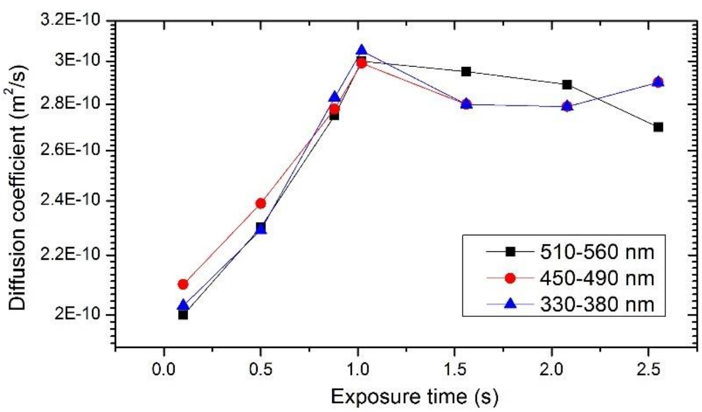


Figure 6.7 Variation of diffusion coefficient with test condition

6.7.2.2 Effect of Temperature

Figure 6.8 shows the change of MGVs with heating time at different temperature. At prolonged times, the MGVs decreased due to asphalt oxidation. To mitigate this effect, the samples were heated in a vacuum oven. This operation possibly minimized oxidation, but could not prevent decrease in MGV due to evaporation.

In order to eliminate the effect of oxidation and evaporation, a data compensation or correction method was proposed. The virgin and aged asphalt were heated under the same condition in the laboratory diffusion experiment, the change in MGV was recorded with heating time. The change in MGV before and after heating was calculated using Equation 6.11 was subtracted from the MGV results in the diffusion experiment to eliminate the influence of oxidation and evaporation.

$$MGV\ variation = MGV_{after\ heating} - MGV_{before\ heating} \tag{6.11}$$

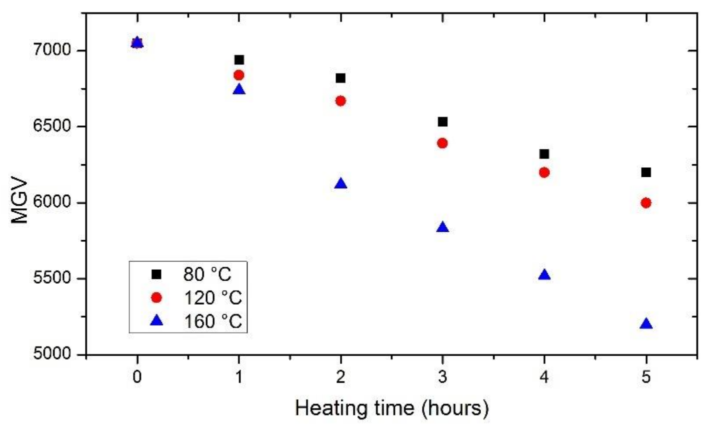


Figure 6.8 Change of MGV with heating time

6.7.3 Diffusion Coefficient Prediction by Free Volume Theory

Figure 6.9 compares the diffusion coefficients as a function of temperatures determined using free volume theory and those determined by fluorescence microscopy. The diffusion coefficients by fluorescence microscopy were generally in good agreement with those predicted by free volume theory within the temperature range of 80 – 160 °C. However, the predicted diffusion coefficients of AAD-1 seemed to deviate from the fluorescence-measured values at high temperatures (140-160 °C). The fluorescence-measured diffusion coefficient of AAK-1 at 160 °C was used to estimate D_{01} in the free volume theory so that an accurate prediction value can be obtained at high temperatures for AAK-1. The assumption of negligible energy effects (E=0) is, therefore, still somewhat questionable at high temperatures. Variation in energy affects the predicted value of diffusion coefficient. It is reasonable to assume that the coefficient in Equation 6.10 needs to be adjusted when the equation is used for another asphalt.

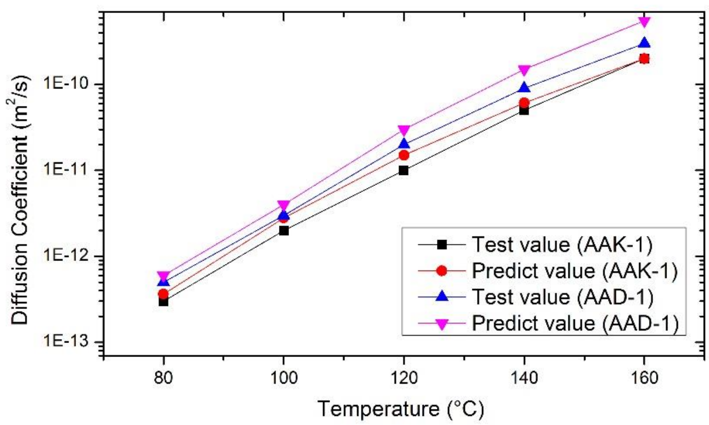


Figure 6.9 Comparison of fluorescence-measured diffusion coefficients and those predicted by free volume theory

6.8 Conclusions and Recommendations

In this study, a new laboratory test method was proposed based on fluorescence microscopy to determine the diffusion coefficient of asphalt. Fick's second law was first applied to obtain the analytical solution of the virgin and aged asphalt distribution in a two-layered model. The concentration of virgin or aged asphalt in the two-layered sample was then back-calculated from the measured MGV of a fluorescence image. Diffusion coefficient was determined by fitting the theoretical solution to the laboratory concentration measurements by the fluorescence microscopy method. The proposed fluorescence microscopy method was verified with the diffusion coefficients determined using the DSR method. In addition, the free volume theory was also utilized to predict the diffusion coefficients of asphalt. From this study, the following conclusions and recommendations can be summarized:

(1) Fick's second law was successfully applied to study diffusion between virgin and RAP binders. A fluorescence microscopy method was developed to determine the diffusion coefficient of the virgin-aged asphalt layered system. Results show that the fluorescence-measured diffusion coefficient was linear with temperature in the log plot within the temperature range of 80–160 °C. The DSR method for determining diffusion coefficient was used to verify the fluorescence microscopy method. The diffusion coefficient from fluorescence microscopy was of the same magnitude to, but slightly lower than that from the DSR method.

