Insights into the Homogeneity of Asphalt Mixtures Containing Reclaimed Asphalt Pavement (RAP)

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Declaration

The work described in this thesis was conducted at the RWTH Aachen University, Institute of Highway Engineering, between October 2017 and July 2021. I declare that the work is my own and has not been submitted for another university degree.

Abstract

Over the past two decades, reclaimed asphalt pavement (RAP) has received increasing attention because of climate change and resource-saving needs. The current high reuse rate of old asphalt fundamentally reduces the landfill areas of the disposal and its related environmental impacts. Hence, in addition to reducing the construction cost and the consumption of natural resources, the use of RAP can also create significant environmental benefits, such as solving the disposal problems.

This thesis was carried out focusing on the homogeneity of asphalt mixture containing RAP materials from multi-scale perspectives. The homogeneity of asphalt mixtures, to a great extent, determines the performance of asphalt mixtures provided that with an appropriate material design. The distribution of aggregates, binder migration, and diffusion of binders in the mixing process of loose asphalt mixtures are influenced by the mixing apparatus, mixing temperatures, and mixing durations, etc. Under the multi-scale framework, therefore, this thesis considered the variables including mixing temperature, mixing time, thermal conductivity, aggregate type to obtain an insight into the homogeneity of asphalt mixtures containing RAP.

The influence of mixing conditions on the macro-scale homogeneity was investigated. The experimental design considered a thermal-equilibrium mixing environment. Multi-direction indirect tensile modulus and morphological characterization were performed. The results indicated that a long mixing time benefited the formation of homogenous state, in particular for the breaking of clusters in RAP materials. As the mixing time increased, the macro-homogeneity of asphalt mixture experienced from 'momentary homogeneity' state to 'real homogeneity' state (Macro-scale mixing model). Whereas, a high mixing temperature played a negative role in the distribution of materials, claimed as that the increase of temperature would obstacle the breaking of clusters and prolong the state shift toward a 'real homogeneity' state.

The influence of mixing conditions on the mesoscale homogeneity in both thermal-equilibrium and thermal-non-equilibrium environments were investigated. The dynamic shear rheometer (DSR) and Fourier Transform Infrared Spectroscopy (FTIR) are adopted as the measurement methods. The results indicated that, in terms of the migration and diffusion, the mixing temperature played a more important role than mixing time. Two-stage model (Micro- and Meso- scale mixing model) were proposed as the migration-dominated stage followed by the diffusion-dominated stage. In addition, the Asymmetric Gaussian Model (AGM) was developed to quantitatively describe the blending rate with mixing time. The diffusion between RAP binder and new bitumen was tightly associated with the meso-scale homogeneity of asphalt mixtures (migration of binders). In another word, the diffusion occurred only if the RAP binder and new bitumen interacted.

The molecular dynamics simulation was performed in the investigation of aging gradient in bitumen and the diffusion between RAP binder and new bitumen. The results indicated that the aging gradient existed along with the depth. At the molecular scale, the interface between virgin bitumen and aged can be quickly achieved due to the migration of resin components. However, the diffusion process was considerably slow compared with the interface formation. Moreover, the aggregate layer, by adhering to the polar molecules in bitumen binders, can accelerate the diffusion process between new and aged bitumen.

In addition to illustrating the achievements, this thesis proposed three relative research topics deserved for future work, which are (1) Quantitative characterization of sample morphology from two-dimension (2D) to three-dimension (3D); (2) The development of Multi-Scale Synchro-adjust Methodology (MSM) towards a near-perfect homogenous asphalt mixture; (3) The use of computer-aided methods in the design of asphalt mixtures containing RAP from begin to the end.

Keywords: Reclaimed asphalt pavement (RAP); Multi-scale homogeneity; Mechanical performance; Mixing temperature; Mixing time; Diffusion; Molecular dynamics simulation

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1 Introduction

1.1 Background

As the raw materials (virgin mineral aggregate and asphalt binder) for asphalt mixtures are non-renewable resources, their availability declines gradually and their prices increase dramatically. For instance, it was reported that the 2006 price ($400 per ton) of asphalt binders in the United States increased by almost 50% over the 2005 prices ($250 per ton) (Apeagyei, Clark and Rorrer, 2013). It is, therefore, necessary to find an alternative substance for these raw materials so that the construction of pavement would not be constrained by the reducing invaluable natural resources and increasing prices.

From the 1930s to the 1980s, reclaimed asphalt pavement (RAP) had been initially used in pavement paving (Nguyen, 2009a; Copeland, 2011; Chen *et al.*, 2019; Ding *et al.*, 2019). However, the use of RAP fell off dramatically in the 1990s on account of the high-performance requirement. Interestingly, over the past two decades, RAP has received increasing attention again because of climate change and resource-saving needs (Bressi *et al.*, 2018; Zheng *et al.*, 2019). By far, it has been extensively used in road construction and rehabilitation. As the RAP was historically disposed of in landfills, the current high reuse rate of old asphalt fundamentally reduces the landfill areas of the disposal and its related environmental impacts (Rinaldini et al., 2014). Hence, in addition to reducing the construction cost and the consumption of natural resources, the use of RAP can also create significant environmental benefits, such as solving the disposal problems (Mantalovas and Di Mino, 2019). However, current practice indicates that recycled asphalt mixtures with a high RAP amount (beyond 50%) are not recommended as that the quality of produced recycled asphalt mixtures cannot be well controlled (Newcomb, Ray Brown and Epps, 2007). Admittedly, the incorporation of RAP in pavement reconstruction encounters varying challenges that attract many researchers working on the asphalt mixtures with RAP (Karlsson and Isacsson, 2006). Such kinds of challenges are attributed to the variabilities of RAP properties, material designs, and recycling procedures. Concerning the recycling procedure, recycled asphalt mixtures are expected to reach a homogeneous state from multi-scale perspectives, therefore, behaving as a satisfying mechanical performance, as shown in Figure 1.1.

The homogeneity of RAP material significantly varies with the original pavements where the RAP obtains. Whether a pavement should be recycled is influenced by many factors, depending on the government policies, industry norms, and the actual pavement service condition in terms of distresses. From this perspective, in the author's opinion, the study of the homogeneity of RAP materials is almost untraceable since the material varies with the sources.

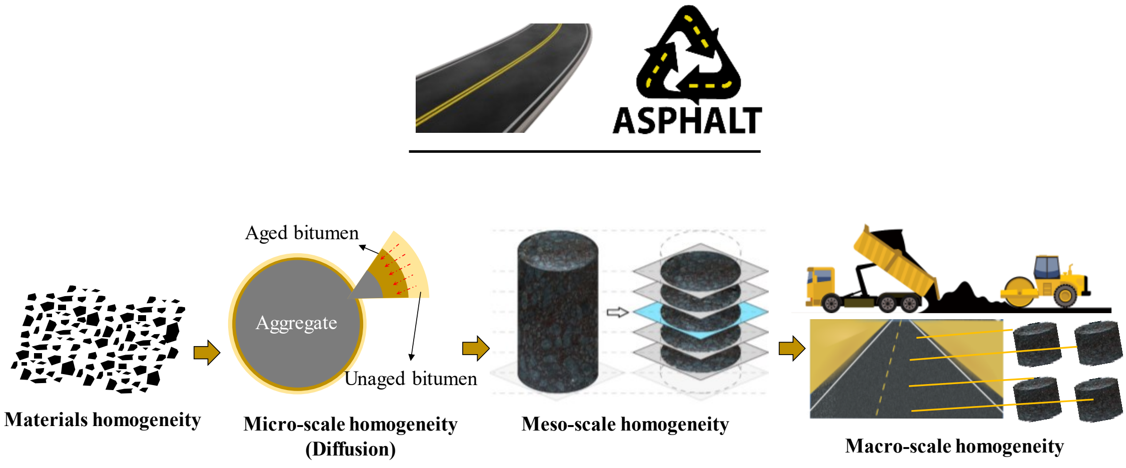

Figure 1.1 Conceptions of homogeneity concerning recycled asphalt mixtures

As illustrated in Figure 1.1, the macro-scale homogeneity refers to the performance consistency of asphalt mixtures paved in a full-scale pavement. It is tightly linked with the mixing and paving of loose mixtures before the compaction. In an in-situ condition, the characterization of macro-scale homogeneity can be estimated by measuring the cored samples from new compacted pavements. At this scale, the research object is the compacted asphalt mixture.

Meso-scale homogeneity of asphalt includes two perspectives. The first one reflects the distribution of aggregates (aggregate skeleton), which is also concerned in conventional asphalt mixtures. The other one, particularly for asphalt mixtures containing RAP, is about the property consistency of binder film at different positions. Usually, at least two types of binders exist in one asphalt mixture containing RAP. At this scale, the research object are aggregates and binder films coating on aggregates.

Micro-scale homogeneity of asphalt mixtures is defined as the property consistency of binder film. This issue has been extensively studied, known as the diffusion of rejuvenator or bitumen in the RAP binders. Under the multi-scale framework, this research included the diffusion issue into the study of micro-scale homogeneity. At this scale, the research object is the diffusion sample extracted from the surface of aggregates. The molecular-scale homogeneity is usually associated with the micro-scale due to that the molecular-scale motion causes the macroscopic diffusion. In addition, the molecular-scale homogeneity of binders is another way to feature the micro-scale homogeneity of recycled asphalt mixtures, which focuses on the mechanism of micro-scale diffusion.

No doubt, the homogeneity of recycled asphalt mixtures basically determines the performance of asphalt mixtures. In practice, the mixing plant cannot be changed easily. However, the mixing temperatures and mixing durations can be altered toward a better production of asphalt mixtures with RAP. Due to the limited mixing time, it can be imaged that the homogeneities seen from each scale are not independent.

1.2 Literature review

1.2.1 Introduction

Reclaimed asphalt pavement (RAP) refers to the old material milled up or ripped off the pavement (Karlsson and Isacsson, 2006). When the pavement reaches its design period, the pavement has to be removed for reconstruction. However, the materials retained are still valuable. In the early 1970s, many countries worldwide encouraged recycling the RAP and stockpiled them for future use (Epps, 1978). The obtained RAP materials can be used in different ways. In general, Table 1.1 presents some definitions concerning pavement recycling.

Table 1.1 Methods and strategies for asphalt recycling

<table>
<tr><th></th><th colspan="3">Methods</th><th>Reference</th></tr>
<tr><td rowspan="3">Early-stage</td><td colspan="3">Surface recycling</td><td rowspan="3">(Epps, 1978; Epps et al., 1980)</td></tr>
<tr><td colspan="3">In-place surface and base recycling</td></tr>
<tr><td colspan="3">Central-plant recycling</td></tr>
<tr><td rowspan="7">Current stage</td><td rowspan="3">In-plant</td><td colspan="2">Cold (below 70°C)</td><td rowspan="7">(Karlsson and Isacsson, 2006)</td></tr>
<tr><td colspan="2">Warm (between 70°C and 120°C)</td></tr>
<tr><td colspan="2">Hot (above 120 °C)</td></tr>
<tr><td rowspan="4">In-place</td><td rowspan="2">Surface recycling</td><td>Remixing</td></tr>
<tr><td>Repaving</td></tr>
<tr><td colspan="2">Cold in-place asphalt recycling</td></tr>
<tr><td colspan="2">Full-depth reclamation</td></tr>
</table>

The research of asphalt mixtures with RAP encompasses many issues. The available literature can be divided into four main topics:1) Performance evaluation of asphalt mixtures incorporated with RAP; 2) Development of innovative rejuvenators; 3) Innovative pavement recycling technology (in production); 4) Enhancement or modification of asphalt mixtures incorporated with RAP. To understand where each research contributes to current work, one must understand how the production process affects the final performance of reproduced asphalt mixtures. Using optimal production procedure for asphalt mixtures is the premise of each topic stated above.

This literature review covers specific areas that either the analysis of influence factors or are involved in the homogeneity estimation of asphalt mixtures. It begins by rounded performance evaluation for asphalt mixtures containing RAP in previous research such as high-temperature anti-rutting performance, low-temperature anti-cracking performance, fatigue performance, and moisture resistance property, etc. The second section of this literature review describes mixing-related studies of recycled asphalt mixtures (RAM). A detailed review is presented from macroscopic to the molecular level, concentrating on the structural homogeneity, blend efficiency, or diffusion (essentially the homogeneity issue) of asphalt mixtures.

1.2.2 Performance-related studies of asphalt mixtures with RAP

Stiffness/rutting resistance

As the presence of aged bitumen in RAP materials, the produced asphalt mixtures would have a higher stiffness modulus than conventional ones. Pham et al. (Pham *et al.*, 2015) investigated the 3D linear behavior of warm mix asphalts produced with the RAP materials and additives. In their research, the time-temperature superposition principle was verified for asphalt specimens. Base on this, modulus derived from a normalized master curve were compared, and the results showed an increased modulus when the RAP materials were used. Huang et al. (Huang, Shu and Vukosavljevic, 2011) studied hot-mix asphalt mixtures with No.4 sieve screened reclaimed asphalt pavement and found that the inclusion of RAP generally increased the stiffness of mixtures but compromised their cracking resistance capacity.

Low-temperature cracking

The low temperature cracking of asphalt mixtures containing the RAP and RAS was evaluated by Tapsoba et al. (Tapsoba *et al.*, 2016) using the Thermal Stress Restrained Specimen Test (TSRST).

0%, 15%, 20%, and 25% RAP contents together with RAS content from 0% to 10% were considered to produce different asphalt mixtures. The investigation results stated that, within limited incorporation of RAP and RAS (15% RAP and 5% RAS), the cracking temperature of asphalt mixtures would not significantly affect the reference mix. However, asphalt mixtures with a high substitution rate of RAP (≥20%) remarkably deteriorated the low-temperature property of mixtures.

Similarly, Stimilli et al. (Stimilli *et al.*, 2017) used 40% RAP content to produce asphalt mixtures with different types and contents of SBS modified bitumen. A mix with 25% RAP content was produced as the reference one. Subsequently, these produced asphalt mixtures were subjected to the Asphalt Thermal Cracking analyzer (ATCA) test to compare the low-temperature performance. It was reported that well-processed RAP materials and appropriate design methods were beneficial in increasing RAP content. Besides, incorporating RAP materials could enhance the capacity to dissipate thermal stresses, which played a favorable role in stress relaxation.

Fatigue resistance

Bankowski et al. (Bankowski, 2018) evaluated fatigue life using 50% RAP content. In specific, asphalt concrete mixtures AC22P and high modulus asphalt concrete ACWMS16 with 50% contents of RAP were measured, which indicating a positive effect in fatigue life. Cao et al. (Cao, Mohammad and Elseifi, 2017; Cao *et al.*, 2018) acquired asphalt mixtures from the full-scale test lanes. The full-scale test lanes included different asphalt mixtures containing RAP and RAS materials. After that, the fatigue life of reproduced asphalt mixtures was estimated based on the continuum damage method. It was found that the incorporation of RAP material would jeopardize fatigue life. Zhao et al. (Zhao *et al.*, 2012) studied asphalt mixtures with a high RAP percentage. They claimed that mixtures with a high RAP content (up to 50%) conduced superior resistance to rutting, moisture, and better fatigue performance. Cong et al. (Cong, Zhang and Liu, 2016) and Mogawer et al. (Mogawer *et al.*, 2012a) reported the decrease of fatigue life, while Aravind et al. (Aravind and Das, 2007) reported the increase of fatigue life when asphalt mixtures were produced with RAP materials. In addition, the reclaimed asphalt pavement has also been successfully applied in warm-mixed asphalt mixtures for sustainable development (López et al., 2019).

Moisture resistance

Doyle and Howard (Doyle and Howard, 2013) attempted to use the reclaimed asphalt pavement to improve the rutting resistance and moisture damage resistance of warm mixed asphalt. For this reason, more than 25% RAP content was used to produce the asphalt mixtures. It was recommended that the PURWheel wet (PW-wet) test proposed in this study was better than the Tensile strength ratio (TSR) test. Based on the PW-wet test, it was found that moisture damage performance of high RAP content WMA appeared to be similar to or not considerably worse than current practice control mixtures.

Singh et al. (Singh, Chitragar and Ashish, 2017) compared the moisture resistance of recycled asphalt mixtures with different RAP contents (0% to 40%). The moisture resistance ability was estimated using the TSR test. Besides, the hot mix asphalt mixture and warm mix asphalt mixture were produced, respectively. Experimental evidence indicated that hot mix recycled asphalt mixture had a better moisture resistance ability than the one produced using warm mix technology.

Kushwaha and Swami (Kushwaha and Swami, 2019) studied the moisture susceptibility of foamed bitumen mix containing RAP. Indirect tensile strength (ITS) test was used to evaluate the mechanical performance of asphalt mixes. Accordingly, this study demonstrated that using 100% RAP materials for reconstruction was possible.

Goli et al. (Goli and Latifi, 2020) combined the warm mix asphalt (WMA) technology and recycling technology to produce asphalt mixtures. In particular, the produced asphalt mixtures against moisture damage were investigated. Results indicated that the incorporation of RAP could enhance the stiffness of asphalt performance in dry conditions, whereas usually inducing poor resistance to the moisture damage. TSR value increased as the increase of RAP content up to 30%.

1.2.3 Mixing-related studies of asphalt mixtures with RAP

The mixing condition between aged and virgin asphalt binders is the main factor that determines the performance of reclaimed mixtures, and it generally contains two major mechanisms: mechanical mixing and diffusion. Mechanical mixing can distribute aggregates and benefit the migration of rejuvenator or virgin bitumen. Diffusion can be referred to as interactions between substances, which are closely related to the mixing temperature. So far, many researchers have attempted to figure out how diffusion takes place in the mixing process. Below some critical research previously reported were concluded regarding these two perspectives.

Mechanical mixing

The mixing mechanism of recycled asphalt mixtures differs from the conventional ones as the incorporation of RAP. Besides, the clusters bonded by aged bitumen essentially exist in the RAP materials, which means more external efforts should be applied before reaching a homogeneity state of all components. On the other hand, the production process of asphalt mixture containing RAP is actually unlike the conventional ones in practice. Usually, the virgin aggregate is superheated to a specific temperature. In what follows, the RAP materials are blended with superheated aggregates. Through the thermal conductivity, the RAP is then softened and subsequently crushed before final mechanical mixing.

There is limited literature that mainly focuses on the influence of mechanical mixing on the homogeneity of asphalt mixtures containing RAP. The blending degree is a more attractive topic for mixing-related studies. Bressi et al. (Bressi *et al.*, 2016; Bressi, Dumont and Partl, 2016; Bueche *et al.*, 2016) defined the clustering phenomenon as the agglomeration of RAP particles formed either before or during the new mixing process and stated that the formation of RAP clusters could decrease the degree of blending between the RAP and the new binders.

Nguyen (Nguyen, 2009a) studied the effects of laboratory mixing methods and RAP materials on the performance of hot recycled asphalt mixtures. The mixing procedures noted as the black rock (BR), complete blending (CB), the SHRP procedure, and field simulation methods were considered to compare different mixing mechanisms that probably existed in practice. The virgin bitumen was intendedly dyed for distinguishing from the aged bitumen in RAP materials. In addition, different sizes of RAP clusters were also invented as the concerned variable of the mixing mechanism. The variation of indirect tensile stiffness modulus measured in four directions examined the heterogeneity of recycled asphalt mixtures. The results indicated that a longer mixing time would reduce the variation of stiffness values.

Eddhahak-Ouni et al. (Eddhahak-Ouni *et al.*, 2012) reported an experimental work focusing on the homogeneity evaluation of asphalt mixtures with high RAP content (70%). A multi-staged extraction and recovery procedure was carried out. After that, conventional tests and FTIR tests were performed for further analysis. The results indicated bad remobilization of the virgin bitumen in the hot recycled bituminous mixture.

Zhang et al. (Zhang, Wen and Hobbs, 2015) used the discrete element method (DEM) to simulate the temperature evolution of superheated virgin aggregate and claimed that a longer mixing time should be applied for the case with higher RAP content and higher RAP moisture.

Wu et al. (Wu et al., 2018) investigated the mixing process under 12 combinations of mixing times and RAP preheating temperatures based on the indirect tensile stiffness modulus test and color image analysis. Results indicated that the asynchronous breaking of clusters caused the deterioration of homogeneity.

Diffusion

Using the Abson recovery method, Zearley et al. (Zearley, 1979) demonstrated the diffusion between virgin and aged bitumen in the hot recycling process. In the case of a new non-recycled mix, the penetrations of bitumen from two increments are identical. In contrast, for the recycled mix, the penetration of bitumen from the first increment was expected higher. Based on comparing different recycling projects conducted during 1977, 1977, and 1978, the selective absorption of the lighter fractions in bitumen reversed the expected results when a large amount of shale was used as virgin aggregates.

Carpenter and Wolosick (Carpenter and Wolosick, 1980) investigated the influence of rejuvenator on the hot-mixed recycled materials. A 20 percent modifier was added directly into 100% recycled asphalt mixtures to soften the aged bitumen in their study. Immediately after the sample preparation, it was reported that the resilient modulus of recycled asphalt mixtures was high. However, the resilient modulus decreased considerably after one week. The research was designated for the study of the diffusion process of rejuvenator coated on the aged bitumen. Accordingly, a significant achievement in this study is the proposed diffusion model, which can adequately explain the evolution of mechanical performance with time. The diffusion model claimed that, after mixing, the amount of rejuvenator penetrating in the aged bitumen is limited.