(2) The diffusion coefficient was predicted using free volume theory. It was shown that the diffusion-temperature function could be reasonably estimated using free volume theory, which allows for a rapid estimate of diffusion coefficient from readily available data.

(3) The two-layered model and the laboratory fluorescence microscopy method developed in this study were validated to be capable of determining diffusion coefficient of two types of SHRP asphalt. It is recommended that more asphalt types, aged binder types, and mixture types be used for validation of the proposed method and investigation of asphalt diffusion phenomenon.

Chapter VII Utilizing of Recycled Asphalt Shingle into Pavement by Extraction Method

A version of this chapter is in the process of being submitted for publication by Yongjie Ding, Baoshan Huang and Xiang Shu:

Yongjie Ding, Baoshan Huang and Xiang Shu. Utilizing of recycled asphalt shingle into pavement by extraction method, Journal of Cleaner Production, 2018

Yongjie Ding was the principle researcher and author of "Utilizing of recycled asphalt shingle into pavement by extraction method". Yongjie Ding's contribution was conducting all literature review, testing, data analysis, and writing the text contained in the manuscript. Dr. Baoshan Huang and Dr. Xiang Shu provided guidance throughout the research process as well as editorial assistance.

7.1 Abstract

The recycling of asphalt shingles in asphalt paving construction is beneficial to the environment and industry by reducing the consumption of virgin materials. A new approach to recycling asphalt shingles in which RAS binder was extracted by a mixed solvent with certain polarity and used as common asphalt binder was developed in this study. In the proposed process, the viscosity of the extracted RAS binder was controlled by the polarity and composition of the mixed solvent. Results indicate that heptane dissolved the soft part and trichloroethylene (TCE) could dissolve the stiff part of RAS binder. The use of the mixed solvent of heptane and TCE with a certain proportion through the proposed method could prepare asphalt binder with desired properties. The current approaches of utilizing RAS which mixes RAS with soft asphalt or rejuvenator were compared with the proposed method. Results indicate that soft asphalt could not dissolve RAS binder at 170 ℃. The binder blend of RAS binder and rejuvenator had a potential antiaging problem because an obvious loss of rejuvenator existed during the aging process.

7.2 Introduction

Asphalt shingle is a type of roofing materials that use asphalt binder for waterproofing and is the most popular roofing covers in the United States. Asphalt shingles are divided into two types according to the base materials: organic and fiberglass (Elseifi et al., 2012). Both shingles are manufactured in a similar manner that asphalt or modified asphalt covers on an asphalt-saturated base. The asphalt content is 30-35% for organic shingles and 15-20% for fiberglass shingles (Hassan et al., 2013). The service life of asphalt shingles varies with the environment from around 14 years to 21 years (Hassan et al., 2013). According to the United States Environmental Protection Agency (EPA), the recycled asphalt shingle (RAS) in the United States achieves a total of 11 million tons annually (Zhou et al., 2013b). The landfill disposal fee of waste shingles may reach as high as $90 to $100 per ton in the United States (Mallick et al., 2000).

Due to the quality and content of asphalt binder and also the environmental pressure, asphalt shingles have been recycled into pavement construction to replace some asphalt binder and fine aggregates (Krivit, 2007). According to National Asphalt Pavement Association, the usage of RAS into the pavement in the United States achieved a total of 2 million tons in 2015, which is a 175 percent increase since 2009 (Hansen and Copeland, 2015). The use of RAS in hot mix asphalt (HMA) is expected to provide significant economic benefits to the asphalt industry by reducing the amount of virgin asphalt binder that is added to the mixture. The fibrous shingle base also contains valuable fibers that may enhance the performance of HMA (Elseifi et al., 2012).

Two strategies have been adopted in the recycling and processing of asphalt shingles. The first strategy is a dry process which is similar to the utilization of recycled asphalt pavement (RAP) into HMA that blending recycled materials with the aggregates before the asphalt binder is added to the batch (Krivit, 2007). The second strategy is named wet process, in which RAS is ground to ultrafine particle sizes then the grounded RAS is blended with the binder at a high temperature prior to mixing with aggregates (Elseifi et al., 2012).

Despite the potential benefits of using RAS in HMA, concerns have been expressed about the impact of RAS on pavement performance. One concern is that air-blown asphalt is typically used in the manufacturing of asphalt shingles. The air-blown process and the further aging during the service life has significantly stiffened the RAS binder and the using of the stiff aged binder from RAS into HMA can cause a series of pavement issues such as cracking failures (Zhao et al., 2013a, Zhou et al., 2013b). Another major concern with RAS relates to the variability in the properties of RAS originating from different sources (Hassan et al., 2013).

Since the early 1990s, a number of studies have evaluated the use of RAS in HMA and its influence on the mix mechanical behavior (Foo et al., 1999). The use of RAS results in a decrease in the required virgin binder content and improved the mixture resistance to permanent deformation. However, mixture resistance to low temperature cracking appears to decrease when asphalt shingles are used (Grzybowski, 1993). Button et al. evaluated the influence of adding 5–10% of asphalt shingles on the mechanical properties of HMA as compared with untreated mixes. The use of RAS results in a decreased tensile strength and creep stiffness of the mixture but it improves the mix resistance to moisture damage (Button et al., 1996). The research indicates that the use of asphalt shingles by dry process improves the rutting resistance of the mixture but the mix has lower fatigue and low temperature cracking resistance (Sengoz and Topal, 2005). The use of RAS modification through the wet process would generally improve or not influence the high temperature grade of the binder, but it also reduces the low temperature grade of the binder. Results of high-pressure gel permeation chromatography (HP-GPC) showed that the wet process produced a slight increase in the high molecular weight content in the prepared blends at higher RAS contents, suggesting that a fraction of the RAS binder contributes to the blend properties (Elseifi et al., 2012). States Agencies are still cautious in the use of high RAS content in asphalt mixtures because of construction and durability concerns (Watson et al., 1998). Usually, the percentage of RAS is limited to less than 5% in practice (Zhao et al., 2014). This concern may be addressed by using the proposed process in this study.

In this study, a new approach to recycling asphalt shingles into asphalt mixtures was proposed. In the new method, part of RAS binder was separated from RAS materials through a dissolve and extraction process using the mixed solvent developed in this study. The properties of the extracted RAS binder such as modules was controlled by the components of the mixed solvent. The extracted RAS binder manufactured using the proposed method could be used as common asphalt in the pavement construction thus there was no limitation on the amount of RAS that can be used.

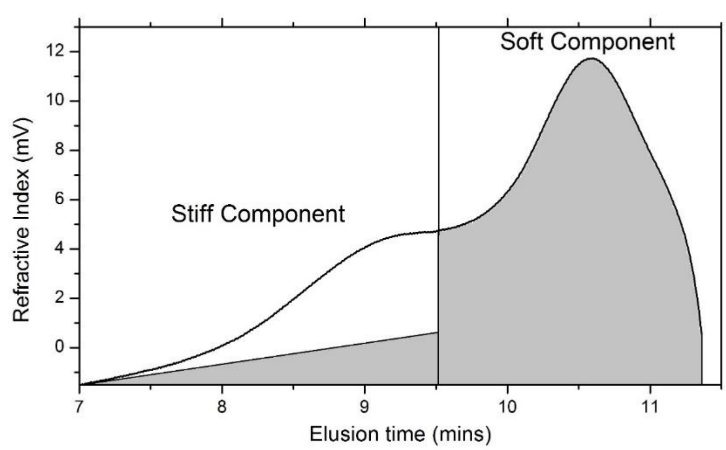


Figure 7.1 GPC chromatogram of RAS binder (The shaded part of the figure represents the RAS binder component that can be dissolved by the mixed solvent.)

The idea behind the proposed method was motivated by the relationship between polarity and viscosity of asphalt fractions. As shown by the gel permeation chromatography (GPC) chromatogram of RAS binder in Figure 1, the soft component of RAS binder is composed of saturates and resins components that with low polarity. The stiff components include asphaltenes and part of resins components that has high polarity. The low polarity solvent such as heptane only dissolved components with low polarity. The high polarity solvent such as Trichloroethylene (TCE) could dissolve all the RAS binder. Therefore, the amount of RAS binder that can be dissolved out could be controlled by the polarity of the solvent. Since the polarity of the mixed solvent was adjusted by the proportion of two solvents with high and low polarity, a mixed solvent composed of heptane and TCE could dissolve part of RAS binder out as shown in the shade of Figure 7.1 and the module of the extracted binder might be controlled by the proportion of TCE in the mixed solvent. The use of RAS through the proposed separation process was expected to act not only as a partial binder replacement but also a common binder alone or rejuvenator for RAP due to the precise control of the binder properties. The proposed process offers the potential to increase the percentage of asphalt shingles used in the mixture and may allow for a better control of the performance of asphalt pavement.

7.3 Objective and Scope

The objective of this study is to investigate the feasibility of using a new approach to recycling asphalt shingles into asphalt mixtures in which RAS binder was separated out of RAS material by a dissolve and extraction process and used as common asphalt. Heptane and TCE were utilized to prepare the mixed solvent. As illustrated above, the properties of the extracted RAS binder might vary with the proportion of the mixed solvent. Accordingly, the mixed solvent proportion was evaluated as a variable of interest. For the comparison purpose, the current method of utilizing RAS into asphalt mixtures in practice which blends RAS binder with soft asphalt or rejuvenator was selected as the reference to illustrate the advantage of the proposed method.

7.4 Experimental Program

7.4.1 Test Materials

The experimental program was designed to evaluate a wide range of asphalt blends prepared using three approaches including the proposed extraction process, mixing RAS binder with soft asphalt, and mixing RAS binder with rejuvenator. One unmodified binder, classified as PG 52-28 according to the Superpave specifications, were selected as the soft binder (Table 7.1). One PG 64-22 unmodified asphalt was used to compared with extracted RAS binder prepared using the proposed method. One tear-off shingle from Tennessee was obtained from Ground Up Recycling plants. An abietic-acid-derived oil called Hydrogreen was adopted as rejuvenators in this study (Cooper et al., 2015).

7.4.1.1 Components Separation of RAS Binder

Heptane dissolved RAS binder component (referred to as DRH) (Table 1) and TCE dissolved RAS binder component (referred to as DRT) (Table 7.1) were prepared referring to AASHTO T 164 method (AASHTO, 2010b) as shown in Figure 7.2. The ground RAS was immersed in heptane at room temperature for 2 hours. The heptane solution was collected using the centrifuge extractor and extracted by the rotavapor to produce DRH. Then the RAS aggregates in the centrifuge extractor was dissolved by TCE for 15 mins and the TCE solution was collected and extracted in the same conditions to prepared DRT. The prepared DRH and DRT were placed in a vacuum oven at 80 °C for 2 hours to evaporate the residual solvent. The abbreviation of binder name is listed in Table 7.1.