In 1983, Lee et al. (Lee, Terrel and Mahoney, 1983) reported designated tests conducted in the laboratory to feature mixing efficiency. For this purpose, a resilient modulus test was carried on samples mixed at different conditions (mixing time, mixing temperature, recycling agent). Although the variation in resilient modulus of inadequately mixed samples was higher than that of adequately mixed ones, the significance seemed insufficient to identify the influence with expected accuracy. Thus, a resilient modulus test was not recommended. Alternatively, they selected the dye print technique to characterize the mixing efficiency. It was demonstrated that the dispersion of the recycling agent no longer occurred or can be ignored after the compaction, and hence, adequately mixing before compaction for recycled asphalt mixture is essential. The dye print technique was also proved a versatile approach successfully used in some field evaluation.

Karlsson and Isacsson (R Karlsson and Isacsson, 2003) proposed using a well-defined substance as markers to monitor the diffusion process in bitumen. To this end, two-layer samples consisted of diffusant and bitumen were prepared and then subjected to the FTIR-ATR (Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance) measurements. It was claimed that using proper substance could effectively trace the diffusion process in bitumen. However, it is challenging work to select a suitable substance. More importantly, many influencing factors were still vague, which induced the variation between results predicted by Einstein-Stokes equation and measurements.

Al-Qadi et al. (Al-Qadi, Elseifi and Carpenter, 2007) published a report focusing on the determination of usable residual asphalt binder in RAP. In this report, a set of mixtures containing RAP (0%, 20%, 40%) was prepared, followed by the dynamic modulus measurement. Also, the recovered, virgin, and binder blends were tested using the dynamic shear rheometer. The results indicated that it was not wise to use the dynamic modulus to indicate how much active RAP binder in the mixing. The reason is the selective absorption effect. Finally, this study claimed that the proportion of binder in RAP attended the mixing and contributed to the final performance of recycled asphalt mixtures.

Navaro et al. (Navaro *et al.*, 2012) qualified the progress in the degree of blending between the virgin bitumen and the RAP binder using the image analysis method. The images used for analysis were taken under white light (WL) and ultraviolet light (UVL). In this case, microscopic observations can be achieved to distinguish the virgin bitumen and RAP binder further. The relationship between temperatures and diffusion efficiency was studied. The results indicated that a temperature reduction by 30°C could result in a mixing time increase by two or three folds.

Bowers et al. (Bowers, 2013; B F Bowers *et al.*, 2014; Benjamin F. Bowers *et al.*, 2014) aimed to use the chemical methodology to identify the diffusion between virgin and aged bitumen. Many analytical chemistry methods were adopted in his research, including Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR). Diffusion samples were obtained using the staged extraction method. It was found that the complex modulus master curve of the diffusion sample showed good agreement with the blending ratios.

Table 1.2 Summary of methods to study the diffusion in the recycling process

Methods	Reference
Mechanical performance (Resilient modulus)	(Carpenter and Wolosick, 1980)
Abson recovery method and penetration characterization	(Zearley, 1979)
Resilient test and Dye print technique	(Lee, Terrel and Mahoney, 1983)
FTIR-ATR and well-defined substance as markers	(R Karlsson and Isacsson, 2003)
Staged extraction and recovery	(Huang *et al.*, 2005a)
Dynamic modulus test, fracture energy test, SEM (not applicable)	(Imad L. Al-Qadi, Mostafa A. Elseifi, 2007) (Castorena, Pape and Mooney, 2016)
Analytical chemistry methods were adopted, including Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR)	(Bowers, 2013; B F Bowers *et al.*, 2014; Benjamin F. Bowers *et al.*, 2014)
DSR	(Ashtiani, Mogawer and Austerman, 2018)
Atomic force microscopy (AFM)	(Nahar *et al.*, 2013) (AbuQtaish *et al.*, 2018)
Image processing method	(Navaro *et al.*, 2012)
Thin-layer chromatography with flame ionization detection (TLC-FID)	(Cong *et al.*, 2016)
Gas Chromatography-Mass Spectrometer (GC-MS) tracer analysis	(Xiao *et al.*, 2017)
Fluorescence Microscopy	(Ding, Huang and Shu, 2017)

Nahar et al. (Nahar *et al.*, 2014) investigated the microstructures between the virgin and the aged asphalt binders from RAP using atomic force microscopy (AFM). They pointed out that a blending zone existed during the process. The morphology of the blending zone (spatial extent of about 50 μm) exhibits domains of a wide range of microstructure sizes (160 nm to 2.07 μm). It can be considered to be a wholly blended new material. Additionally, a design formula is proposed that relates the spatial dimensions of the blending zone to temperature and mixing time.

In recent five years, the diffusion characteristics of rejuvenators in aged bitumen were studied by many innovative methodologies. With the aid of thin-layer chromatography with flame ionization detection (TLC-FID), Cong et al. (Cong *et al.*, 2016) illustrated the effects of the thickness and types of rejuvenators on the diffusion rate. In the recycled asphalt mixtures, the temperature has a significant influence on the diffusion coefficient. However, the effect of the thickness of the rejuvenator on the diffusion coefficient is not apparent. Xiao et al. (Xiao *et al.*, 2017) performed the study by image thresholding and Gas Chromatography-Mass Spectrometer (GC-MS) tracer analysis. The results showed that image threshold analysis and tracer method could visualize the diffusion process intuitively.

Molecular dynamic simulation

In the past decades, molecular dynamic simulation was popularized in the study of bituminous materials since some reasonable molecular models of bitumen were proposed. For this reason, molecular dynamics simulation has been introduced to study the diffusion process. Ding et al. (Ding *et al.*, 2016) used molecular dynamics (MD) to simulate the diffusion between virgin and aged asphalt binders, which further revealed that applying rejuvenator into aged binder first is capable of significantly accelerating the diffusion between virgin and aged asphalt binders. Also, Ding et al. (Ding, Huang and Shu, 2017) applied the Fluorescence Microscopy (FM) for quantifying the mobilization rate of aged asphalt binder.

Xu et al. (Xu and Wang, 2018a) constructed a three-layer model consisted of rejuvenator, virgin bitumen, and aged bitumen to study the diffusion and interaction mechanism. In this study, the radial distribution functions (RDF), Mean square displacement (MSD), and inter-diffusion coefficients were used to characterize the nanoaggregate and translation mobility. Furthermore, in another study, a two-layer model composed of the rejuvenator and RAP binders was built (Xu, Wang and Sun, 2018). Subsequently, the effect of rejuvenators on the molecular interaction of saturate, aromatic, resin, and asphaltene (SARA) fractions was investigated. Using the molecular dynamics simulation, Cui et al. (Cui *et al.*, 2020) studied physical conditions on rejuvenators' diffusion behavior in aged bitumen. The coupled effect of water and temperature were mainly discussed in the results. Xu et al. (Xu *et al.*, 2019) also performed the molecular dynamics simulation to study bitumen rejuvenators' diffusion. The results claimed that, apart from the thermal motion, the molecular forces also drive the diffusion process. Besides, it was reported that the temperature was the decisive factor determining the motion of aged bitumen at the molecular scale.

1.3 Objectives

By far, many researchers focus on varying research topics such as new technologies for higher incorporation of amount, performance evaluation of asphalt mixtures, the blending efficiency of asphalt mixtures with RAP, the development of high-efficiency rejuvenators, the diffusion mechanism between rejuvenators and RAP binders. Nevertheless, a limited number of studies center on the homogeneity of asphalt mixtures containing RAP materials. Moreover, the blending efficiency and diffusion were concluded in the conception of multi-scale homogeneity proposed in this thesis. Enlightened by the background, this thesis was conducted to provide an insight into the multi-scale homogeneity of asphalt mixtures blended with RAP. Fundamentally, the research in this thesis is concerned with four areas:

- Estimation of multi-scale homogeneity for recycled asphalt mixtures
- The influence of mixing conditions on the multi-scale homogeneity
- The influence of thermal conductivity on the multi-scale homogeneity
- The influence of aggregate characteristic on the multi-scale homogeneity

1.4 The present work

The scope of the thesis consists of a literature review followed by five chapters, each focusing on one or two of the four objectives of the thesis, and finally, a chapter presenting the final discussion, conclusions, and recommendations for future work.

Chapter 1 presents state of the art concerning the present knowledge about the application of RAP in the pavement, homogeneity issues of asphalt mixtures containing RAP, and current use of molecular dynamics simulation in bitumen and asphalt.

Chapter 2 investigates the influence of mixing conditions on the macro-scale homogeneity. The experimental design considers a thermal-equilibrium mixing environment. Multi-direction indirect tensile modulus is used as the estimation indicator. In addition, morphological characterization is performed to evaluate the macro-scale homogeneity of produced asphalt mixtures.

Chapter 3 introduces the influence of mixing conditions on the mesoscale homogeneity of asphalt mixtures. The experimental design considers a thermal-equilibrium mixing environment. The dynamic shear rheometer (DSR) and Fourier Transform Infrared Spectroscopy (FTIR) are adopted as the measurement methods.

Chapter 4 also pays attention on the influence of mixing conditions on the mesoscale homogeneity of asphalt mixtures. Unlike the Chapter 3, the experimental design considers a thermal-non-equilibrium environment. The dynamic shear rheometer (DSR) and Fourier Transform Infrared Spectroscopy (FTIR) are also used. Besides, in the chapter, the blending efficiency and the evolution of blending rate are discussed in detail.

Chapter 5 studies the thermal-oxidative aging mechanism of virgin bitumen through experiments and molecular dynamic simulation. This study is performed to see whether the aging gradient exists in RAP binders. From the micro-scale, the aging gradient could contribute to the inhomogeneity of asphalt mixtures with RAP.

Chapter 6 shows a molecular-scale investigation of diffused samples in the mixing. The molecular scale cannot be qualified through experiments, and therefore, the molecular dynamics simulation is carried out. In specific, the influence of temperature on the diffusion process is analyzed. However, the influence of simulation time was not included in this study, which contributes little to the purpose of this study.

Chapter 7 summarizes the conclusions achieved from chapter 2 to chapter 6. Also, some recommendations concerning future work are proposed.

Figure 1.2 presents the research framework of this thesis.

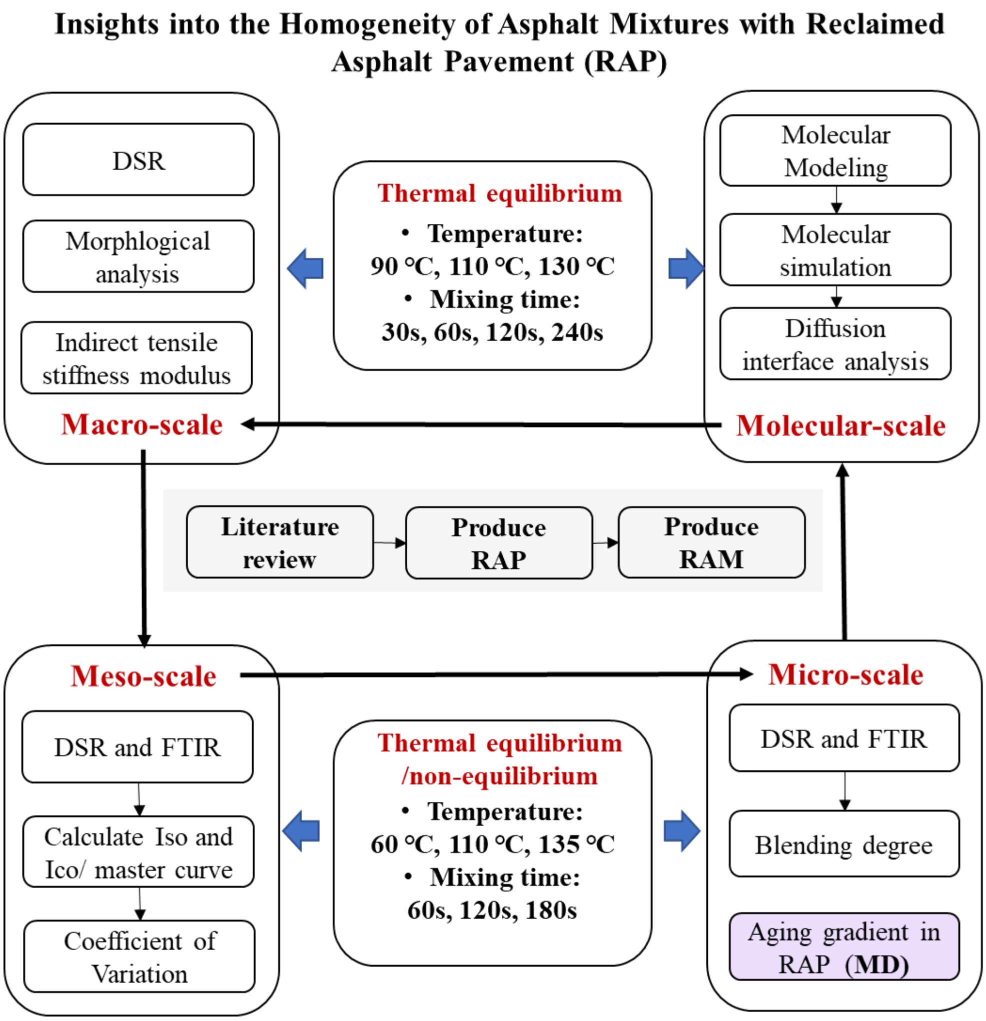

Figure 1.2 Research framework of the thesis

2 The Influence of Mixing Conditions on the Macro-Scale Homogeneity of Asphalt Mixtures Blended with Reclaimed Asphalt Pavement (RAP)

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2 The Influence of Mixing Conditions on the Macro-Scale Homogeneity of Asphalt Mixtures Blended with Reclaimed Asphalt Pavement (RAP)

2.1 Abstract

The homogeneity of asphalt mixtures blended with reclaimed asphalt pavement (RAP) is affected by many factors. Due to the complicated compositions of recycled asphalt mixtures, the inhomogeneity issue might cause insufficient mechanical properties of asphalt mixtures, even though a design method was appropriately adopted. Therefore, it is of great significance to study the influence of mixing conditions on the homogeneity of asphalt mixtures blended with RAP materials. This study focused on the macro-scale homogeneity of produced asphalt mixtures. Specifically, asphalt mixtures incorporated with 40% RAP content were produced in a laboratory using different mixing times and mixing temperatures. A multi-direction indirect tensile stiffness modulus (ITSM) test was proposed to quantify the homogeneity of produced samples. In addition, the digital image processing (DIP) method was used to identify the distribution of aggregates and RAP binder. The results indicated that the influence of mixing time on the macro-homogeneity of asphalt mixtures indicated that a longer mixing time was favorable for the material dispersion. The influence of mixing temperature mainly rested on two perspectives. One was that the temperature variation induced the change of binder viscosity. The other was that the temperature influences the diffusion process between RAP binder and new bitumen, which further affected the mechanical performance of produced asphalt mixtures.

2.2 Introduction

Asphalt mixtures have been extensively used in the construction of pavements. However, when pavement suffers severe distress and, as a result, no longer functions with satisfactory quality, pavement has to be reconstructed (Wu *et al.*, 2021). On the other hand, to address increased environmental concerns, an economic solution to deal with reclaimed asphalt pavement (RAP) is to reuse recycled materials in construction (Abed, Thom and Lo Presti, 2018). Specifically, a certain amount of RAP can be incorporated into the production of new asphalt mixtures, aiming to reduce resource consumption. Additionally, the reuse of RAP materials also has environmental benefits, as landfill usage for recycled materials can be reduced remarkably (Song, Huang and Shu, 2018; Li *et al.*, 2020).

In the conventional production of asphalt mixtures, bitumen is evenly coated on the aggregate surface, and the aggregates are uniformly distributed, forming a relatively homogenous structure. A previous study demonstrated that the homogeneity issue played a critical role in the mechanical properties of produced asphalt mixtures (Peng, Xu and Chen, 2011). Commonly, the homogeneity of asphalt mixtures is estimated by quantifying the segregation of air voids and aggregates (Peng and Sun, 2014, 2017; Peng *et al.*, 2014). Therefore, studies addressing the homogeneity of asphalt mixtures can be simplified as the distribution of aggregates and air voids. To date, many technologies have been developed to characterize the distribution of aggregates and air voids. Among these, digital image processing (DIP) technology is the most widespread method used to quantify the microstructure of asphalt concrete (Feng, Ye and Hao, 2013; Kou, Kang and Zhang, 2015; Peng and Sun, 2016). Yue et al. applied DIP to calculate the distribution, orientation, and shape of coarse aggregates in mixtures (Yue, Bekking and Morin, 1995). Their results indicated that major cross-sections of coarse particles preferred to lie horizontally in mixtures. Masad et al. (Masad *et al.*, 2002) adopted X-ray computed tomography (CT) to measure air void distributions. It was reported that the air void distributions conformed to a bathtub shape, whereby larger voids existed at the top or bottom parts of a specimen. Liu et al. (Liu *et al.*, 2014) analyzed CT images based on fractal dimension methods. Accordingly, a segregation indicator based on a fractal dimension method was proposed, which was feasible for defining the segregation of pavement. Peng et al. conducted a comprehensive investigation of the homogeneity of asphalt mixtures (Peng and Sun, 2014, 2016, 2017). The effect of vertical aggregate homogeneity on penetration strength was studied, based on the discrete element method (DEM) method. In addition, an aggregate homogeneity index was introduced and it verified a good correlation with penetration strength.

Due to clusters in RAP and the property variation between RAP materials and new mixtures, the segregation issue in production could possibly be more significant. Li et al. (Li *et al.*, 2020) adopted DIP technology to study the homogeneity of in-place recycling of asphalt mixtures. It was reported that, using DIP technology, virgin and RAP aggregate could be identified, respectively. An increase in RAP temperature and mixing time was able to improve the homogeneity of asphalt mixtures. They also concluded that the quantitative homogeneity of aggregates could control the quality of recycled asphalt mixtures. The variation in RAP materials also affected the homogeneity of asphalt mixtures produced with RAP. Vislavičius and Sivilevičius studied the effect of reclaimed asphalt pavement gradation variation on the homogeneity of recycled asphalt mixtures (Vislavicius and Sivilevicius, 2013). In that study, a stochastic simulation technology was carried out, and the simulation results claimed that the formal standard requirements were not sufficient to guarantee the homogeneity of the produced batch. Apart from the variation in RAP materials and the mixing procedure, the homogeneity issue was no longer limited to aggregates and air-void segregation; it also including binder homogeneity. Mohammadafzali et al. discussed the effect of rejuvenation and aging on the binder homogeneity of recycled asphalt mixtures (Mohammadafzali *et al.*, 2018). It was found that a rejuvenator could be absorbed by the outer binder layers and continued to diffuse as time elapsed.

According to the studies introduced above, it can be concluded that many factors influence the homogeneity of asphalt mixtures incorporated with RAP materials. Comparing with conventional asphalt mixtures, the homogeneity issue concerning the recycled asphalt mixtures should be extended to a multi-scale solution. On the other hand, it is known that the production of recycled asphalt mixtures continues to use conventional mixing devices, which could be unfavorable for the homogeneity of the produced asphalt mixtures. Therefore, it is necessary to study the effect of mixing, including mixing time, mixing temperature, and mixing procedure, on the homogeneity of recycled asphalt mixtures. Additionally, the homogeneity of the mix from a multi-scale perspective should be considered in the investigations.

This study aims to investigate the macro-homogeneity of asphalt mixtures incorporated with reclaimed asphalt pavement, considering different mixing conditions. Specifically, the influence of mixing temperature and mixing time on the mechanical performance of produced asphalt mixtures will be discussed. To this end, asphalt mixtures incorporated with 40% RAP content were produced in a laboratory at different mixing times and mixing temperatures. The thermal equilibrium state was intended to eliminate the influence of thermal conductivity on the final performance of asphalt mixtures, although it deviated from actual mixing condition. In this case, the variation of macro-scale homogeneity caused by mixing could be qualified. RAP production was completed in a laboratory to avoid material variation. After producing asphalt mixtures, a multi-direction indirect tensile stiffness modulus (ITSM) test was carried out, followed by variation analyses of the obtained data. In addition, a morphological analysis of sliced asphalt mixtures was conducted, aiming to present an intuitive visualization of the morphological structures of the produced asphalt mixtures.

2.3 Materials and Experimental Methods

2.3.1 Materials

2.3.1.1 Bitumen

PG 70-22 bitumen was used to produce the RAP materials, and new bitumen was added to the mixing. In order to distinguish between the new bitumen and the aged bitumen in RAP materials, dyeing technology was applied for the bitumen in RAP. The dyeing technology was invented to change the color of bitumen by adding chemical additives. The use of iron oxide powder was introduced in the literature (Nguyen, 2009b). Specifically, iron oxide powder was added to the bitumen before RAP production. According to the preliminary trial, the optimal iron oxide powder was determined to be 30% by mass of bitumen, as shown in Figure 2.1. It could be found that when the amount of bitumen reached 30%, the bitumen could be well dyed.

9.3% 17.1% 27.6% 43.8% Dyed mixtures

Figure 2.1 Visualization of dyed bitumen with different contents of iron oxide

Table 2.1 presents conventional indicators for the new bitumen and the dyed bitumen. After dyeing, the penetration decreased and the ductility was reduced, indicating an increase in stiffness. In addition, the viscosity-temperature curves (Figure 2.2) (International, 2015) indicated an increase in viscosity after dyeing, while the temperature sensitivity did not change significantly.

Table 2.1 Empirical parameters of PG70-22 bitumen and the dyed binder

	Penetration @25oC (dmm) (ASTM International, 2020a)	**Softening Point (°C)** (ASTM International, 2014)	**Ductility @15 °C (cm)** (ASTM International, 2017)
New bitumen	68	49.2	158.4
Dyed bitumen	52	49.7	26.4

Although the variation between the new bitumen and the dyed bitumen could alter the flowability of binders, which further affected the mixing, this study used significantly different mixing temperatures to alter the influence of mixing temperature on the macro-homogeneity of the produced asphalt mixtures. It is worth noting that the incorporation of iron oxide increased the stiffness of the produced mixtures. Therefore, the incorporated amount of iron oxide was fixed for different mixing conditions. In this case, the difference in the measured modulus was mainly ascribed to the variation of the mixing conditions. For the evaluation of the homogeneity of asphalt mixtures based on the measured modulus, the coefficient of variation (CoV) was accordingly calculated for the parallel samples.

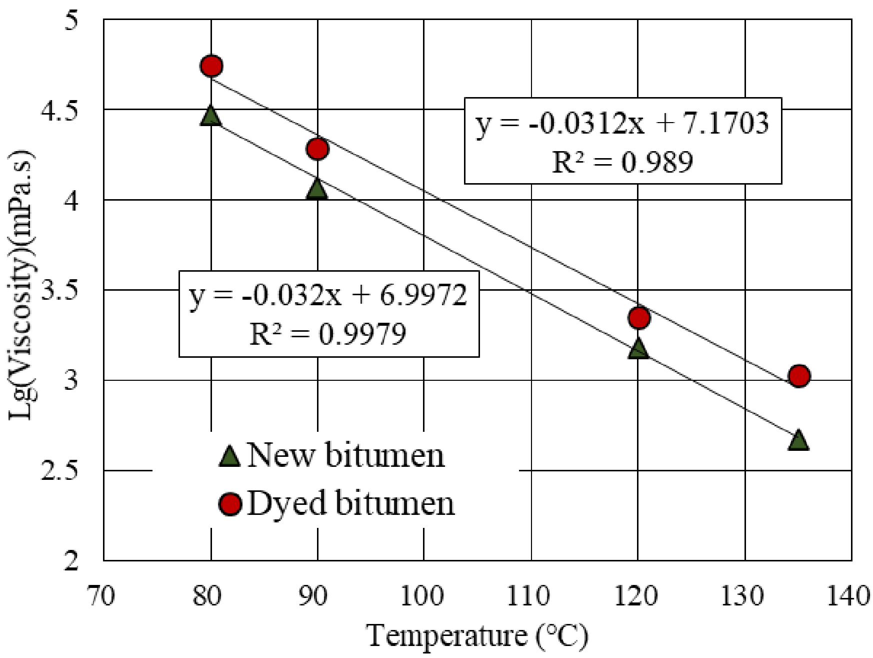

Figure 2.2 Viscosity-temperature curves for new bitumen and dyed bitumen

2.3.1.2 Mineral Aggregate and Filler

This study used basalt as the aggregate and limestone as the filler. The objective gradation curve shown in Figure 2.3 is in line with the gradation of AC-13 from the specifications (Standard, 2011). The binder was fixed at 4% for the production of mixtures, and the filler-binder ratio was 1.0 in this study.

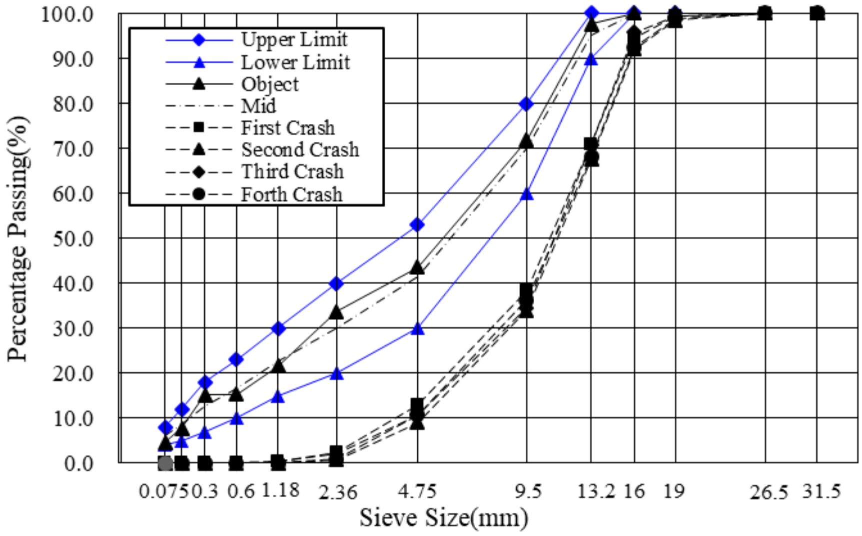

Figure 2.3 Grading curves for aggregates and crushed RAP

2.3.1.3 RAP Preparation

Following the gradation used in this study, sufficient asphalt mixtures were mixed with 4% binder content. In what follows, part of the asphalt mixtures was subjected to SHRP short-term aging (at 135 °C for four hours) in a loose state (Wu *et al.*, 2021). After that, the short-term aged loose asphalt mixtures were compacted into cylindrical specimens (150 mm diameter, 115 ± 5 mm height, and 4.5% target air void) using a Superpave Gyratory Compactor (SGC) (AASHTO, 2011). The compaction parameters were set to 1.25° (angle of gyration), 0.6 MPa (vertical pressure stress), and 30 rpm (gyration speed). The RAP materials were then produced after applying SHRP long-term aging (at 85 °C for 5 days) on the compacted asphalt mixtures with at least 1 day at ambient temperature (Wu *et al.*, 2021). The variation of gradations for the RAP materials was examined as the indicator to control the material homogeneity. Specifically, four samples were heated to 135 °C for four hours and crushed into pieces. Four samples were randomly taken from the crushed RAP and subjected to gradation tests; the results are shown in Figure 2.3. It can be seen that the grading results are very close to each other. The whole process is illustrated in Figure 2.4.

Figure 2.4 The process illustrating RAP production

2.3.2 Experimental Program

2.3.2.1 Fabrication of Specimens Containing RAP

The new aggregate was heated to 150 °C for eight hours to eliminate moisture to avoid thermal conductivity. The virgin bitumen was firstly heated to 135 °C to obtain sufficient flowability. The crushed RAP materials and new aggregates were preheated to targeted temperatures (90, 110, and 130 °C) for two hours. In order to produce the asphalt mixtures containing the RAP, the crushed RAP materials and new aggregate were firstly blended using a mechanical mixer. After that, flowable bitumen was added to the blend for a specific amount of time (30, 60, 120, and 240 s). The proportion of RAP was maintained at 40%. In this case, 12 kinds of mixing conditions were considered in the production of recycled asphalt mixtures. Four cylindrical specimens (with 150 mm diameter and 115 ± 5 mm height) were compacted using a gyratory compactor for each case. The specimens were conditioned at room temperature for one day and then cored into cylindrical specimens with a diameter of 100 mm. After that, two specimens were cut into two cylindrical specimens with a height of 40 mm, and another two specimens were sliced into 10-disc specimens with a thickness of 20 mm.

2.3.2.2 ITSM Tests

As shown in Figure 2.5, the ITSM test was applied to two specimens from four different directions at 20 °C using UTM-25. The test was carried out following the standard for indirect tensile tests for the resilient modulus of bituminous mixtures (ASTM International, 2020b). In this case, eight ITSM values for one mixing condition could be obtained. Based on the variation analysis on the eight ITSM values, the macro-homogeneity of the asphalt mixtures in terms of mechanical performance could be quantitatively estimated. Herein, this study defined macro-homogeneity as the overall performance of the asphalt mixtures. Corresponding micro-scale homogeneity was defined by the migration and diffusion behavior of binders in the asphalt mixtures.

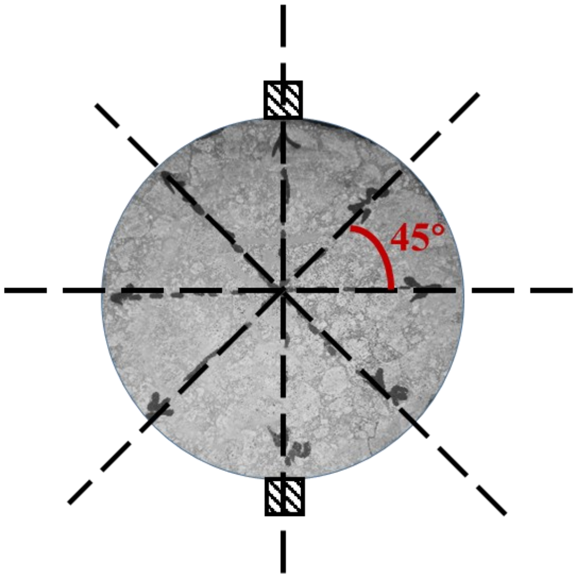

Figure 2.5 ITSM test from four directions

2.3.2.3 Color Image Analysis

High-quality pictures were taken for both sides of each disc specimen using a digital camera with carefully controlled lighting and exposure conditions. It was found that the binder was easier to identify when the specimen was wetted. Therefore, water was sprayed before pictures were taken. In total, 240 pictures of the specimens were collected.

The obtained 240 images were subjected to the image analysis using MATLAB, which conformed to the following steps.

Step 1: Preliminarily enhance the image quality: Image contrast is enhanced using the histogram equalization function. The histogram equalization method processes the image to adjust the contrast of the image by modifying the intensity distribution histogram. The purpose of this technique is to give an image of the cumulative probability function related to a linear trend.

Step 2: Calculate sample color in L*a*b color space for each region: for the image segmentation, the RGB image was firstly convert to the CIE L*ab space. CIE L*ab was defined by the lightness and the color-opponent dimensions a and b. The CIE L*ab space of an image is usually calculated for specific purpose, such as the image segmentation.

Step 3: Classify each pixel using the nearest neighbour classification: By calculating the Euclidean distance between that pixel and each color marker. The smallest distance could determine that the pixel most closely matched that color marker.

Step 4: Display results of nearest neighbour classification: The label matrix contains a color label for each pixel in the image. Based on this, the label matrix was calculated to separate objects in the original image by color.

Step 5: Convert each classification region into binary images.

Following the above steps, the aggregate component and RAP binder component can be successfully identified and segmented, as shown in Figure 2.6.

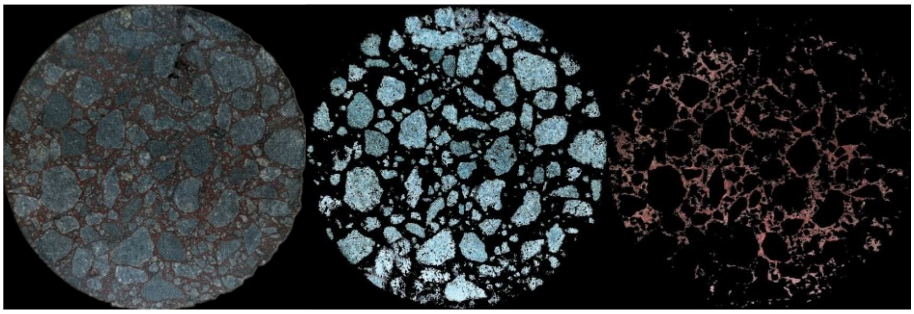

Figure 2.6 Montage of original image, aggregate, and RAP binder

2.4 Results and Discussion

2.4.1 Macro-Scale Homogeneity Based on ITSMs

According to ITSM measurements, the mean value, standard deviation (SD), and coefficient of variation (CoV) of ITSMs were calculated for each mixing condition. Figure 2.7 shows the mean values of the ITSM for all cases. It could be found that the mixing conditions significantly influenced the stiffness of the asphalt mixtures. Therefore, it is essential to use appropriate temperature and time parameters, regardless of the recycling types. It is worth noting that the maximum mean value of ITSM (7794 MPa) was observed when the mixing temperature and time were 90 °C and 240 s, respectively. In previous studies, the increase of RAP content increased the stiffness of asphalt mixtures due to aged bitumen in the RAP materials.

Similarly, the high stiffness obtained at a low temperature might be attributed to the low blending degree between the aged bitumen and the new bitumen. In contrast, mixing the asphalt mixture at high temperatures accelerated the diffusion between the aged bitumen and the new bitumen. Hence, a high stiffness modulus was observed at low temperatures.

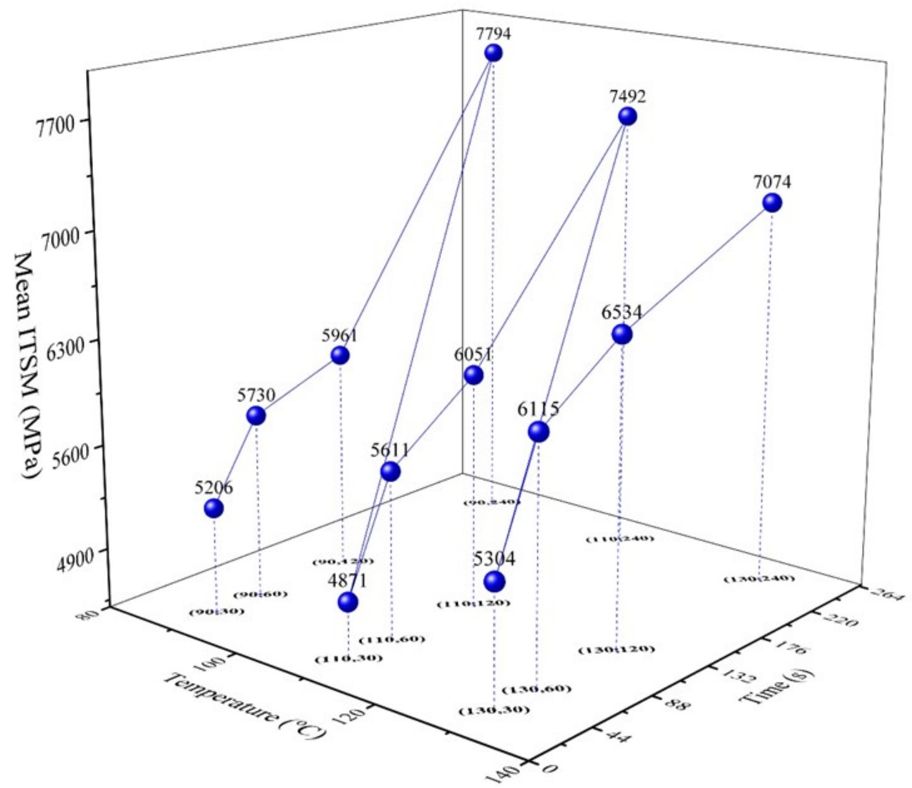

Figure 2.7 The average ITSM versus mixing temperature and time

The minimum mean value of ITSM occurred at a temperature of 110 °C and a mixing time of 30 s. This observation indicated that the influence of temperature on the stiffness modulus of the asphalt mixtures was not monotonic. Therefore, a critical temperature was most unfavorable for forming asphalt mixture stiffness, for instance, 110 °C in this study. The mixing time benefited the formation of asphalt stiffness. There are two plausible reasons for this. With the increase in mixing temperature, the bitumen binders suffered secondary aging. Additionally, a longer mixing time made it easier to achieve a better morphological distribution, although morphological distribution on the stiffness formation requires further investigation.

2.4.2 Effect of Mixing Time on Stiffness

This section discusses the influence of mixing time on the stiffness of asphalt mixtures. Figure 2.8 and Figure 2.9 interpret the same results in two different presentations for the benefit of analysis. Figure 2.8 shows the trend of stiffness modulus as the mixing time increased. It can be seen that, at all temperatures in this study, the average stiffness modulus increased progressively when extending the mixing time from 20 s to 240 s, which indicated that the extension of mixing time positively influenced the stiffness formation of asphalt mixtures containing RAP. In the mixing process, particles included in both new aggregates and RAP experienced complicated movements, during which time, the RAP clusters broke and simultaneously mixed with new aggregates. Therefore, the extension of mixing time was favorable for achieving a homogenous aggregate skeleton of asphalt mixtures. The increase in the modulus was also ascribed to the secondary aging of binders stated above.

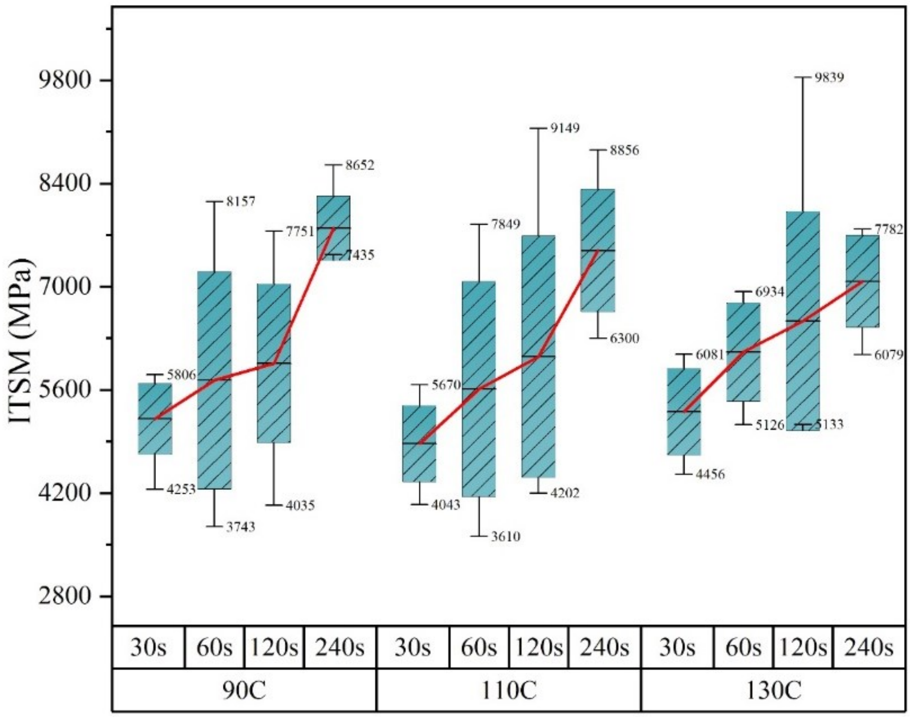

Figure 2.8 The stiffness values versus mixing time at different mixing temperatures

Apart from the average ITSMs, the error bar and value boundary of ITSMs measured at specific mixing conditions are shown in Figure 2.9 to estimate the data variation. At 90 and 110 °C, the maximum standard error and data difference were observed when the mixing time was 60 s, indicating the worst homogeneity of the specimens. While at 130 °C, the worst homogeneity of the asphalt mixtures happened at 120 s. In conclusion, the homogeneity of the asphalt mixtures first increased then decreased with mixing time. In addition, the increase in temperature prolonged the mixing time when the worst state took place. In the beginning, the clusters could not be crushed in time and, therefore, acted as large particles existing in the asphalt mixtures after compaction. The asphalt mixtures produced with a short mixing time were deemed to be in the momentary homogeneity state. When the mixing continued, the clusters would be crushed under external mechanical forces and progressively blended with newly added mixtures. Immediately after the breaking of clusters, the momentary homogenous state disappeared until a further mixing effort was applied. This assumption perfectly explained the homogeneity evolution of the asphalt mixture with mixing time. As for the influence of temperature, the termination of the momentary state prolonged as the cluster breaking could significantly interfere with binders' viscosity variations at different temperatures.