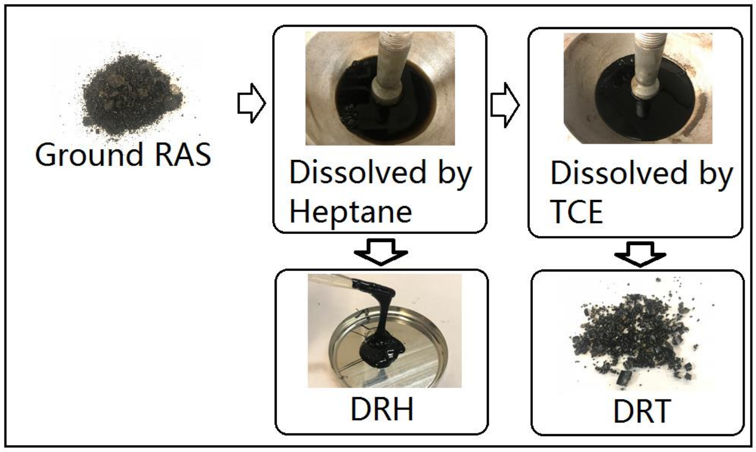


Figure 7.2 Preparation of RAS binder component using the proposed dissolve process

7.4.1.2 RAS Binder Extraction Using Mixed Solvent

Heptane and TCE were mixed according to volume ratio. The extraction method was designed referring to AASHTO T 164 (AASHTO, 2010b). The ground RAS was immersed in heptane at room temperature for 30 mins. The collected solution from the centrifuge extractor was recovered by the rotavapor to produce extracted RAS binder (referred to as ER) (Table 7.1). The prepared ER were placed in a vacuum oven at 80 ℃ for 2 hours to evaporate the residual solvent.

7.4.1.3 Mixing RAS Binder with Soft Asphalt or Rejuvenator

RAS binder was extracted in accordance with AASHTO T 164 (AASHTO, 2010b). The RAS materials were firstly dried up to constant weight at the temperature of 105±5 ℃ and then dissolved in TCE for 15 mins. Centrifuge extractor was used to perform asphalt extraction test. The solvent collected from the extractor was recovered using a rotavapor. The prepared RAS binder were placed in a vacuum oven at 80 ℃ for 2 hours to evaporate the residual solvent.

Table 7.1 Description of the test materials

Binder abbreviation	Description
Soft binder	PG 58 – 28 Asphalt
DRH	RAS binder component dissolved and extracted using heptane
DRT	RAS binder component dissolved and extracted using TCE
SAR	Binder blend of soft asphalt and RAS binder
RAR	Binder blend of rejuvenator and RAS binder
ER	Extracted binder using mixed solvent

The extracted RAS binder was ground to fine particles (passing No. 100 sieve) to mix with rejuvenator and soft binder. The soft binder was heated in an oven at 165 ℃. Then the RAS binder particles were blended into the soft binder at target concentrations using a shear mixer with high shear rate (Huang et al., 2007) in the laboratory. The RAS binder particles blended with rejuvenator at room temperature using the shear mixer. The binder blends (referred to as SAR/RAR) (Table 7.1) were stored in an airtight container at 170 ℃ for 2 hours. The binders on the top and bottom of the binder blend were collected to test after SAR/RAR cooled down to room temperature. The soft binder was heated in the same conditions as a reference test.

7.4.2 Laboratory Testing

Laboratory testing activities in this study compared the rheological properties, molecular and fractional compositions of prepared binder and binder blends.

7.4.2.1 Mechanical Properties Testing

Prepared binder and binder blends were tested by dynamic shear rheometer (DSR) to characterize the mechanical properties as per AASHTO T 315-10 (AASHTO, 2011). The high temperature grade and modules of ER were compared with SAR and RAR. The binders were subjected to a short term aging process using the rolling thin film oven (RTFO) following AASHTO T 240-03 standard (AASHTO, 2010a) and a long-term aging process at 100 ℃ using pressure aging vessel (PAV) according to ASTM D 6521 - 13 standard (ASTM, 2010a) to investigate the antiaging performance.

7.4.2.2 Gel Permeation Chromatography

Gel permeation chromatography (GPC) was conducted for the prepared binder and binder blends to detect the delicate change of molecular size distribution within the asphalt. TOSOH EcoSEC GPC with two 4.6 mm I.D. x 15 cm-multipore columns packed with 4μm polystyrene divinylbenzene copolymer was used. The elution time was converted to molecular weight using the calibration spectrum obtained from the standard polystyrene GPC testing (Daly et al., 2013). The asphalt solution for GPC test was prepared at a concentration of 1 mg of asphalt per 1 mL of solvent tetrahydrofuran (THF). The 1 mg/mL solutions injected into a 2-mL vial and inserted in an automatic sample injector. The samples were eluted with THF, and the components concentration in the eluent was recorded.

The molecular weight distribution of asphalt was divided into three fractions, a larger molecular size (LMS) fraction, a medium molecular size (MMS) fraction and a low molecular size fraction (LMS). The proportions of LMS and SMS were adopted for the chemical structure investigation of the binder. The LMS fraction comprised components with molecular weights greater than or equal to 3000. The LMS fraction contained the components with molecular weights less than 1000. The proportion of fraction was calculated by dividing the fraction area to the total area of the chromatogram. Two replicates were measured for each sample and the average was used in the analysis.