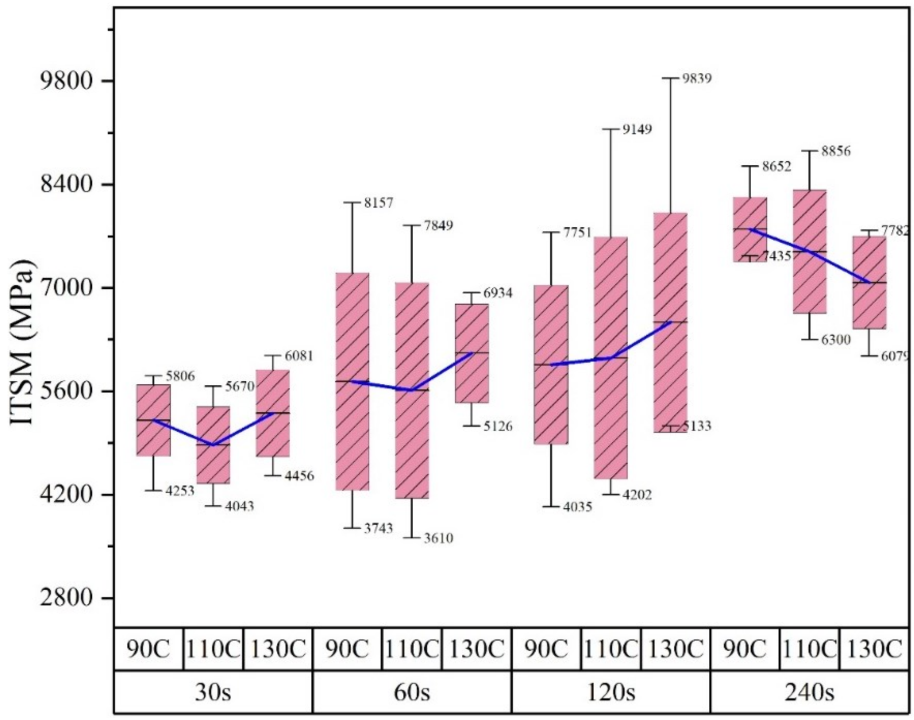

Figure 2.9 The stiffness values versus temperature at different mixing times

(1) Momentary homogeneity with insufficient temperature

As stated above, when the mixing time was very short, the produced asphalt mixture might achieve a momentary homogeneous state due to the clusters in RAP not being wholly crushed under external forces. In such a state, the aged bitumen in RAP and new bitumen were separated with limited interactions. Therefore, the diffusion process between them was limited. In this case, the temperature dominantly contributed to the flowability of aggregates both in RAP and in the newly added ones. Within an insufficient temperature range, the increase in temperature increased the flowability of particles. However, this improvement negatively influenced the breaking of clusters in RAP. As a result, the stiffness decreased, although the temperature increased.

(2) Momentary homogeneity with sufficient temperature

If the temperature continued to increase to a sufficient range, the clusters would be softened and would lose the adhesive force inside. In this case, the temperature played a positive role in the breaking of clusters in RAP. The momentary homogeneous state would shift into an unbalanced state when the blending degree of RAP and new aggregates started to grow. Therefore, the stiffness modulus increased when the temperature was at 130 °C, as seen in Figure 2.9.

(3) Near-real homogeneity with insufficient temperature

Extending the mixing time is helpful for the formation of real homogeneity in asphalt mixtures. The mixing time and temperature mutually determined the homogeneity state of asphalt mixtures. As seen in Figure 2.9, when the mixing time was 120 s, the asphalt mixture experienced a change from a momentary homogeneous state to a real homogeneous state called a near-real homogeneous state in this study. In such a state, the temperature played two roles. One rested on the speed of the state shift. The other one contributed to the diffusion between new and aged bitumen. The role of temperature concerning the state shift was more explicit than the diffusion.

(4) Real homogeneity with sufficient temperature

When the mixing time was 240 s, the asphalt mixtures almost achieved real homogeneity since the error bars were small. In this condition, the temperature mainly contributed to the diffusion between aged bitumen and new bitumen. With the increase in temperature, the diffusion rate would be accelerated, during which the aged bitumen would be softened, inducing a decrease in the stiffness modulus.

Figure 2.10 presents the calculated coefficient of variation (CoV) for different mixing conditions. The CoV was used herein to evaluate the homogeneity of the asphalt mixtures. As seen in Figure 2.10, the red areas indicated the inhomogeneous state, while the blue ones referred to the homogeneous asphalt mixtures. It should be noticed that Figure 2.10 cannot tell the difference between momentary homogeneity and real homogeneity. When the mixing time was from 0 s to 30 s, momentary homogeneity was observed. Furthermore, when the temperature increased to 125 °C, the momentary homogeneity state would last a long time, extending to around 75 s. The real homogeneous state took place when the mixing time was beyond 150 s for a low temperature (90 °C) and 175 s for a high temperature (135 °C).

The inhomogeneous state occurred in the rest area. It can be seen that the combination of temperature (110 °C) and mixing time (120 s) was the most unfavorable mixing condition in terms of the homogeneity. Additionally, the inhomogeneous state area was shown in a 'Z' shape. The most inhomogeneous state can be achieved quickly at a low temperature or a longer time at a high temperature. It is believed that Figure 2.10 can be improved further if more and more mixing conditions could be considered in one research study. This construction of a homogeneity pattern as a mixing time and temperature function can efficiently guide the mixing procedure in practice.

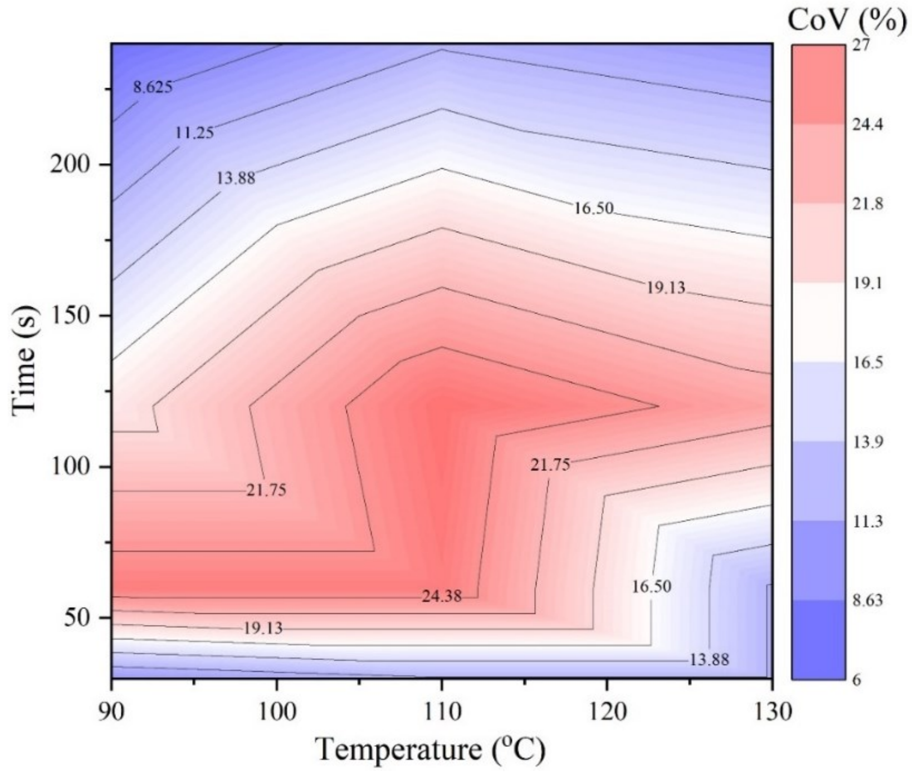

Figure 2.10The stiffness variation caused by mixing time and mixing temperature

2.4.3 Visualization of the Homogeneity of Asphalt Mixtures

In total, 240 images were subjected to image processing to identify aggregates and RAP binder morphologies, respectively. Figure 2.11 presents one image for each mixing condition. Significant variation among the 12 images was not observed. This indicated that, for a conventional asphalt mixture, 30 s was sufficient to disperse the aggregate, forming a typical asphalt mixture structure. This complied with actual situations since mixing, in practice, was usually controlled within 1 min.

It can be seen that it is not possible to tell the difference caused by the mixing condition. The primary reason for this was that the aggregates in RAP or newly added aggregates could not be further distinguished. From another perspective, aggregates in RAP had identical properties to the newly added ones. Given that the binders were well coated on the aggregate surface, the mechanical performance of asphalt mixtures was mainly determined by the skeleton structure of aggregates, which was not a critical problem with a well-designed mixing procedure.

Another limitation of examining the aggregate distribution shown in this study was that the dimension reduction from 3D to 2D might lose considerable structural information. Therefore, it is not recommended to evaluate the homogeneity of asphalt mixture by visualizing aggregate morphology.

Figure 2.12 shows a visualization of RAP binder morphology. The red area indicated the place where the RAP binder was located. It can be seen that the RAP binder, even with the mixing time of 240 s, can be dispersed uniformly in the asphalt mixtures. Based on the visualization of the RAP binder, it is not easy to achieve a complete mixing even the mixing time was 240 s and the temperature was 130 °C. Additionally, it can be observed that there is no significant rule for the RAP binder pattern when the mixing conditions varied. However, it is clear that when the mixing time is short (30 s or 60 s), the phenomena "partial missing of RAP binder" quickly occurred, which demonstrated the presence of RAP clusters.

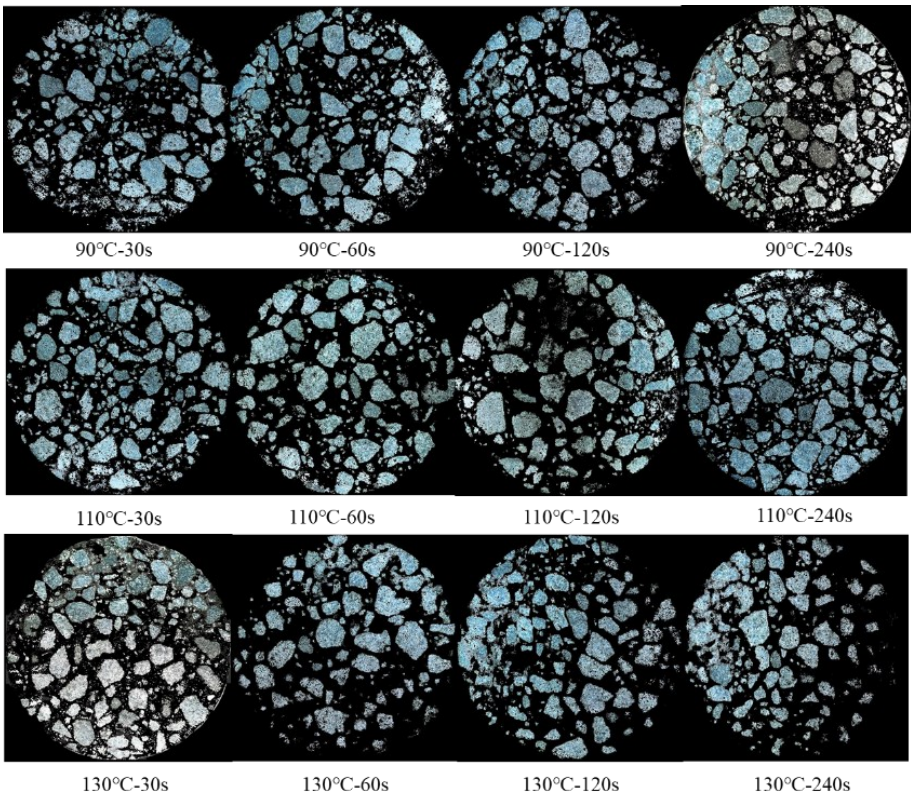

Figure 2.11 Visualization of aggregate distribution at different mixing conditions

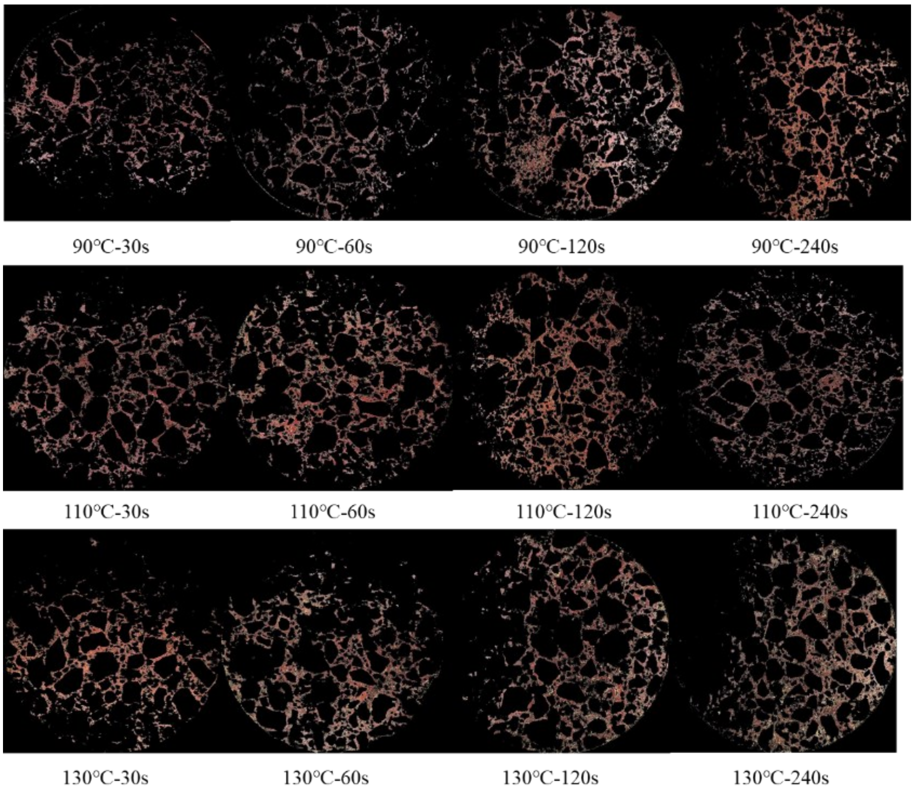

Figure 2.12 Visualization of RAP binder distribution at different mixing conditions

When the temperature was 90 °C, a relatively homogenous distribution of RAP binder was observed at 120 s. According to the last section's analysis, the RAP binder's viscosity was high, and the migration of RAP binders was mainly attributed to external force. Thus, extending the mixing time was beneficial to the migration of RAP binders. It is worth noting that the RAP binder was not detected in some parts of the image at 240 s, indicating that the cluster of new aggregate and new bitumen also occurred in the mixing process. Similar phenomena were observed at other mixing temperatures.

2.5 Conclusions

Based on the results and discussion in this study, the following conclusions can be drawn:

(1) The macro-homogeneity of asphalt mixtures is associated with mixing temperature and mixing time. The asphalt mixtures produced with different mixing conditions show distinct mechanical performance.

(2) A long mixing time benefited the distribution of aggregates in both RAP materials and new mixtures. The increase of mixing temperature induced binder flowability, which improved the migration and diffusion of binders. According to the results, the influence of mixing time and temperature should not be determined separately. An optimal combination of mixing time and temperature exists to achieve a satisfying mechanical performance of asphalt mixtures containing RAP materials.

(3) Although many efforts have been made to repeat the production of asphalt mixtures with RAP materials in the laboratory. The addition of iron oxide into bitumen significantly changed the binder properties. Therefore, it should be promising to use other technologies to identify the difference between RAP materials and newly added mixtures. The laboratory investigations provided a basic understanding of the macro-homogeneity of asphalt mixtures with different mixing temperatures and mixing times. However, in situ mixing procedures are different from laboratory ones. For a deep understanding of the homogeneity of asphalt mixtures containing RAP materials, carrying out a full-scale investigation in the field is recommended.

3 Study of Migration and Diffusion during the Mixing Process of Asphalt Mixtures with RAP

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<u>Individual contributions:</u>

Quan Liu and Jiantao Wu conceptualized research idea and designed the experiments. Quan Liu also contributed to the experiment completion, data analysis, manuscript writing and editing. Shuai Yang contributed to the assistance of experiments. Cadnel Ago contributed to the proofread of manuscript. Markus Oeser contributed to the supervision and final manuscript check.

3 Study of Migration and Diffusion during the Mixing Process of Asphalt Mixtures with RAP

3.1 Abstract

The mixing degree of virgin and aged asphalt binders is one of the main factors that can significantly affect the performance of reclaimed asphalt pavement (RAP). On the other hand, an important factor that contributes to the mixing is diffusion, which dominantly determines the general performance of asphalt mixtures with RAP. In this study, twelve different lab-mixing conditions were deliberately adopted to investigate the impact on the diffusion between virgin and aged bitumen binders, including three mixing temperatures (110°C,130°C,150°C) and four mixing times (30s,60s,120s,240s). Specially fabricated cubic aggregates were designed and deposited for collecting pure binders, so that virgin or aged binders can be tracked and the effect of chemical reagents be avoided. Based on the Dynamic Shear Rheometer (DSR) and Fourier Transform Infrared Spectroscopy (FTIR) tests, the performance and blending rate of binders under various conditions were clearly shown. The results show that blending temperature can play a more crucial role in diffusion than mixing duration, which means the higher temperature is capable of accelerating the inter-diffusion rate between virgin and aged bitumen binders, thus increasing the efficiency of recycling ulteriorly. The blending degree investigated in this study could not achieve the complete mixed state with the highest value being around 50%. Furthermore, the Asymmetric Gaussian Model is proposed to mathematically describe the change of blending rate with the mixing time.

3.2 Introduction

From the 1930s to the 1980s, reclaimed asphalt pavement (RAP) had been initially used in pavement paving (Nguyen, 2009a; Copeland, 2011; Chen *et al.*, 2019; Ding *et al.*, 2019). However, the use of RAP fell off dramatically in the 1990s on account of the high performance of Superpave and its low cost. Over the past two decades, RAP has received increasing attention because of the change of economic climates and resource saving (Bressi *et al.*, 2018; Zheng *et al.*, 2019) and therefore, it has been extensively used in road construction. In addition to the reduction in the construction cost and the consumption of valuable natural resources, the use of RAP can also create significant environmental benefits, such as solving the disposal problems (Mantalovas and Di Mino, 2019).

The mixing condition between aged and virgin asphalt binders is the main factor that determines the performance of reclaimed mixtures, and it generally contains two major mechanisms: mechanical mixing and diffusion between molecules. Karlsson and Isacsson (R. Karlsson and Isacsson, 2003; Karlsson and Isacsson, 2006) stated that the effectiveness of mechanical mixing was influenced by several factors, such as temperature and mixing time, etc. Huang (Huang *et al.*, 2005b) studied that effective mechanical mixing time is very short in the process of actual engineering. Diffusion can be referred to as interactions between random molecules, which is closely related to temperature. Al-Qadi (Al-Qadi, Elseifi and Carpenter, 2007) and Bowers (Bowers, 2013) both found that only partial blending mixing occurs between aged and virgin binders during the mixing process, and this observation was supported by many other researchers as well. Nahar et al. (Nahar *et al.*, 2014) investigated the microstructures between the virgin and the aged asphalt binders from RAP and pointed out that a blending zone existed during the process. In fact, the aged and virgin binders began to diffuse into each other as soon as they came into contact and then the penetration and diffusion process takes place. Among the characteristics of diffusion, diffusion efficiency is the focus of an investigation by researchers. Wu et.al (Wu *et al.*, 2018a) investigated the 12 combinations of mixing times and mixing temperatures based on the indirect tensile stiffness modulus test and color image analysis. The results indicated that the deterioration of homogeneity was on account of the asynchronous breaking of clusters. Meanwhile, the mixing temperature was decisive in determining the resistance of clusters to breaking. Navaro et al. (Navaro *et al.*, 2012)studied the relationship between temperatures and diffusion efficiency with UV and white light microscopy, which proved that a temperature reduction by 30°C could result in a mixing time increase by two or three folds. Cong et al. (Cong *et al.*, 2016) illustrated the effects of the thickness and types of rejuvenators on the diffusion rate. In the recycled asphalt mixtures, the temperature has a great influence on the diffusion coefficient, but the effect of the thickness of the rejuvenator on the diffusion coefficient is not obvious. Ding et al. (Ding *et al.*, 2016) used molecular dynamics (MD) to simulate the diffusion between virgin and aged asphalt binders, which further revealed that by applying rejuvenator into aged binder first is capable of significantly accelerating the diffusion between virgin and aged asphalt binders.

It should be noticed that most existing studies related to RAP binder diffusion have adopted binder recovery techniques (Noureldin and Wood, 1987; Kriz *et al.*, 2014; Zhao *et al.*, 2016). However, chemical reagent recycling asphalt method, which is the most commonly used method, has been frequently questioned due to its great influence on bitumen binder properties. The destruction of molecular structure and the secondary aging of bitumen binders both might lead to inaccurate experimental results.

This study proposed a new method, which can avoid chemical reagent recycling asphalt, to study the influence of different mixing conditions on the diffusion law between virgin and aged asphalt binders. Specially fabricated cubic aggregates were deposited in old and new asphalt mixtures at different mixing condition combinations (3 temperatures and 4 times), as tracking markers. DSR and FTIR tests were then applied on asphalt binders directly scraped from cubic aggregates, based on which, statistical analyses were carried out to characterize the performance of different binders. Finally, the blending rate was then quantified with the Asymmetric Gaussian Model (AGM) developed in this study.

3.3 Materials and Experimental Program

3.3.1 Materials

(1) *Bitumen and Aggregates*

Bitumen binder PG70-22 was used in both the RAP production and the new bitumen. Basalt aggregates were used in both the RAP production and the original aggregates.

(2) *Synthetic Aggregate Gradation*

To avoid the influence of fine materials and mineral powder when obtaining bitumen samples, this study only selected aggregates with grain sizes above 2.36mm as the final gradation. The bitumen content was calculated to be 1.2% based on the assumption of 20μm bitumen film thickness. The synthetic gradation is shown in Table 3.1.