7.5 Results and Discussions

7.5.1 Properties of RAS Components

Figure 3 shows the measured frequency sweeping modules of the DRH and DRT components as well as their mixture with a certain proportion based on laboratory testing conducted at 25 ℃. Results are presented for 5 types of blends: PG 64-22 conventional, DRH, DRH + 20%, 40% and 60% DRT. As shown in Figure 7.3, the addition of DRT into DRT increased its complex modules, stiffened the binder at all frequency range. This was expected as the DRT component mainly composed of asphaltene with high molecular weight and modules. These results indicate that the use of TCE as a solvent would generally improve the modules of extracted RAS binder. The modules of PG 64-22 asphalt were in the range of mixed binder DRH + 40% and 60% DRT.

Figure 7.4 shows the GPC chromatograms for the whole RAS binders, DRH and DRT. Heptane dissolved almost all the small molecular part and TCE dissolved most of the large molecular part of RAS binder. This result can explain the conclusion above that the module of DRT was larger than DRH because the stiffness of component usually increased with molecular weight.

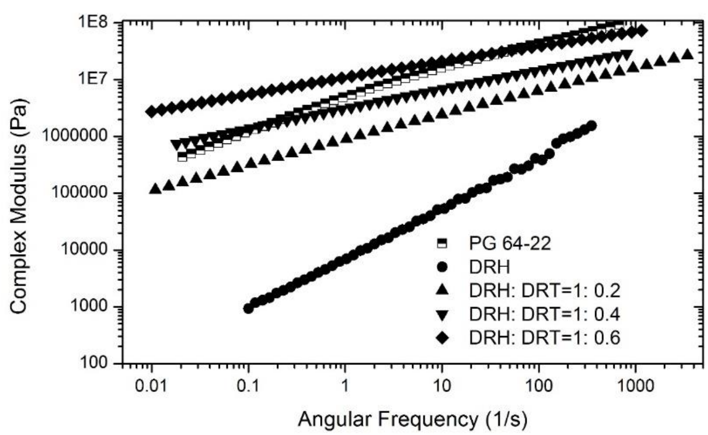


Figure 7.3 Frequency sweeping modules of binder blends (25 ℃)

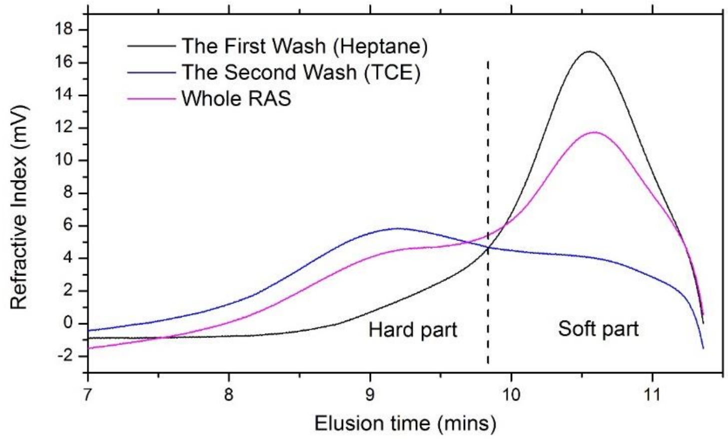


Figure 7.4 GPC chromatogram of RAS components

7.5.2 Properties of Extracted RAS Binder of Various Mixed Solvent

As heptane and TCE can obtain the soft and stiff components of RAS binder respectively, this study intended to use a mixture of two solvents to directly manufacture the extracted RAS binder with desired properties. Figure 7.5 shows the frequency sweeping modules of the RAS binders dissolved and extracted using the mixed solvent. The ratio of heptane and TCE in mixed solvent was 1: 0.1, 1: 0.2 and 1: 0.3 separately. The use of TCE as a component of the mixed solvent significantly increased the module of extracted RAS binder, stiffened the binder at all frequency range. This was expected as TCE can dissolve asphaltene which is a stiff component out of RAS. These results indicate that the use of TCE in mixed solvent would generally improve the stiffness of the binder and the properties of the extracted RAS binder could be controlled by the proportion of TCE in the mixed solvent.

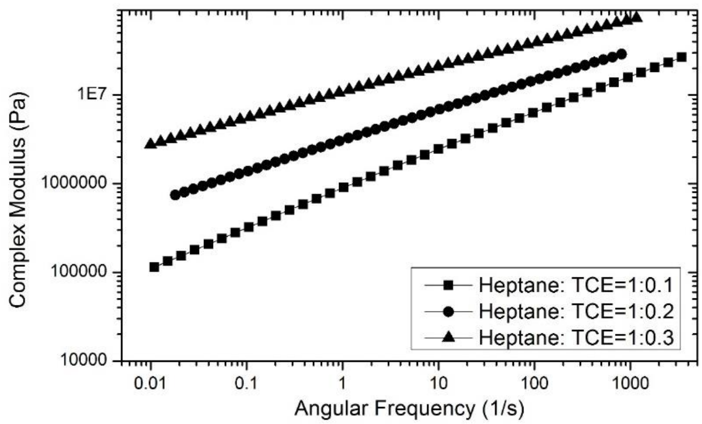


Figure 7.5 Frequency sweeping modules of extracted RAS binder of various mixed solvent

7.5.3 Properties of SAR and RAR

Table 7.2 presents the high temperature grade of the binder blend on the top and bottom of RAR and SAR sample. The results indicate that rejuvenator dissolved the RAS binder completely because the high temperature grade of binder on the top and bottom of RAR was close to each other. On the opposite, there was a significant difference on the properties of binder on the top and bottom of SAR, which suggests that RAS binder could not be effectively dissolved by the soft asphalt used in this study.