Table 3.1 Synthetic gradation design

Sieving size (mm)	16	13.2	9.5	4.75	2.36	1.18	0.5	0.3
Passing ratio (%)	100	90-100	60-80	30-53	20-40	15-30	10-23	7-18
The median value (%)	100	95	70	41.5	30	22.5	16.5	12.5
Synthetic gradation (%)	100	97.7	70.87	43.5	2.9	0	0	0

(3) *RAP Preparation*

To prepare enough RAP materials for the following studies, AC-13 asphalt mixtures with the objective gradation of aggregate and 1.2% binder content were firstly mixed and then subjected to the short-term aging (at 135℃ for four hours) per the Strategic Highway Research Program (SHRP). After that, the loose mixtures were compacted into cylindrical specimens (150mm diameter, 115±5mm height, and 4.5% target air void) using a gyratory compactor. The compacted specimens were then subjected to SHRP long-term aging (at 85℃ for five days), followed by at least 1-day conditioning at room temperature. Finally, the specimens were heated at 135℃ for four hours and manually crushed. The grading of crushed samples was proved homogenous enough as illustrated in Chapter 2.

(4) Aggregate Tracking Method

This study proposed a method to track and obtain the bitumen directly from the aggregate surface by using regular shape aggregates. The method shown in Figure 3.1 can be illustrated as follows:

Step 1: RAP mixtures with a specific amount of cubic tracking aggregates (20mm length) were produced.

Step 2: RAP mixtures were mixed with new bitumen and aggregates according to the designed RAP content. Meanwhile, another type of tracking aggregates with 15mm length were added to the new aggregates.

Step 3: After the mixing procedure, all the tracking aggregates were collected, and diffusion samples were obtained from the surface of cubic tracking aggregates.

Step 4: The diffusion sample were characterized by DSR and FTIR tests.

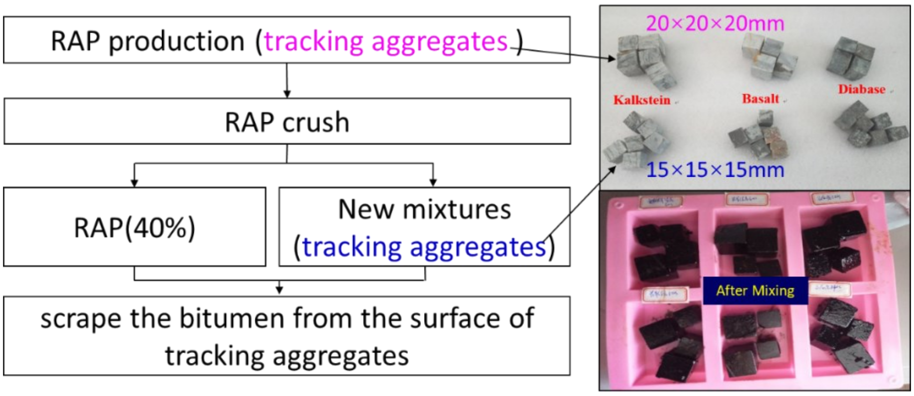


Figure 3.1 Flow chart of aggregates tracking method

3.3.2 Experimental Program

Based on the aggregate tracking method, diffusion samples blended using various mixing conditions can be obtained. Four mixing times (30s, 60s, 120s, and 240s) and three mixing temperatures (110°C, 130°C, and 150°C) were considered according to practical experience. Subsequently, 20 mm and 10 mm tracking aggregates were taken out, respectively. In what follows, the diffusion sample was immediately scraped from the surface of the tracking aggregates with a silicon knife. Finally, collected diffusion samples were subjected to the DSR and FTIR tests to avoid further disturbance on samples. As shown in Figure 3.2 (a), the diffusion samples from the aggregate surface were ideally composed of three parts: virgin bitumen, aged bitumen in the RAP, and the mixed bitumen on account of the diffusion process. As the mixing time proceeded or the mixing temperature increased, proportions of three parts varied. As a result, the FITR and DSR results were capable of differentiating the variation of samples.

On the other hand, the extend of mixing time also affects the probability of collision between aggregates. The collision between aggregates is the premise of the diffusion process. Therefore, it is possible to obtain some non-ideal scraped samples, as illustrated in Figure 3.2 (b). In conclusion, the DSR and FTIR results were influenced by both diffusion and migration actions during the mixing process.

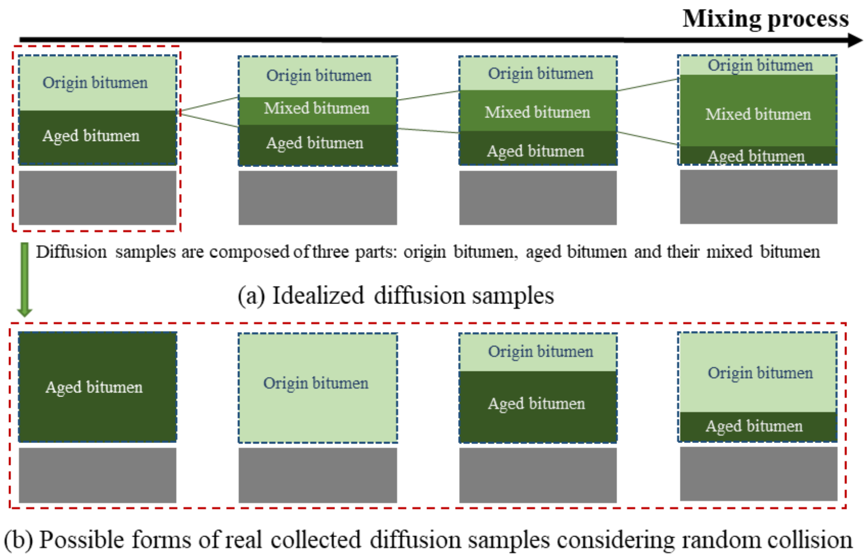


Figure 3.2 Schematic of diffusion samples scraped from the aggregate surface

The detailed experimental plan is shown in Figure 3.3. It should be noted that, to avoid sample variation, at least four cubic aggregates for one mixing condition were collected. The representative diffusion sample is a mixture of binders from all the collected aggregates.

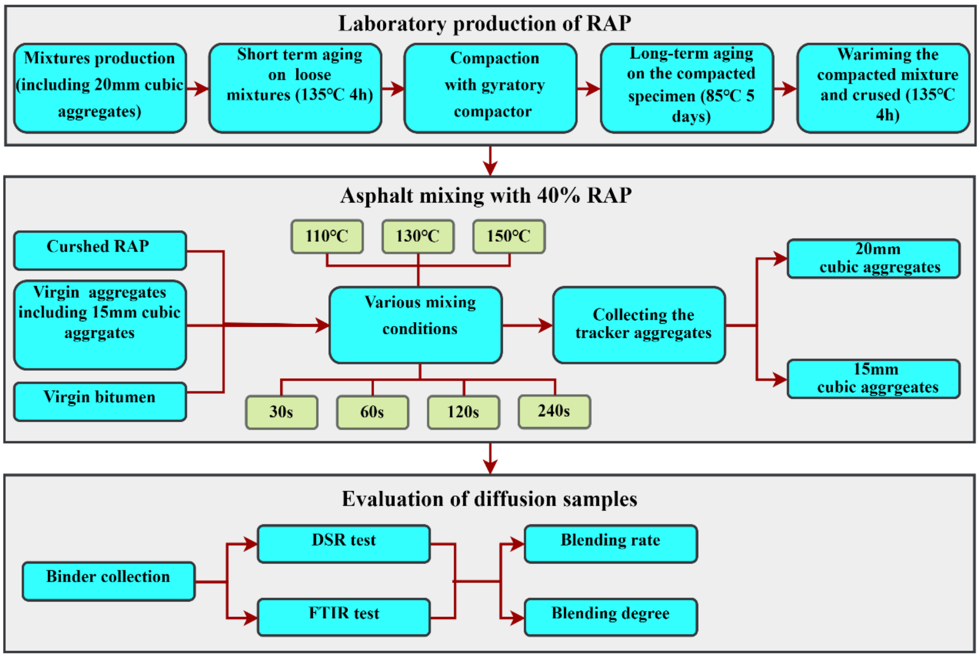


Figure 3.3 Experimental plan

As seen in the experimental plan, a total of 12 mixing condition combinations were investigated. For the benefit of the analysis, the mixing conditions were numbered, as shown in Table 3.2.

Table 3.2 The condition number of mixing conditions

Temperature (°C)	110				130				150			
Time (s)	30	60	120	240	30	60	120	240	30	60	120	240
Condition Number	1	2	3	4	5	6	7	8	9	10	11	12

3.4 Evaluation Methods

3.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared Spectroscopy is an analytical technique through which the functional groups of organic molecules are identified (Robert Karlsson and Isacsson, 2003). In this study, the ATR (Attenuated Total Reflectance) technique was carried out, a commonly used IR procedure. The wavenumber scan range is 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. For quantitative analysis, two indicators can be used to identify the difference between bitumen (Ruau, Landais and Gardette, 1997).

Carbonyl Index:

$$Ico = \frac{Area\ around\ 1700\ cm^{-1}}{Area\ around\ 1460\ cm^{-1} + Area\ around\ 1375cm^{-1}} \quad \text{Equation 3.1}$$

Sulfoxide Index:

$$Iso = \frac{Area\ around\ 1030\ cm^{-1}}{Area\ around\ 1460\ cm^{-1} + Area\ around\ 1375cm^{-1}} \quad \text{Equation 3.2}$$

Lu et al. (Lu and Isacsson, 2002) investigated the effect of aging on bitumen chemistry and rheology using Thin Film Oven Test (TFOT) and Rolling Thin Film Oven Test (RTFOT). The aging index, which is defined as the ratio of a chemical or rheological parameter after aging, was adopted to characterize the aging effect quantitatively. Compared with the accelerated aging method, in this mixing procedure, the maximum mixing temperature and mixing time are 130°C and 240s. Therefore, it is assumed that oxidation is neglected, which means no obvious aging process occurs during the mixing of asphalt mixtures containing RAP. The change of functional groups merely depends on the diffusion process. In this case, the amount of C=O and S=O in both virgin and aged bitumen is relatively constant. Therefore, the blending rate can be indicated as:

$$Blending\ rate = \frac{I_{n+1} - I_n}{t_{n+1} - t_n} \qquad \text{Equation 3.3}$$

Where I indicate the value of I_{SO} or I_{CO}, the subscript denotes the time interval.

3.4.2 Dynamic Shear Rheometer (DSR)

The dynamic mechanical analysis was applied to evaluate the diffusion sample. Frequency sweep tests were carried out at frequencies from 0.1Hz to 10Hz, and temperatures ranging from 20 to 80 °C (with 10°C intervals) within the binder's linear viscoelastic (LVE) limit. Parallel plates with a diameter of 25mm and a gap size of 1mm were used.

Similar to the FTIR analysis, in this study, the complex modulus measured at 20°C and 10rad/s was selected as the typical indicator. Accordingly, the blending degree and blending rate can be described with the following equations:

$$Blending\ degree = \frac{\log G_{exp} - \log G_{target}}{\log G_{aged} - \log G_{virgin}} \qquad \text{Equation 3.4}$$

$$Blending\ rate = \frac{\log G_{n+1} - \log G_n}{t_{n+1} - t_n} \qquad \text{Equation 3.5}$$

The blending degree is calculated according to Equation 3.4. The target value of complex modulus is calculated according to the following equation (Karlsson and Isacsson, 2006).

$$\ln(G_{mix}) = x_1 \ln(G_1) + x_2 \ln(G_2) \qquad \text{Equation 3.6}$$

Where: G_{mix} is complex modulus of the binder mixture; G_1 and G_2 represent complex modulus of both bitumen; x_1, x_2 refer to volume percentages of both bitumen.

3.5 Results and Discussion

3.5.1 Analysis of blend degree during the mixing process

In Chapter 2, the macroscale homogeneity of asphalt mixtures including RAP materials, was investigated. Due to the adhesion of aged bitumen and insufficient heating, RAP materials cannot be crushed into their original gradation completely. Therefore, those that have not been crushed composed the cluster. On account of the presence of clusters, asphalt mixtures containing RAP behaved different homogeneity states at the macro-scale as illustrated in Figure 3.4.

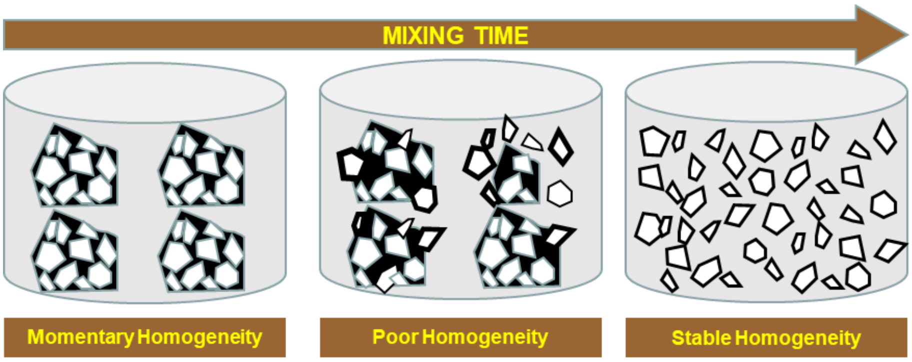


Figure 3.4 Three stages of asphalt mixtures during the mixing process

With the increase of mixing time, asphalt mixtures basically experienced three stages which are momentary homogeneity, poor homogeneity, and stable homogeneity, respectively. Meanwhile, the mixing temperature dominated the flowability of binders which played a critical role in the cluster breaking in the mixing process. According to the macroscale investigation, it can be demonstrated that the migration process makes a significant contribution to the diffusion process. The migration process always happens before the diffusion process.

Figure 3.5 shows the schematic of the mixing process at the meso-scale based on above analysis. Two stages proceeded during the mixing process. The first stage is the migration stage. In this stage, bitumen coating on the new aggregates migrates to the surface of RAP aggregates and vice versa. The second stage is the diffusion stage, in which the diffusion between virgin bitumen and aged bitumen dominants until reaching the equilibrium state.

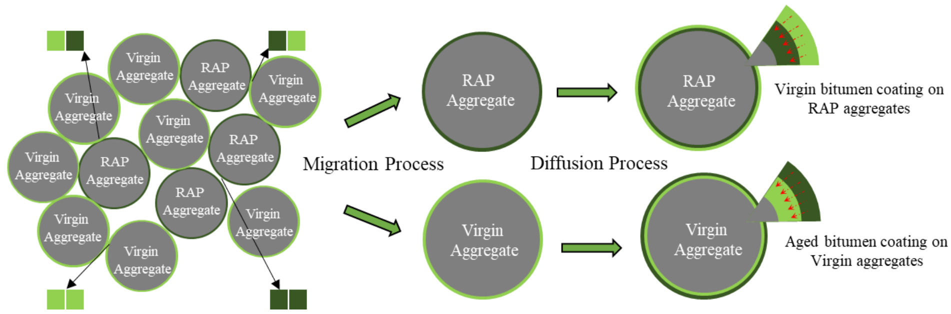


Figure 3.5 Schematic of mixing process containing RAP

Table 3.3 summarizes the modulus measured for diffusion samples obtained from both virgin and RAP aggregates, as well as the blending degree calculated according to Equation 3.4. The target modulus assumes the complete mix of virgin and aged bitumen.

Table 3.3 Modulus and blending degree at different mixing conditions

Number	Virgin Aggregates		Aged Aggregates	
	Moduli @ 20°C, 10rad/s (Pa)	Blending degree	Moduli @ 20°C, 10rad/s (Pa)	Blending degree
1	16846872	31.49%	5848000	0.51%
2	5627560	1.67%	13510000	24.81%
3	13788700	25.43%	10150000	16.16%
4	11228000	19.22%	9845000	15.24%
5	11831300	20.80%	22537000	40.29%
6	2989880	20.80%	10058700	15.89%
7	2847920	22.27%	16481000	30.83%
8	4298330	9.82%	6976650	4.83%
9	17383900	32.44%	32020300	50.91%
10	12201600	21.73%	22638100	40.43%
11	13419600	24.61%	30401900	49.34%
12	19377600	35.72%	20456100	37.36%
Virgin bitumen			1584893	
Aged bitumen			43241000	
Target Modulus			5947826	

With the increase of mixing time, the final modulus will reach an equilibrium state. However, this kind of equilibrium state differed when the temperature changes. The blending degrees for all the investigated mixing conditions were calculated and shown in Figure 3.6. It can be seen that the diffusion samples obtained from the RAP aggregates showed higher blending degrees. The new bitumen has superior flowability to the aged bitumen at the same temperature. Consequently, more virgin bitumen migrated and coated on the RAP aggregates leading to a higher blending degree. Besides, it was also proven that the highest blending degree was around 50%, and a similar conclusion was reported previously (Zhao *et al.*, 2016).

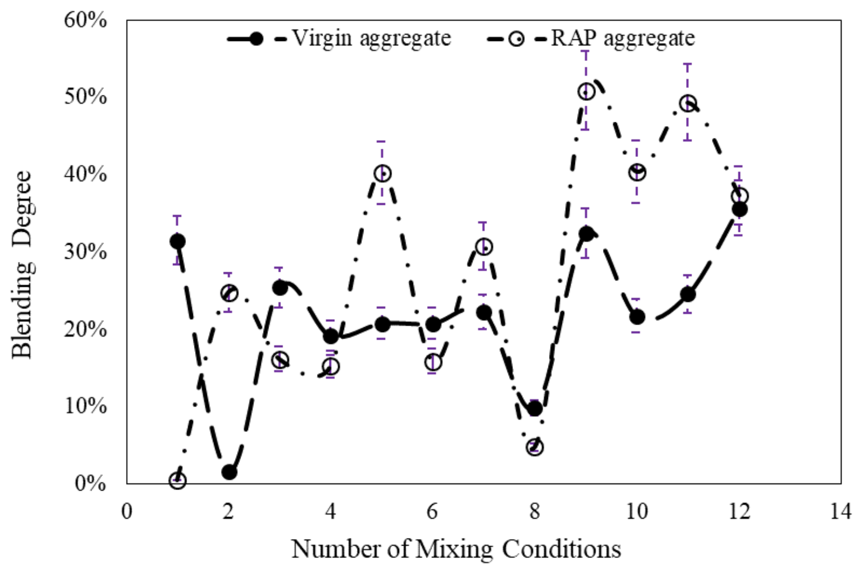
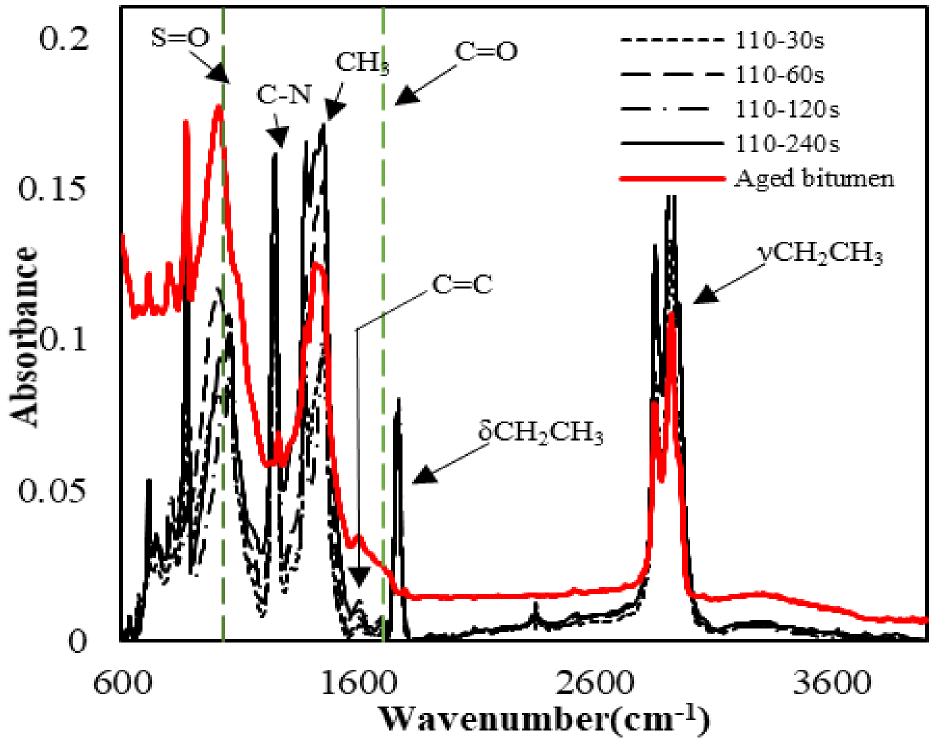


Figure 3.6 Blending degree at different mixing conditions

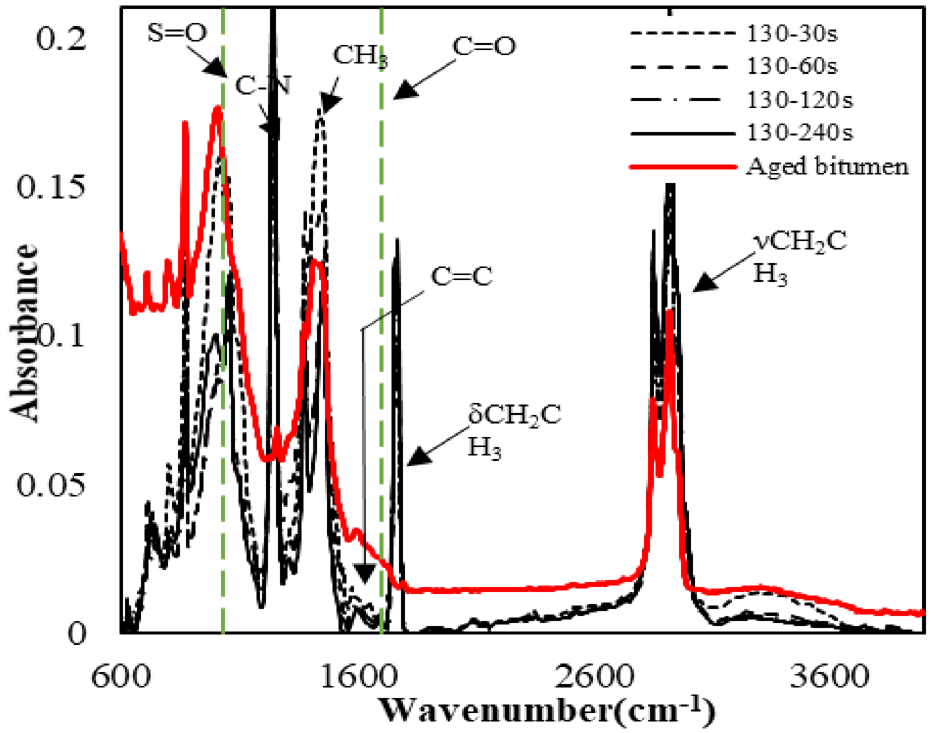
3.5.2 Blending rate based on the FTIR

Figure 3.7 presents the FTIR test results with different mixing conditions. Typical functional groups like carbonyl, sulfoxide and carbon-carbon double bond were observed in the aged bitumen and diffusion samples.