To further investigate the effect of soft asphalt on RAS binder, the RAS binder was mixed with an increased proportion of soft asphalt to produce binder blends. Figure 7.6 shows the changes of high temperature grade of binder blend on the top of SAR with RAS binder content as well as their complex modules at 25°C. The increase of RAS binder content caused a slight decrease in the high temperature grade and complex module of binder blend, which further indicates that soft asphalt used in this study did not dissolve RAS binder.

Table 7.2 Properties of binder on the top and bottom of RAR and SAR

Materials	High temperature grade (℃)
Binder on the top of RAR (5% rejuvenator)	70.9
Binder on the bottom of RAR (5% rejuvenator)	71.6
Binder on the top of SAR (10% soft asphalt)	55.1
Binder on the bottom of SAR (10% soft asphalt)	106

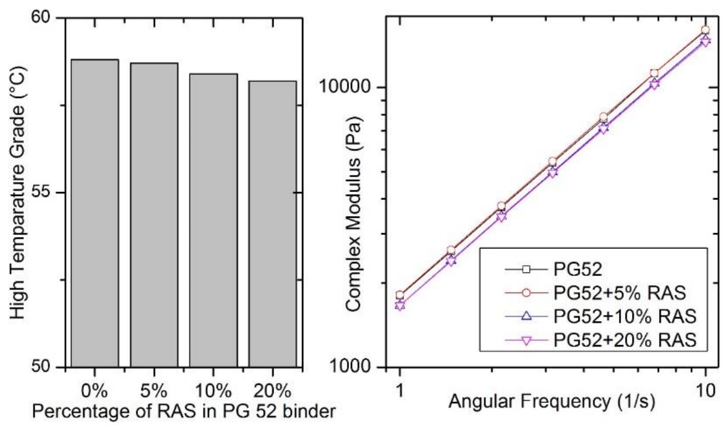


Figure 7.6 Properties of binder on the top of SAR

7.5.4 Antiaging Properties

Rejuvenator used in this study could dissolve RAS binder and produce binder blend with desired properties. Therefore, the ER produced using the proposed method was compared with RAR. The content in the mixed solvent was 12% and the rejuvenator percentage in RAP was 7%. The original stiffness of two binders was close thus was selected as the comparison objects. Figure 7.7 shows a comparison between the module changes of RAR and ER during the aging process. The module increase of RAR was obviously larger than that of ER, which suggests that the antiaging properties of ER were much better.

Figures 7.8 shows the changes of GPC chromatograms for ER and RAR during the aging process. The aging process resulted in an ignorable change in the molecular size distribution of ER but a significant decrease in a small molecules peak of RAR which of the same elision time with rejuvenator. The significant decrease in the small molecules peak of the RAR is indicative that the rejuvenator fraction of the binder blend lost due to aging or evaporation effect. Table 7.3 presents the molecular distribution and mass changes of two binders during the aging process. As shown in Table 3, the mass loss of RAP was obviously larger than ER, which can be attributed to the evaporate of rejuvenator. Two binders both expressed an increase in the large molecules percentage (LMS (%)), which was expected as polymerization process occurred due to aging effect. However, the decrease of small molecules percentage (SMS (%)) of RAR during TFOT test was obviously larger than that of ER. Small molecules can soft binder blend and decrease the module of materials. The decrease of small molecular percentage can explain the module increase of RAR during the aging process.

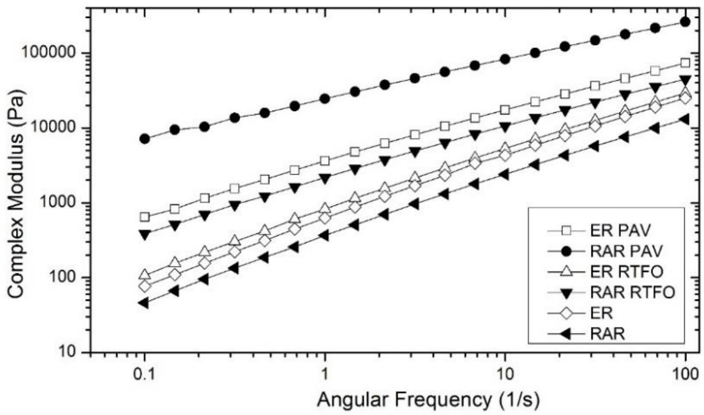


Figure 7.7 Comparison of antiaging properties of two binder blend

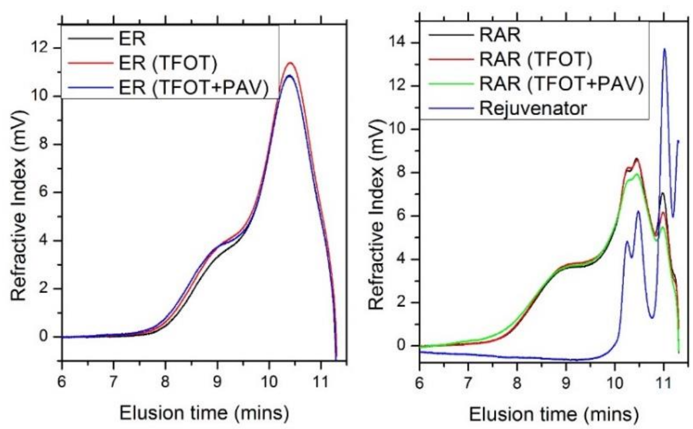


Figure 7.8 GPC chromatograms of ER and RAR during aging process

Table 7.3 Molecular distribution changes during aging process

Material	LMS (%)	SMS (%)	Mass Loss (%)
Original ER	30.51%	25.38%	0
ER (TFOT)	31.74%	26.61%	0.98%
ER (TFOT+PAV)	33.52%	25.59%	-0.35%
Original RAR	37.08%	29.16%	0
RAR (TFOT)	38.29%	25.55%	2.55%
RAR (TFOT+PAV)	40.14%	26.43%	-0.66%

7.5.5 Comparison to Common Asphalt

The creep test at low temperature is a simple approach to investigate the low temperature degree of asphalt. One ER with tested high temperature degree 75.2 ℃ and three commercial asphalt binders with various low temperature degree were subjected to RTFO and PAV aging process then tested by creep test using DSR. The shear stress was set as 50 Pa and the test was conducted at 10 ℃ and 0 ℃. Result in Figure 9 indicates that the ER with high temperature degree of 75.2 ℃ exhibits consistent creep performance at low temperature with PG 58-28 asphalt.