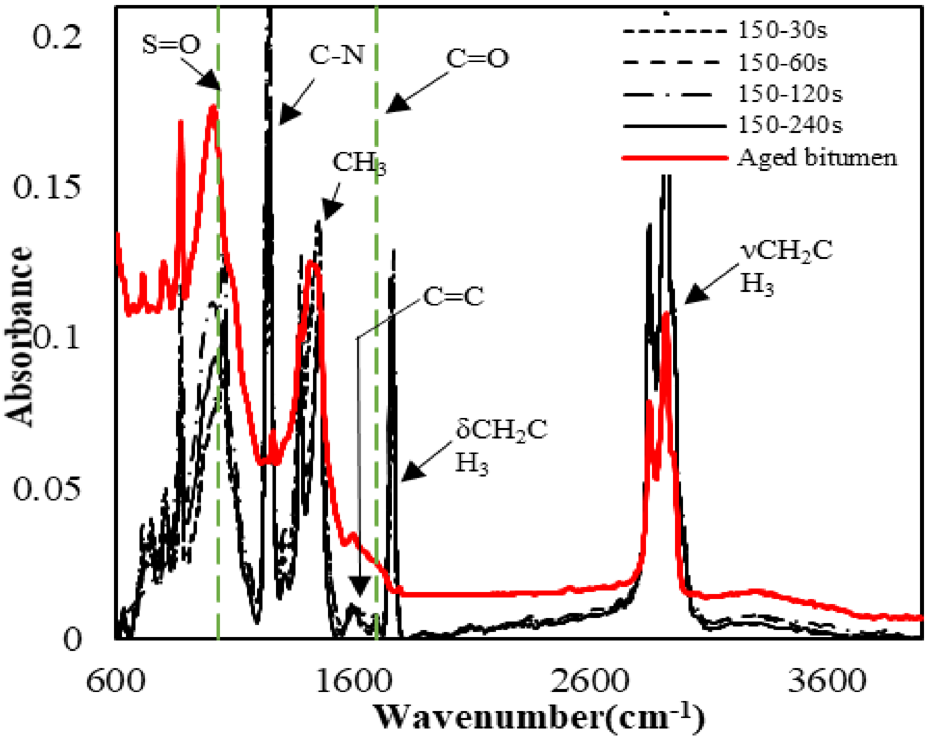
According to Equation 3.3, the blending rates based on the *Iso* and *Ico* were calculated and presented in Figure 3.8. After 30s mixing, all the values of the blending rate were negative, which indicated a decline of *Iso* and *Ico*. It was assumed that the oxidation of binders was neglected during the limited mixing time, and therefore, the changes of *Iso* and *Ico* proved that diffusion happened. After the 120s mixing duration, the blending rate gradually decreased to zero. When the blending rate reaches 0, the *Iso* and *Ico* kept constant, which demonstrated that the diffusion process almost stopped. Thus, it can be speculated that the diffusion process mainly happened within the 240s. Afterward, the diffusion process became very slow.



(a) 110°C



(b) 130°C (continued)

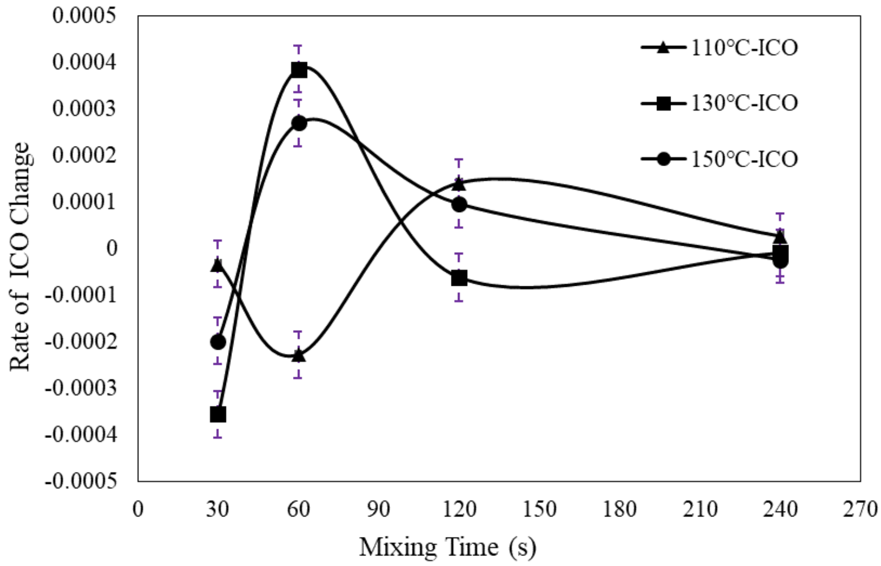


(c) 150°C

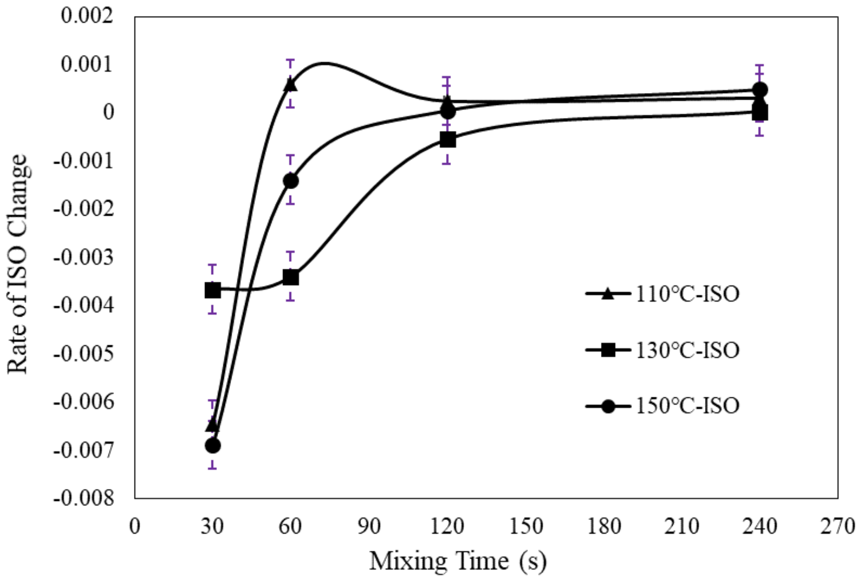
Figure 3.7 FTIR results of samples with different mixing conditions

The mixing time of the 60s is another critical point judging from Figure 3.8. It was observed that around the mixing time of the 60s, the blending rate reached its inflection value. This phenomenon illustrated that at this time point, the diffusion processed the most tempestuously.

However, when comparing the *Iso* and *Ico* change rates, the characterization of the diffusion process based on these two indicators was not consistent. Several reasons can explain this. Firstly, sulphoxides are primarily formed in the saturate fraction, and the carbonyl functional groups are usually found to be in the more polar fractions (Petersen, 2000a). In bitumen, the more polar fractions can be viewed to be dispersed (or buried) in the more nonpolar fractions (Petersen and Harnsberger, 1998); Fisher observed the distribution of chemical species in a nano-scale and different micro-phases presented in the bitumen-aggregate system (Fischer and Cernescu, 2015). Therefore, it was reasonable that, because of the micro-phases distribution inside the diffusion samples, the *Iso* and *Ico* induced inconsistent evaluation results. In addition, the rate of *Ico* change at 110°C seemed abnormal to others; the change rate increased at the beginning and achieved the inflection value around the 60s. The increase or decrease of the *Iso* and *Ico* value relied on the diffusion between the new and aged bitumen. It depends on the migration of new or aged bitumen during the mixing process. In fact, with the same mechanical mixing force, the migration behavior was affected by the flowability of bitumen binders. Thus, temperature played an essential role in the migration and diffusion of bitumen binders in terms of the viscosity change. With regard to the change rate of *Iso* at 150°C, there was no inflection value observed. Bitumen binder performed the best flowability at 150°C. The migration process speeded up and reached a stable situation at an earlier time, even before the 30s, which clarified those different tendencies were observed.



(a) ICO



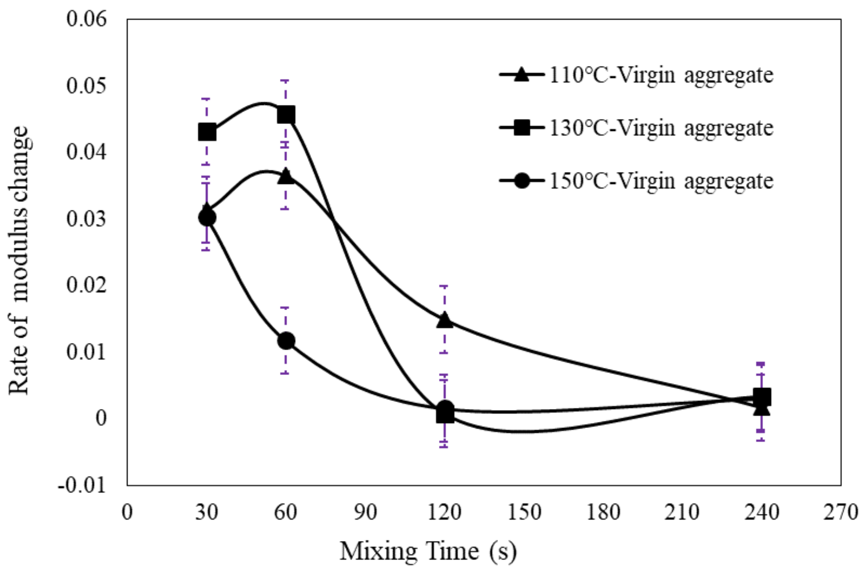
(b) ISO

Figure 3.8 The blending rate on RAP aggregate at different temperatures

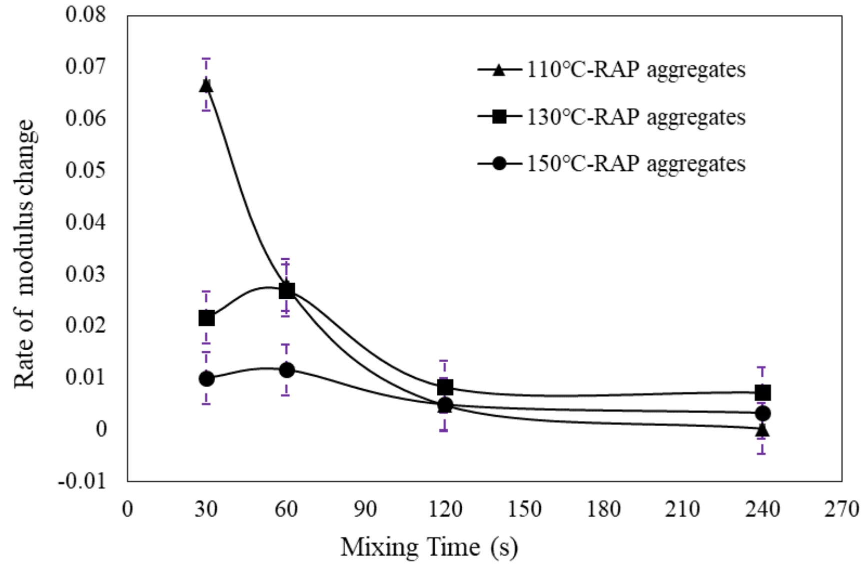
3.5.3 Blending rate based on the DSR

The above analysis based on the *Iso* and *Ico* showed that the diffusion process would reach a stable rate near zero with a sufficient mixing process. At a critical mixing duration, the migration of bitumen binders achieved a stable state where the blending rate reached an inflection value. The mixing temperature played a dominant role in both the migration and diffusion processes. However, the analysis of the FTIR results can only be the support information to trace the migration and diffusion process. The essential motivation of the diffusion study was to evaluate the blending efficiency, expecting a high quality of mechanical performance. Figure 3.9 shows the rate of modulus change for both the virgin aggregates (15cm ×15cm×15cm) and RAP aggregates (20cm ×20cm×20cm). Concerning diffusion samples from the virgin aggregates, the critical time (the 60s) was observed when the mixing temperature was 110℃ and 130℃. In terms of the mixing temperature of 150℃, a monotonical decrease indicated that the critical time at 150℃ was smaller than the 30s. When the mixing time exceeded 120s, it can be seen that a higher temperature induced an earlier equilibrium state.

In the case of virgin aggregate, the critical time, which occurred at 150℃, where the change rate achieved the highest value was less than 30s. In the case of RAP aggregates, the critical mixing time for 150℃ was around the 50s. Meanwhile, the critical mixing time for 110℃ was less than 30s. In terms of the critical mixing time, the diffusion samples collected from virgin aggregates and RAP aggregates exhibited contrary tendencies. It was not difficult to understand due to that, except for the diffusion process, the migration of new bitumen from virgin aggregates to RAP aggregates and bitumen from RAP aggregates to virgin aggregates happened simultaneously. The interaction between new and aged bitumen affected by the migration might result in contrary conclusions.



(a) virgin aggregates



(b) RAP aggregates

Figure 3.9 The blending rate of modulus change from new and RAP aggregates

3.5.4 Plausible Asymmetric Gaussian Model (AGM) for predicting blending rate

According to the analyses above, it is possible to develop a mathematical model to describe and predict the blending rate precisely. The main scheme for the blending rate during the mixing process was depicted in Figure 3.10. This figure represented two Gaussian functions before and after the critical mixing time δ_t while performing the asymmetric property. The scheme can be mathematically expressed as Asymmetric Gaussian Model (AGM):

$$DR = DR_{max}\left[H(t-\delta_t)e^{-\frac{(t-\delta_t)^2}{2S_L^2}} + H(\delta_t - t)e^{-\frac{(t-\delta_t)^2}{2S_R^2}}\right] \quad \text{Equation 3.7}$$

Where the DR_{max} is the critical value of the blending rate. δ_t denotes the critical mixing time. Before the critical time, the migration due to the mechanical force dominates, while after the critical time, the diffusion process plays a pivotal role. S_L and S_R indicate the shape of Gaussian curves related to work of mixing and the temperature. $H(u)$ represents two Heaviside step functions defined as:

$$H(u) = \begin{cases} 1, & u < 0 \\ 0, & u \geq 0 \end{cases} \quad \text{Equation 3.8}$$

$$u = t - \delta_t \quad \text{Equation 3.9}$$

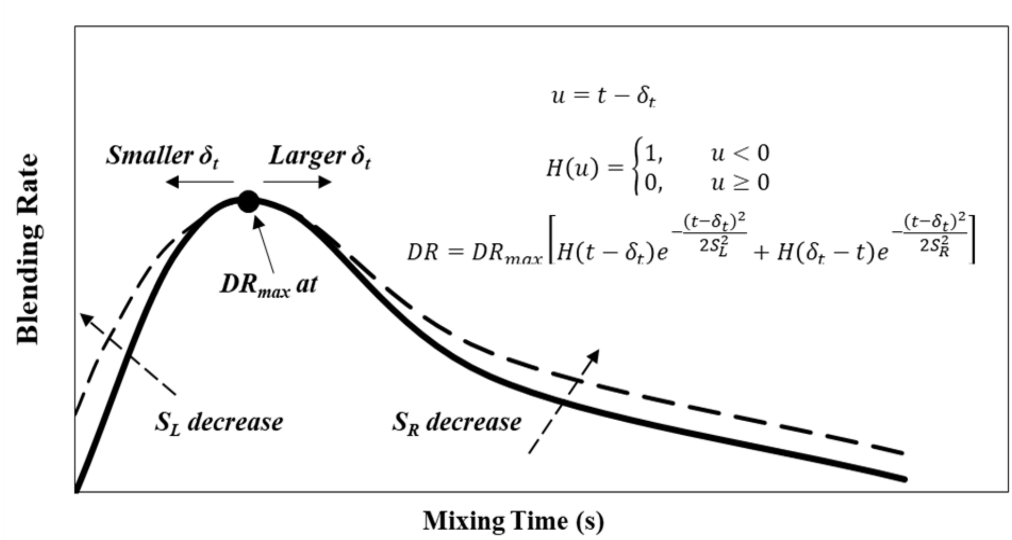


Figure 3.10 Schematic of Asymmetric Gaussian Model

For the model validation, an Asymmetric Gaussian Model was applied to the mixing temperatures of 110°C, 130°C, and 150°C, respectively (diffusion samples obtained from virgin Aggregates). Table 3.4 concludes the modeling results and model parameters of the Asymmetric Gaussian Model.

Table 3.4 Model parameters of the developed mathematical model

	110℃	130℃	150℃
DR_{max}	0.0375	0.0485	0.0303
δ_t (s)	60	48	30
S_L	50.4	37.4	50
S_R	44.2	28.1	21.9
R^2	0.999	0.993	0.994

As can be seen from Table 3.4, the model parameters can be estimated by fitting the blending rate curve. The fitting results are sufficient with all the correlation coefficients above 0.9. By comparing these model parameters, it is easy to distinguish the difference between different mixing conditions.

3.6 Summary and Conclusions

This chapter investigated the migration and diffusion behaviours during the asphalt mixing process containing RAP. Specially fabricated cubic aggregates were mixed with virgin and RAP aggregates at different mixing combinations (three mixing temperatures and four mixing times) as tracking markers. Diffusion samples were subjected to DSR and FTIR tests. The following conclusions were obtained in this chapter.

(1) In general, it can be divided into two stages when the asphalt mixtures containing RAP were mixed. In the first stage, the migration of virgin and aged bitumen occurred while the diffusion of bitumen mainly dominated the second stage.
(2) The mixing temperature is crucial for the migration and diffusion behavior during the mixing process, and it is also directly related to the diffusion rate. The increase of temperature leaded to a decrease in the viscosity of bitumen binders and, therefore, the increase of binder flowability.
(3) The change of blending rate with the mixing time follows the Asymmetric Gaussian Model proposed in this study. The AGM described two stages during the mixing process: the migration-dominated and diffusion-dominated stages. The migration-dominated stage was mainly affected by the temperature and mixing work, while the diffusion-dominated stage was determined by the temperature and bitumen properties.

4 Micro- and Meso-scale Homogeneity of Asphalt Mixtures with RAP in Thermal-non-equilibrium Condition

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Individual contributions:

Quan Liu conceptualized research idea, completed the simulation, conducted data analysis, contributed to writing and editing. Jiantao Wu contributed to the proofread of manuscript. Markus Oeser contributed to the supervision and final manuscript check.

4 Micro- and Meso-scale Homogeneity of Asphalt Mixtures with RAP in Thermal-non-equilibrium Condition

4.1 Abstract

Reclaimed asphalt pavement (RAP) is a promising material that can be partially substituted into the newly constructed pavement. An appropriate production procedure is of great significance to produce high-quality recycled asphalt mixtures. This study performed an investigation on the micro and mesoscale homogeneity of asphalt mixtures produced by different mixing conditions. To this end, 36 mixing combinations, including three preheated RAP temperatures, three mixing times, and two aggregate types, were considered in this study. The diffusion sample composed of new and aged bitumen was obtained non-destructively using the aggregate tracking method (ATM). In what follows, the Fourier Transform Infrared Spectroscopy (FTIR) and Dynamic Shear Rheometer (DSR) tests were conducted to quantify the diffusion sample from the mechanical and chemical aspects, respectively. Accordingly, the homogeneity of asphalt mixtures containing RAP was analysed at the micro and mesoscales. The results indicated that mixing temperature dominantly controlled the migration behavior of binders, further determining the diffusion behavior between new bitumen and aged bitumen. Notably, the estimation of homogeneity of asphalt mixtures was found to be indicator-dependent. Using different indicators could induce distinct evaluation results or even opposite results. In general, the increase of mixing time would improve the complex modulus of the diffusion sample. The worst homogeneity was observed when the mixing temperature was around 110°C. Due to the variation in adhering to the bitumen binder, the aggregate type also influenced the micro and mesoscale homogeneity of asphalt mixtures.

4.2 Introduction

Due to the increase of the rehabilitation projects, reclaimed asphalt pavement (RAP) is extensively applied to substitute a certain amount of new asphalt mixtures in reconstructed roads (Zaumanis, Mallick and Frank, 2014). Many practical experiences and research achievements have demonstrated that the use of reclaimed asphalt mixtures is an advanced approach from technical, economic, and environmental perspectives (Wang *et al.*, 2020; Lin *et al.*, 2021).

Previous studies indicated that incorporating a certain percentage of RAP had a positive influence on asphalt mixtures' mechanical performance (Mogawer *et al.*, 2012b; Guo *et al.*, 2014). Nejad et al. characterized the permanent deformation of warm-mixed asphalt mixtures containing varying RAP amounts and concluded that the high viscosity of aged bitumen in the RAP contributed to increasing anti-rutting properties of asphalt mixtures (Moghadas Nejad *et al.*, 2014). Zhao et al. studied the asphalt mixtures with RAP and claimed that mixtures with a high RAP content (up to 50%) conduced superior resistance to rutting, moisture, and better fatigue performance (Zhao *et al.*, 2012). Tapsoba et al. adopted the Thermal Stress Restrained Specimen Test (TSRST) to evaluate the thermo-mechanical behavior of asphalt mixtures with RAP. Results showed that asphalt mixtures with a high substitution rate (≥20%) of RAP significantly deteriorated the low-temperature property of asphalt mixtures (Tapsoba, Sauzéat, Benedetto, *et al.*, 2012). Huang et al. studied hot-mix asphalt mixtures with No.4 sieve screened reclaimed asphalt pavement and found that the inclusion of RAP generally increased the stiffness of mixtures but compromised cracking resistance capacity. Researchers also investigated the fatigue performance of asphalt containing RAP. However, it is not easy to unify consistent conclusions from these studies (Huang *et al.*, 2005a). Cong et al. (Cong *et al.*, 2016) and Mogawer et al. (Mogawer *et al.*, 2015) reported the decrease of fatigue life, while Aravind et al. (Aravind and Das, 2007) reported the increase of fatigue life when asphalt mixtures were produced with RAP materials. In addition, the reclaimed asphalt pavement has also been successfully applied in warm-mixed asphalt mixtures for sustainable development (López *et al.*, 2019).

Nonetheless, existing achievements failed to reach a consensus on the impact of RAP on the final performance of mixtures which might attribute to the diversities of RAP properties, materials designs, and recycling procedures. Concerning the recycling procedure, recycled asphalt mixtures are expected to reach a homogeneous state from a multi-scale perspective, behaving as satisfying mechanical performance. As illustrated in Figure 4.1, the material's homogeneity is determined by RAP sources and processing methods, while the macro-scale homogeneity is mainly related to the paving and compaction of pavements. Herein, the mesoscale homogeneity of recycled asphalt mixtures was defined as the homogeneity of one asphalt mixture sample. It consists of the homogeneity of aggregates, air voids, and binders. Concerning the definition of micro-scale, this study referred to it as the blending degree caused by diffusion between aged bitumen and virgin bitumen.

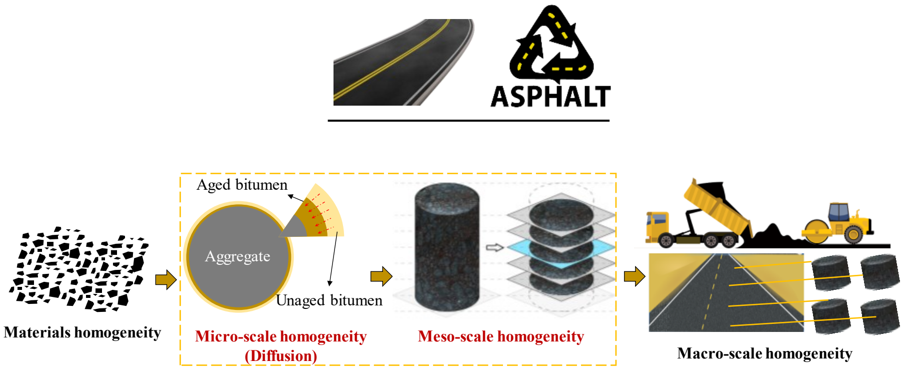


Figure 4.1 Conceptions of homogeneity concerning recycled asphalt mixtures

An optimal mixing procedure to produce recycled asphalt mixtures can improve the homogeneity at micro and mesoscale. Therefore, it is necessary to figure out the evolution of the micro and mesoscale homogeneity of recycled asphalt mixtures as the mixing proceeded. Attempts have been made to reveal the basic rule of the mixing process for asphalt recycling. Bressi et al. (Bressi *et al.*, 2015, 2016; Bressi, Dumont and Pittet, 2015) defined the clustering phenomenon as the agglomeration of RAP particles formed either before or during the newly mixing process and stated that the formation of RAP clusters could decrease the degree of blending between RAP and new binders. Wu et al. (Wu *et al.*, 2018b) investigated the mixing process under 12 combinations of mixing times and RAP preheating temperatures based on the indirect tensile stiffness modulus test and color image analysis. Results indicated that the deterioration of homogeneity was on account of the asynchronous breaking of clusters.

Meanwhile, the RAP preheating temperatures were decisive in determining the resistance of clusters to breaking as the increase of temperature would decrease the binder viscosity. Huang et al. (Huang *et al.*, 2005a) experimentally analyzed the blending process of RAP with virgin mixtures. The staged extraction and recovery technology was adopted, and it was concluded that a small portion of aged bitumen participated in the remixing process. Al-Qadi et al. (Al-Qadi, Elseifi and Carpenter, 2007) also concluded that only partial blending occurs during the mixing process. Nahar et al. (Nahar *et al.*, 2013) reported a blending zone during the mixing process by investigating the microstructures of recycled asphalt mixtures.

Fundamental knowledge of the mixing process has been investigated from multi perspectives. However, a minimal number of studies focused on how the mixing conditions and aggregate characteristics affect the mesoscale homogeneity of recycled asphalt mixtures. Accordingly, this study considered the variables of mixing time, mixing temperature, and aggregate characteristics. Notably, this study adopted the tracking aggregate method to obtain the diffusion samples from aggregates' surfaces (Wu *et al.*, 2021). In this case, the influence of chemical reagents on bitumen properties can be avoided. This study attempted to re-appear the mixing process as close as practical ones. The Fourier Transform Infrared Spectroscopy (FTIR) and Dynamic Shear Rheometer (DSR) tests were then carried out to measure diffusion samples.

4.3 Materials and Test Program

4.3.1 Materials

4.3.1.1 Bitumen

Laboratory-produced RAP materials were designed to avoid the variation of the materials. A PG 70-22 bitumen named ZH70 was used for the laboratory production of RAP. Asphalt mixtures prepared with ZH70 were subjected to the short-term and long-term aging process, after which laboratory production of RAP was completed. A PG 64-22 bitumen named SK70 was adopted as the new bitumen. Conventional properties of both unaged ZH70 and SK70 are listed in Table 4.1. Since the SK70 had a low-performance grade, the diffusion process can be tracked more explicitly.

Table 4.1 Conventional properties for bitumen in this study

Items		ZH70	SK70
Penetration (25°C,0.1mm)		62.3	73.3
Ductility (15°C, cm)		＞100	＞100
Softening Point (°C)		49.1	48.3
RTFO (163°C,5h)	Mass loss (%)	-0.2	-0.3
	Penetration ratio (%)	66	62
	Residual ductility (15°C, cm)	17	25

4.3.1.2 Aggregates used and the synthetic gradation

Two types of aggregates, limestone and basalt, were used. A typical dense gradation of asphalt mixture with the nominal maximum aggregate size (NMAS) of 16 mm was selected. However, the presence of fine aggregate and fillers would contaminate the diffusion sample when using the tracking aggregate method (details in Figure 4.3). Therefore, to reduce the fine aggregates and filler, only particle sizes above 2.36 mm were used as the final synthetic gradation, as shown in Table 4.2 and Figure 4.2.

Table 4.2 Synthetic gradation design of mixtures

Sieving size/mm		19	16	13.2	9.5	4.75	2.36	1.18	0.5	0.3	0.15
Passing ratio/%	Max	100	100	92	80	62	48	36	26	18	14
	Min	100	90	76	60	34	20	13	9	7	5
	Design	100	95	84	70	48	0	0	0	0	0

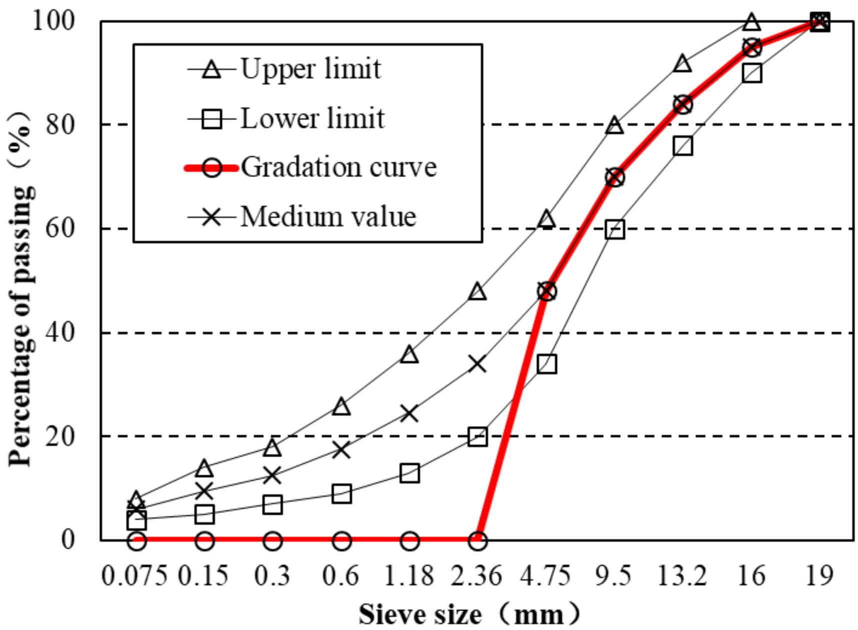


Figure 4.2 Gradation curves of asphalt mixture used for investigation

4.3.2 Determination of the binder content

As seen in Figure 4.2, the aggregate gradation adopted the coarse aggregate part of conventional aggregate gradation. For this reason, this study determined the bitumen content provided that the bitumen film thickness was 30 μm (determined by preliminary trials). Accordingly, the binder content can be derived by calculating the total surface areas of aggregates following Equation 4.1 and Equation 4.2 (Highway research institute of the transportation department, 2004). Consequently, the bitumen content used for the mixing was 1.26% by mass of the total weight.

$$SA = (2 + 0.02a + 0.04b + 0.08c + 0.14d + 0.3e + 0.6f + 1.6g)/48.74 \qquad \text{Equation 4.1}$$

$$P_b = h \times SA \qquad \text{Equation 4.2}$$

Where the SA means the specific surface area, m^2/kg; P_b is the calculated bitumen amount, %; a, b, c, d, e, f indicates the percentage of passing sieve for 4.75mm, 2.36mm, 1.18mm, 0.6mm, 0.3mm, 0.15mm respectively, %; h is the designed bitumen film thickness, μm.

4.3.3 Production of recycled asphalt mixtures

Aiming to obtain the diffusion samples of bitumen in recycled asphalt mixtures, the aggregate tracking method was adopted. Figure 4.3 illustrated the laboratory production of RAP materials. Tracking aggregates with the dimension of 20mm were prepared preliminarily by cutting large stones into small cubic shapes. The virgin aggregates with tracking aggregates were mixed with bitumen, and mixes in the loose state were subsequently subjected to the SHRP short-term aging process at 135°C for 4 hours, followed by the long-term aging process in the compacted state at 85°C for 120 hours. The compaction of asphalt mixtures was conducted using a gyratory compactor. In the end, the RAP materials were produced by crushing the compacted mixtures.

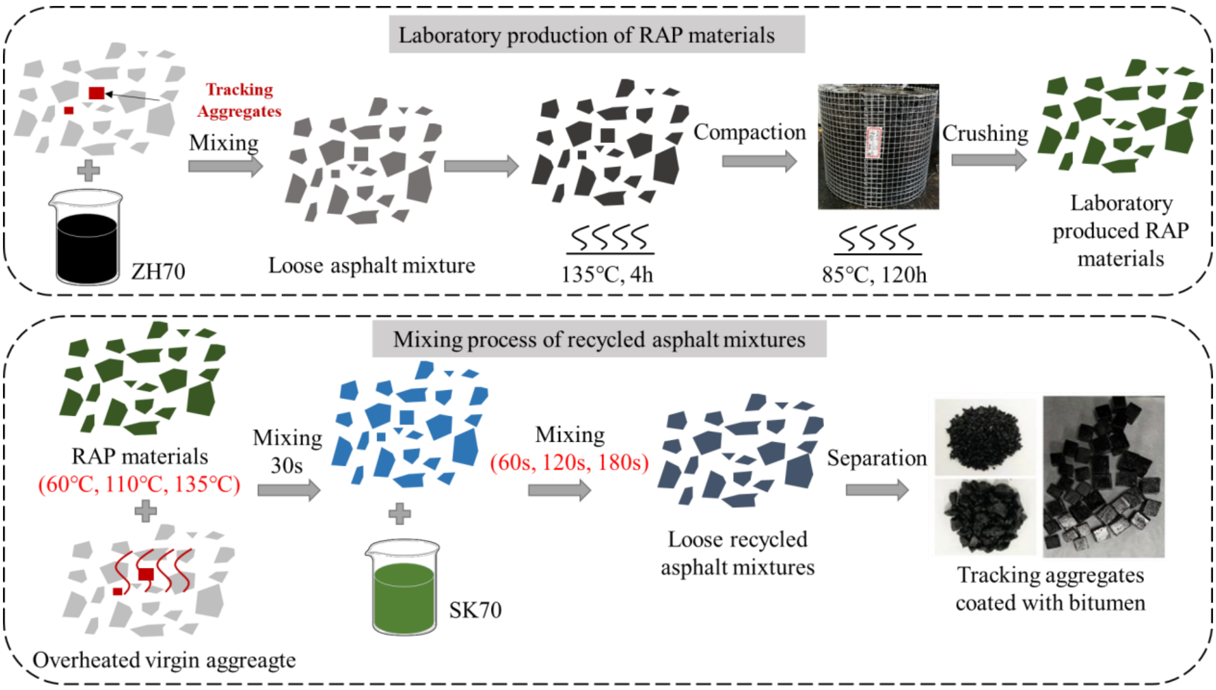


Figure 4.3 Schematic of recycled asphalt mixtures production

After obtaining sufficient RAP materials, the production of recycled asphalt mixtures in the laboratory can be carried out, as seen in Figure 4.3. The recycled asphalt mixture was composed of 30% RAP materials. It was worth noting that current practice suggests the use of RAP with an incorporation percentage below 20%. However, the homogeneity issue would become more significant when a high replacement rate was adopted. Therefore, this study used the 30% RAP dosage. In the beginning, the RAP materials were preheated to the investigated temperatures (60°C, 110°C, 135°C). To achieve sufficient flowability for mixing, the virgin aggregate should be overheated to a specific temperature, determined by the thermal conductivity, as seen in Equation 4.3.

$$T_a = T_{mix} + \frac{C_R P_R (T_{mix} - T_R) + C_f P_f (T_{mix} - T_f)}{(0.0078r + 0.504) C_a P_a} \quad \text{Equation 4.3}$$

Where T_a is the temperature of virgin aggregates, T_{mix} is the target mixing temperature (165°C). The low case of R, a, and f represents the RAP, virgin aggregates, and fillers, respectively. Symbols C, P, and T illustrate the specific heat capacity, mass percentage, and initial temperature, respectively. r is the content of RAP (30%). According to literature, the specific heat capacities used in this study for basalt, limestone, and bitumen were 0.89 kJ·(kg·°C)$^{-1}$, 0.84 kJ·(kg·°C)$^{-1}$, and 1.67 kJ·(kg·°C)$^{-1}$, respectively. Based on this, the overheated temperature of virgin aggregates relative to the investigated temperature can be determined as listed in Table 4.3.

Table 4.3 Determination of overheated temperature for virgin aggregates

T_R (°C)	Determined overheated temperature T_a (°C)	
	Basalt	Limestone
60	255.9	256.0
110	212.6	212.7
135	191.0	191.0

The RAP materials and overheated aggregates were mixed for 30s to transfer the heat. After that, the virgin bitumen was incorporated for an additional mixing duration. Consequently, the recycled asphalt mixtures were produced. The tracking aggregates were then recognized according to their shape and taken out for further tests. In total, 36 mixing conditions were considered as the combinations of RAP temperatures (60°C, 110°C, 135°C), mixing time (60s, 120s, 180s), and aggregate types (basalt and limestone), the dimension of tracking aggregates (20mm). For each mixing condition, five tracking aggregates were used. The diffusion sample with varying mixing conditions was collected directly from the aggregate surface using a silicone knife.

4.4 Experimental methods

4.4.1 Dynamic Shear Rheometer (DSR)

The mechanical properties were characterized by performing a DSR frequency sweep on diffusion samples obtained from tracking aggregates' surfaces. Specifically, the frequency sweep was conducted from 0.1Hz to 10Hz strictly within the linear range of viscoelastic under the strain control mode. Five samples were measured using parallel plates of 8mm diameter and 2mm gap size for each mixing condition. The measured temperature was from 10 to 50℃ with an interval of 10℃.

Moreover, the master curves were constructed using Williams-Landel-Ferry (WLF) equations (Zhang and Leng, 2017) for comparison in a broad frequency range. The sigmoidal model was used to smooth the mater curves with a reference temperature of 15℃. Mechanistic-Empirical Pavement Design Guide (MEPDG) recommended the sigmoidal model to fit the master curve, and it mainly describes the rate dependence of the modulus master curve. Mathematically, the sigmoidal model is described as Equation 4.4 (Yusoff *et al.*, 2013):

$$\lg |G^*| = \delta + \frac{\alpha}{1 + e^{\beta + \gamma\{\lg \omega\}}} \qquad \text{Equation 4.4}$$

where ω is the reduced frequency, δ is the lower asymptote, α is the difference between the values of the upper and lower asymptote, the shape between the asymptotes and the location of the inflection point is dependent on β and γ, respectively. The master curve of phase angle was established based on the Kramer-Konig relationship expressed in Equation 4.5 (Yang and You, 2014).

$$\delta(\omega) \approx \frac{\pi}{2} \int_0^\infty \frac{\pi dlog|E^*|}{dlog(\omega)} \qquad \text{Equation 4.5}$$

The entire construction process was optimized with the aid of the Solver function in Microsoft Excel by minimizing the sum of square error (SSE) (Yusoff, Shaw and Airey, 2011; Yusoff *et al.*, 2013), as shown in Equation 4.6.

$$SSE = \sum \frac{\left(log\left|G^*_{exp}(f,T)\right| - log\left|G^*_{model}(f,T)\right|\right)^2}{\left(log\left|G^*_{exp}(f,T)\right|\right)^2} + \sum \frac{\left(log\left|\delta^*_{exp}(f,T)\right| - log\left|\delta^*_{model}(f,T)\right|\right)^2}{\left(log\left|\delta^*_{exp}(f,T)\right|\right)^2} \quad \text{Equation 4.6}$$

4.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

The diffusion between aged bitumen and unaged bitumen was characterized by monitoring the functional groups in the diffusion sample from the chemical perspective. Lamontagne et al. (Lamontagne *et al.*, 2001) stated that the chemical evaluation of road bitumen has a good correlation with the aging degree. Two oxidation indices are obtained by calculating defined areas: carbonyl and sulfoxide, respectively, as seen in Equation 4.7 and Equation 4.8. In this study, an FTIR spectrometer was used to determine diffusion samples' functional characteristics considering different mixing conditions with the wavenumbers ranging from 4000 to 600 cm^{-1}.

$$Ico = \frac{Area\ around\ 1700\ cm^{-1}}{Area\ around\ 1460\ cm^{-1} + Area\ around\ 1375cm^{-1}} \quad \text{Equation 4.7}$$

$$Iso = \frac{Area\ around\ 1030\ cm^{-1}}{Area\ around\ 1460\ cm^{-1} + Area\ around\ 1375cm^{-1}} \quad \text{Equation 4.8}$$

4.4.3 Evaluation methods applied in this study

Coefficient of Variation (CoV)

The coefficient of variation (*CoV*) measures a probability distribution or frequency distribution (Reed, Lynn and Meade, 2002). It is often expressed as a percentage and is defined as the standard deviation ratio to the mean expressed in Equation 4.9. The mesoscale homogeneity was estimated by calculating the *CoVs* of oxidation indices for a specific mixing condition.

$$CoV = \frac{\sigma}{\mu} \quad \text{Equation 4.9}$$

Where the σ represents the standard deviation, and μ is the mean value.