The creep performance at low temperature can be an indicator of low temperature degree of asphalt. The low temperature degree of the ER used in this test was approximately -28 according to creep test, which suggests that the temperature range of ER could reach 103.2 ℃ (75.2+28=103.2) and satisfy the requisites for common asphalt used in pavement.

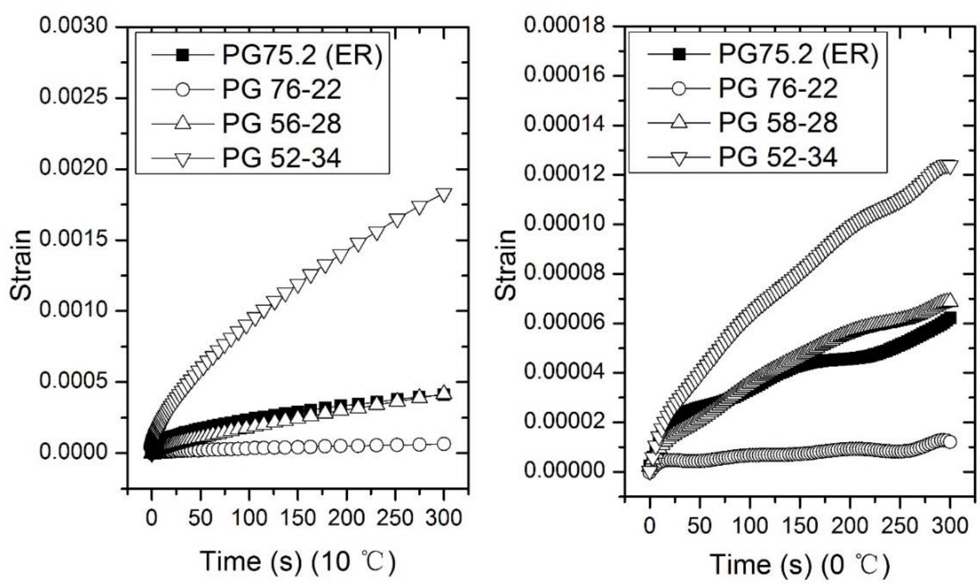


Figure 7.9 creep test at 10 ℃ and 0 ℃

7.6 Conclusions

The recycling of asphalt shingles in HMA is a very valuable approach for technical, economic, and environmental reasons. However, conventional practices of dry or wet blending tear-off asphalt shingles with the aggregates or asphalt binder prior to adding into the batch are often criticized due to the large variability of asphalt shingles properties. The amount of RAS that allowed to be added usually is limited owing to the brittle and stiff properties of RAS binder. The objective of this study is to introduce a new approach to recycling asphalt shingles in asphalt paving construction in which RAS binder was extracted using a mixed solvent and used as common asphalt. In the proposed extraction process, the recycled shingle material was dissolved using a mixed solvent of heptane and TCE and then extracted to obtain a binder with desired properties. The proposed extraction process allows for a better control of the properties and performance of asphalt binder and HMA. The performance two other approaches of using RAS into HMA, including mixed RAS binder with soft asphalt and rejuvenator, was compared with proposed extraction method. Based on the results of the experimental program, the following conclusions may be drawn:

(1) Results of DSR and GPC testing indicate that heptane dissolved the soft part (small molecule) and TCE could dissolve the stiff part (large molecule) of RAS binder.

(2) The stiffness of ER increased with the proportion of TCE in the mixed solvent, which indicates that the properties of the ER could be controlled by the proportion of the mixed solvent.

(3) The high temperature grade and module of binder blend of RAS binder and soft asphalt had no obvious increase comparing with original asphalt, which suggests that soft asphalt could not dissolve RAS binder.

(4) The antiaging properties of extracted binder using the proposed method were better than that of binder blend of RAS binder and rejuvenator because an obvious loss of rejuvenator existed during the aging process.

Chapter VIII Conclusions and Recommendations

8.1 Conclusions

A series of studies were conducted to address the blending and diffusion issues hot mix asphalt containing RAP and the utilization strategy of RAS. Several new methods including fluorescence microscopy and molecular simulation were developed to characterize the blending and diffusion process. Based on the results obtained from the aforementioned studies, the following conclusions can be summarized:

(1) The variation of aging index (AI) of asphalt on virgin aggregates were used to evaluate the blending efficiency using FTIR. The variation of AI was found to decrease with the blending degree between RAP and virgin binders. RAP particles varied in the degree of oxidation of RAP binder, and mixing RAP binder with virgin binder could reduce the heterogeneity. Comparing with hot mix, warm mix with foaming technology showed a higher blending efficiency.

(2) A new procedure was developed using fluorescence microscopy to differentiate between RAP and virgin binders as well as their blends. A new parameter, MGV based on fluorescence image, was utilized to quantitatively determine the mobilization rates of aged asphalt binder in RAP. A "Blending Chart" was generated, showing the change of MGV with RAP binder content. Ultimately, a new method was proposed to quantitatively determine the mobilization rate of aged binder in RAP by directly measuring the MGV of the binder blend.

(3) The sensitivity of MGV to aged binder content was affected by test conditions. One index, Differentiation Factor, was used to measure the sensitivity of MGV to aged binder content. Results indicate that the MGV measured at the wavelength of 450-490 nm and the exposure time of 0.5-1.5 s was most sensitive to aged binder content.

(4) For construction of a blending chart, it was found that there existed a linear relationship between MGV of a binder blend and its RAP binder content, and a quadratic relationship between MGV of a binder blend and its RAS binder content. Therefore, the relationship between MGV and aged binder content of a binder blend could be different for asphalt from diverse sources.

(5) Glass cullet was selected as a special aggregate and added into the mixtures because it has two parallel planes and can be tested by a fluorescence microscope directly. The results indicate that the mobilization rate increased with the increase of mixing time and temperature.

(6) The overall mobilization rate of a mixture could be determined by considering the surface area of large and small aggregate. Three plant-produced asphalt mixtures were tested for their blending efficiency, which included a hot mix with rejuvenator, a hot mix without rejuvenator, and a warm mix with foaming technology. Addition of rejuvenator showed a slight improvement in blending efficiency of recycled mixtures. However, the mixtures with and without rejuvenator showed only a slight difference in the degree of oxidation. Therefore, compared with warm mix, adding rejuvenator had a limited effect on blending efficiency.

(7) A study has been conducted to investigate the diffusion process of virgin and aged binders using MD simulations. The results of simulation indicate that the diffusion rate of asphaltic molecules increase with the rising molecular weight. The influence of temperature on the diffusion of asphaltenes was obvious larger than resin and oil, which suggests that the diffusion of large molecules was the critical step that controlled the diffusion rate of the whole structure. The results of MD simulation

were in agreement with the GPC conclusions, and thus can be applied to investigate the diffusion between virgin and aged binders.

(8) In the single model, the diffusion coefficient of virgin binder was higher than aged binder; whereas, the diffusion coefficient of virgin binder has the same diffusion rate with aged binder in layer model stage II. This result indicates that, in an inter-diffusion process of binders, the diffusion coefficient was not only determined by the diffusion ability itself, but also influenced by properties of the acceptor on the opposite side.

(9) The simulation results show that applying rejuvenator into virgin binder first had no obvious benefit for increasing the diffusion rate of the whole layer; whereas, adding rejuvenator into aged binder first could significant accelerate the diffusion of the whole model.

(10) A new laboratory test method was proposed based on fluorescence microscopy to determine the diffusion coefficient of asphalt. Fick's second law was first applied to obtain the analytical solution of the virgin and aged asphalt distribution in a two-layered model. The concentration of virgin or aged asphalt in the two-layered sample was then back-calculated from the measured MGV of a fluorescence image. Diffusion coefficient was determined by fitting the theoretical solution to the laboratory concentration measurements by the fluorescence microscopy method. The proposed fluorescence microscopy method was verified with the diffusion coefficients determined using the DSR method. In addition, the free volume theory was also utilized to predict the diffusion coefficients of asphalt.

(11) Fluorescence-measured diffusion coefficient was linear with temperature in the log plot within the temperature range of 80–160 °C. The DSR method for

determining diffusion coefficient was used to verify the fluorescence microscopy method. The diffusion coefficient from fluorescence microscopy was of the same magnitude to, but slightly lower than that from the DSR method. The diffusion-temperature function could be reasonably estimated using free volume theory, which allows for a rapid estimate of diffusion coefficient from readily available data.

(12) A new approach to recycling asphalt shingles in asphalt paving construction in which RAS binder was extracted using a mixed solvent and used as common asphalt was proposed. In the proposed extraction process, the recycled shingle material was dissolved using a mixed solvent of heptane and TCE and then extracted to obtain a binder with desired properties. The proposed extraction process allows for a better control of the properties and performance of asphalt binder and HMA. The performance two other approaches of using RAS into HMA, including mixed RAS binder with soft asphalt and rejuvenator, was compared with proposed extraction method.

(13) Results of DSR and GPC testing indicate that heptane dissolved the soft part (small molecule) and TCE could dissolve the stiff part (large molecule) of RAS binder. The stiffness of ER increased with the proportion of TCE in the mixed solvent, which indicates that the properties of the ER could be controlled by the proportion of the mixed solvent. The high temperature grade and module of binder blend of RAS binder and soft asphalt had no obvious increase comparing with original asphalt, which suggests that soft asphalt could not dissolve RAS binder.

(14) The antiaging properties of extracted binder using the proposed method were better than that of binder blend of RAS binder and rejuvenator because an obvious loss of rejuvenator existed during the aging process.

8.2 Recommendations

On the basis of the conclusions obtained in this study, the following recommendations can be made:

(1) The glass cullet used as tracking aggregates may not be able to fully represent the mixing scenario. The shape, size, absorption, surface texture, and other characteristics of aggregates could affect the mobilization rate of aged binder. Further research is needed to investigate the effects of these factors and to find more suitable tracking materials.

(2) The two-layered model and the laboratory fluorescence microscopy method developed in this study were validated to be capable of determining diffusion coefficient of two types of SHRP asphalt. It is recommended that more asphalt types, aged binder types, and mixture types be used for validation of the proposed method and investigation of asphalt diffusion phenomenon.

(3) This study represents a first step toward evaluating the proposed extraction process to utilize RAS in asphalt paving construction. Based on the results of this study, further research is recommended to evaluate the performance of asphalt mixture prepared using the asphalt binder manufactured with the proposed approach.

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Vita

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