Blending degree

A blending degree was used to qualify the blending efficiency. Complex moduli measured at 20°C and 10rad/s were selected as the fundamental indicator, based on which the blending degree can be calculated by the following Equation (see in Chapter 3):

$$Blending\ degree = \frac{\log G_{exp} - \log G_{target}}{\log G_{aged} - \log G_{virgin}} \quad \text{Equation 4.10}$$

Where G_{aged} and G_{virgin} are the complex moduli of aged and virgin bitumen, and G_{aged} means the measured complex modulus for the blending sample. G_{target} indicates the mixed complex modulus in the logarithm coordinate, providing the virgin and aged bitumen was thoroughly mixed.

4.5 Results and Discussion

4.5.1 Micro-scale homogeneity (diffusion) of recycled asphalt mixtures

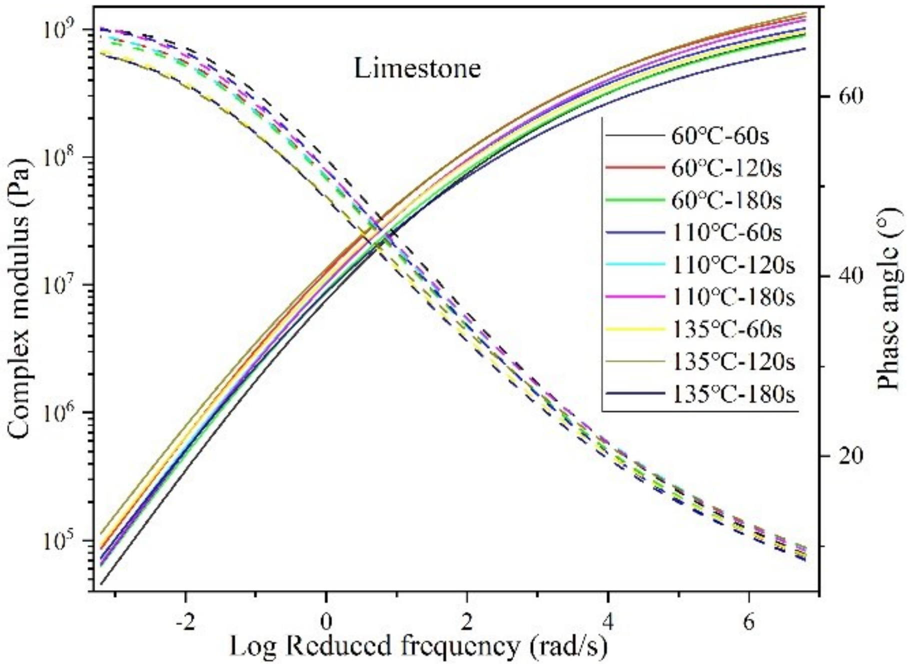
Many existing studies have been carried out to study the diffusion between virgin and aged bitumen. For the benefit of terminology consistency, this study preferred to use the micro-scale homogeneity to include the binder diffusion in asphalt mixtures' homogeneity issue. As seen in Table 4.4, the sigmoidal model's parameters for different mixing conditions were summarized. Accordingly, Figure 4.4 shows constructed master curves of complex modulus and phase angle.

Due to that, the DSR test requires a sufficient number of binders. Therefore, diffusion samples collected from the tracking aggregates were mixed preliminarily. The measurement results represented the overall rheological properties of the diffusion sample for a specific mixing condition. It can be seen from Figure 4.4 that diffusion samples obtained from the tracking aggregate surface showed distinct master curves of complex modulus, demonstrating the diffusion process that occurred during the mixing. Furthermore, the mixing condition significantly influenced the rheological properties of diffusion samples, which indicated that the diffusion process was associated with the mixing condition. Hence, it is essential to design an optimal mixing condition to satisfy the initial mechanical performance of recycled asphalt mixtures, which comprises the mechanical performance and economical cost.

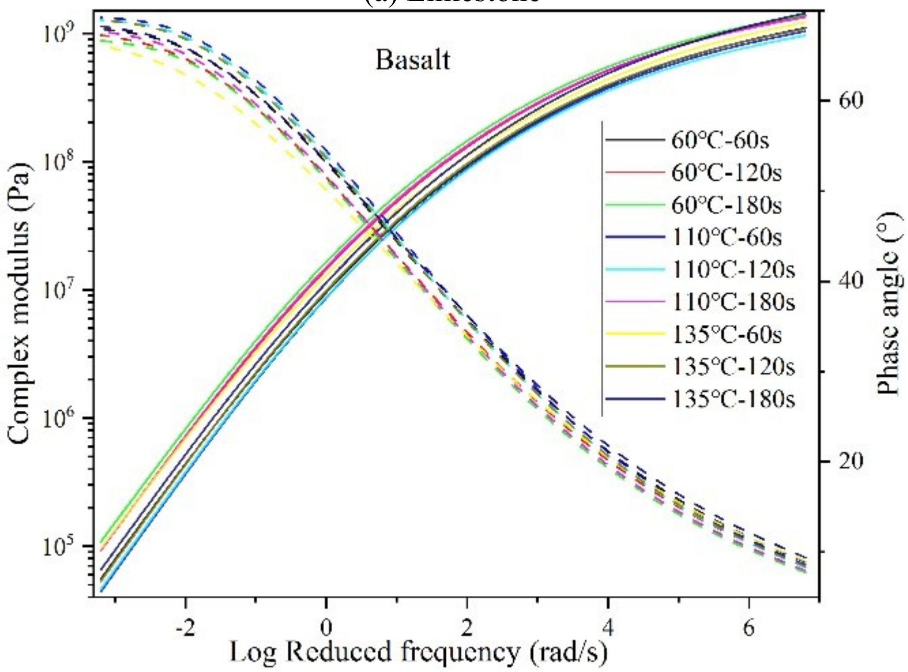
Table 4.4 Sigmoidal parameters for master curves construction

Mixing conditions		Limestone				Basalt			
		δ	α	β	γ	δ	α	β	γ
60°C	60s	0.46	8.81	-1.00	-0.34	0.55	8.79	-1.01	-0.34
	120s	0.60	8.81	-1.05	-0.34	0.76	8.65	-1.05	-0.35
	180s	0.46	8.80	-1.05	-0.33	1.10	8.29	-1.05	-0.36
110°C	60s	0.62	8.66	-1.04	-0.35	0.58	8.71	-1.00	-0.35
	120s	0.17	9.25	-1.05	-0.32	0.65	8.60	-1.01	-0.36
	180s	0.19	9.21	-1.05	-0.33	0.88	8.51	-1.06	-0.35
135°C	60s	0.34	8.97	-1.10	-0.32	0.46	8.95	-1.07	-0.33
	120s	0.16	9.34	-1.09	-0.31	0.63	8.68	-1.02	-0.35
	180s	0.46	8.69	-1.09	-0.33	0.46	9.02	-1.01	-0.34

On the other hand, it can be observed that (although not explicit) neither mixing temperature nor mixing time affects the rheological properties of diffusion samples monotonously. For instance, the diffusion sample relative with 135°C and 120s (clay bank line) showed the highest stiffness modulus in limestone, whereas the corresponding condition turned out to be 60°C and 180s (green line). Honestly speaking, it does not make much sense herein to discuss the influence of mixing conditions on diffusion samples' rheological properties. Figure 4.5 gives a schematic to demonstrate the insignificance of the discussion.



(a) Limestone



(b) Basalt

Figure 4.4 Master curves (15°C) of complex modulus and phase angle

As indicated in Figure 4.5, the mechanical force drives the random motions of aggregates during the mixing process; thus, the aggregates interacted. Simultaneously, the migration of binders happened. The aggregate surfaces progressively formed a two-layer structure, which was composed of unaged and aged bitumen binders. Although the new aggregates were added before the new bitumen; Probably, new aggregates were partially coated with aged bitumen before incorporating the new bitumen due to the high viscosity of aged bitumen. It can be imagined that realistic conditions could be more complicated than those illustrated in Figure 4.5. Therefore, merely comparing the mater curves is unneutral.

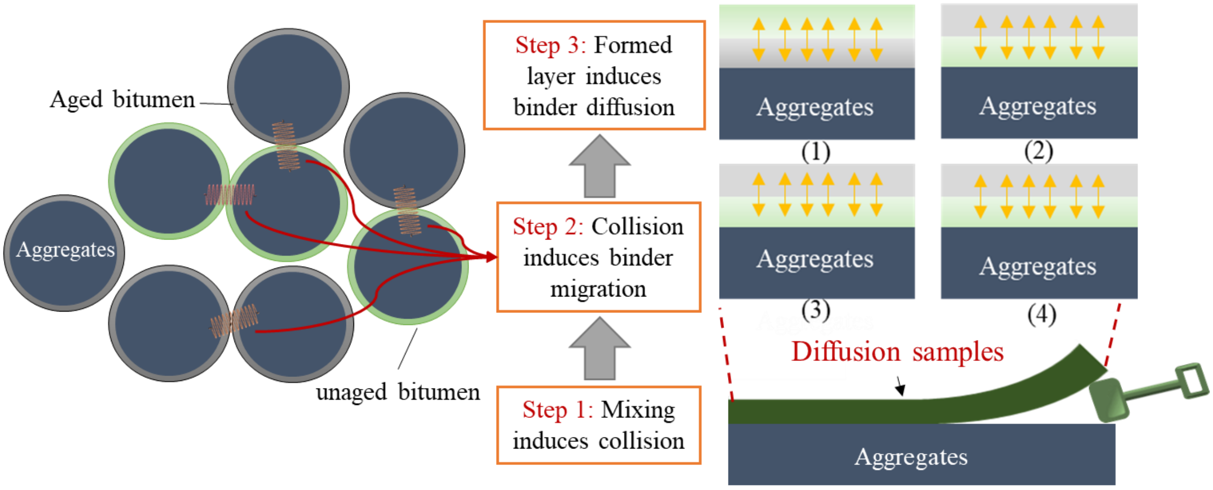


Figure 4.5 Schematic of migration and diffusion in the mixing process

Previous studies introduced the blending degree to evaluate the blending efficiency of recycled asphalt mixtures. Therefore, this study used the moduli measured at 20°C and 10rad/s to calculate the blending degree as a function of mixing time and temperatures, as shown in Table 4.5. The target modulus was calculated assuming the idealized blending of new and aged bitumen with the RAP proportion of 30%. Following Equation 4.10, corresponding blending degrees were then derived for limestone and basalt aggregates. It can be intuitively seen from Table 4.5 that the aggregate type played a crucial role in the diffusion between virgin and aged bitumen binders. The influence of mixing conditions on the complex moduli or blending degree was untraceable, ascribed to the complicated migration and diffusion behaviours explained in Figure 4.5.

Nevertheless, the tendency of blending degree, to some extent, can identify the specific migration or diffusion process, as seen in Figure 4.6. The higher mixing temperature led to low flowability of binders and further determined the migration behavior of new and aged bitumen. Besides, the temperature is also the decisive factor of the binder diffusion. Therefore, the analysis on the blending degree was generally divided into three groups based on the temperature. It is noticeable that, in the current mixing procedure, the final mixing temperature was theoretically the same, given that the temperature equilibrium can be reached in a very short time. However, the idealized condition is too perfect to achieve. In the mixing practice, the RAP temperature determined the viscosity of aged bitumen; Moreover, the unbalanced thermal conductivity also induced the thermal non-equilibrium.

Table 4.5 Moduli and blending degrees for different mixing conditions

Mixing Conditions		Moduli @ 20°C, 10rad/s		Blend Degree	
Temperature/°C	Time/s	Limestone	Basalt	Limestone	Basalt
60	60	8312300	10505000	15.14%	25.72%
60	120	13418000	15356000	36.79%	42.89%
60	180	9617600	17505000	21.73%	48.82%
110	60	11160000	9526100	28.46%	21.30%
110	120	11157000	9723300	28.45%	22.23%
110	180	11061000	16026000	28.06%	44.83%
135	60	11689000	13443000	30.55%	36.88%
135	120	13859000	10862000	38.26%	27.24%
135	180	9243100	12322000	19.94%	32.94%
Aged bitumen		27510000		-	-
Virgin bitumen		3014200		-	-
Target modulus		5947826		-	-

When the RAP temperature was at 60°C, the viscosity of aged bitumen was relatively low. Most of the flowing bitumen was the new bitumen. Therefore, in the case of the basalt, the blending degree increased with the mixing time. Besides, it can be found that the increasing rate was reduced, which conformed to the Fick law. However, when the aggregate was limestone, the blending degree remarkably decreased. It is plausible that a third new bitumen layer was added due to the migration of new bitumen. Besides, the abnormal phenomenon was probably ascribed to two reasons. Firstly, the aggregate tracking method can only collect the outer layer of binders. Therefore, the precise proportion of the mix of fresh and aged bitumen was uncertain. Furthermore, due to a low mixing temperature, a perfect coating of new bitumen on the RAP aggregates cannot be guaranteed, which resulted in the uniformly distribution of new bitumen. Referring to Table 4.3, it can be found that the overheated temperature of aggregates for basalt and limestone was almost the same. The apparent variation between basalt and limestone can be attributed to two reasons. One was due to the variation of thermal conductivity, and the other one rested on the difference of absorption ability to bitumen.

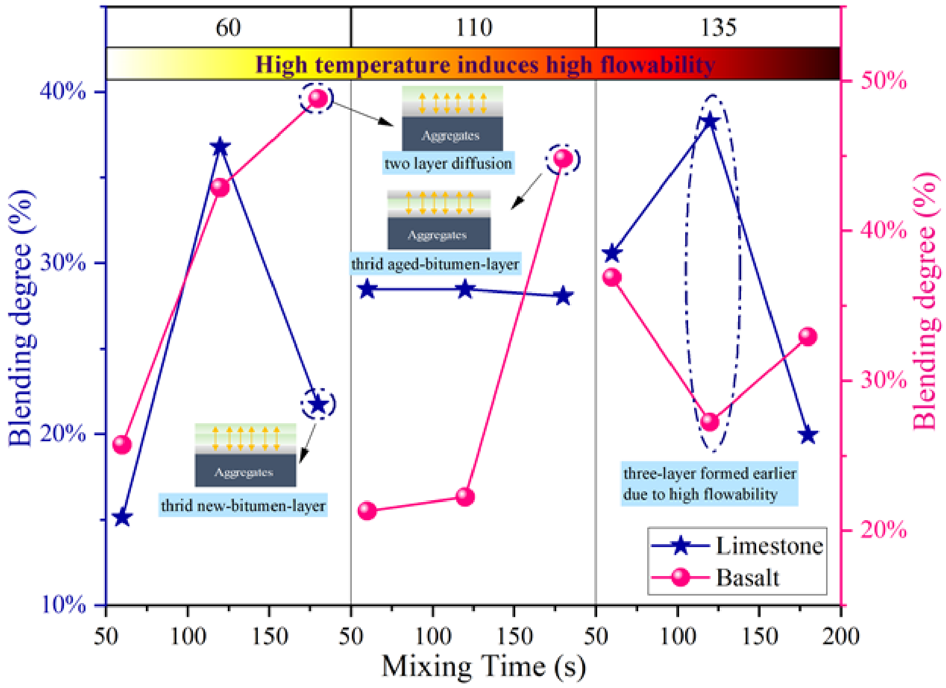
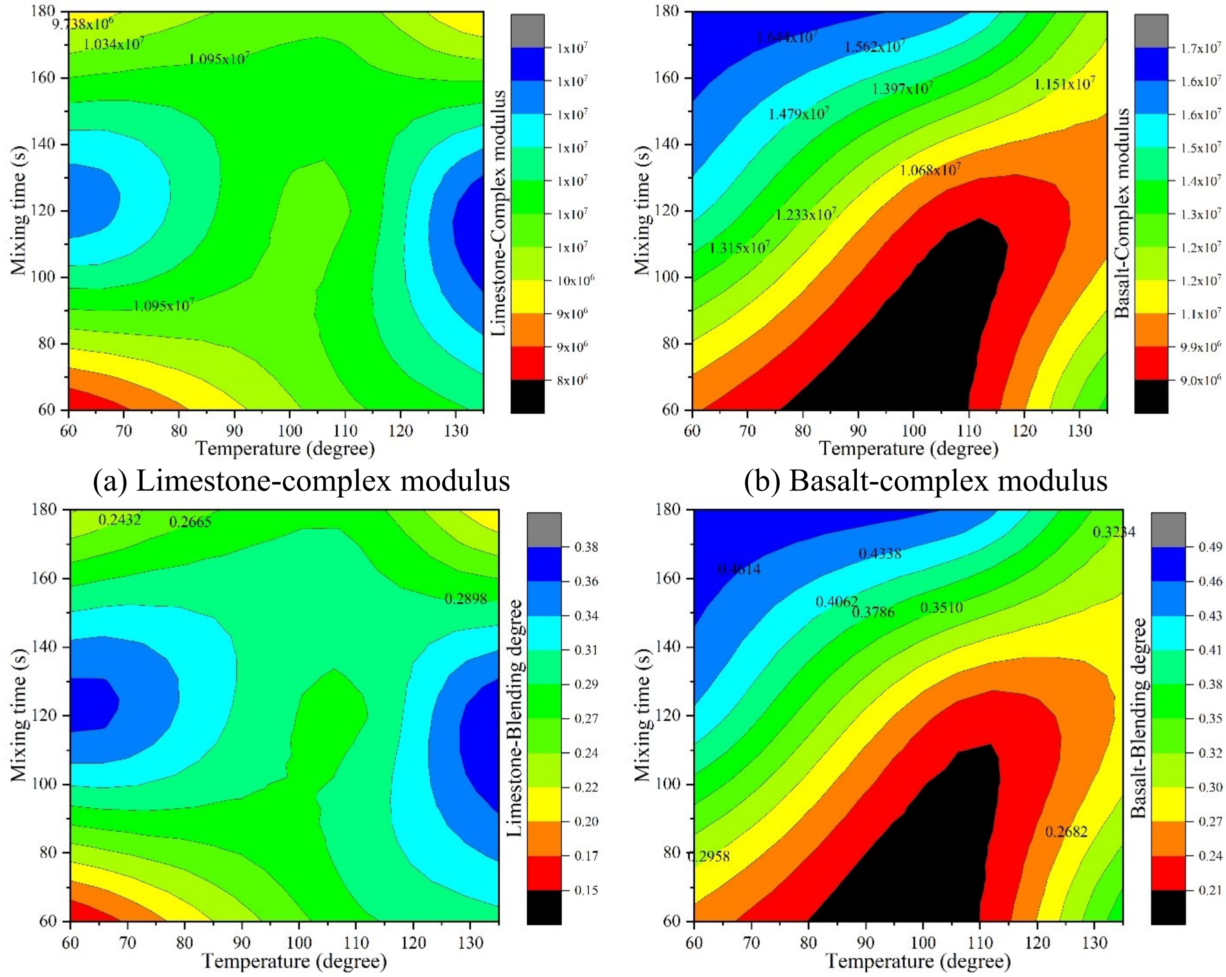


Figure 4.6 Schematic of possible migration and diffusion in the mixing process

At 110°C, the increasing rate was observed with a dramatically increasing tendency. At this temperature, aged bitumen started to flow, and thus, the aged bitumen was possible to be added as the third outer layer, as indicated in Figure 4.6. It is interesting to notice that the blending degrees almost kept unchanged as the mixing time increased. This phenomenon claimed that increasing the mixing time does not mean the increase of blending degrees, dependent on the aggregate type and mixing temperatures. This finding stressed that, for the production of recycled asphalt mixtures, the mixing condition could not be specific. In other words, no mixing procedure could be universally adapted to the production of recycled asphalt mixtures.

When the temperature increased to 135°C, the blending degree tendency was not consistent with the previously introduced two conditions. As explained in Figure 4.6, the reason was ascribed to that three-layer formed earlier due to high flowability for both aged bitumen and new bitumen. In conclusion, the blending degree evolution was untraceable due to the complicated migration behaviours associated with the aggregate types and preheated RAP temperatures.

Figure 4.7 summarized the influence of mixing conditions on a specific indicator measured by DSR using the contour plots. The contour plots of limestone were remarkably distinct from basalt, indicating that the aggregate type should be considered when discussing the influence of mixing conditions on the diffusion samples.



(a) Limestone-complex modulus (b) Basalt-complex modulus

(c) Limestone-blending degree (d) Basalt-blending degree

Figure 4.7 Influence of mixing on complex modulus and blending degree

Since the blending degree was calculated based on the complex modulus, the blending degree and complex modulus would show a similar contour pattern. It can be intuitively observed that how the mixing condition affects specific indicators. For limestone, low temperature and mixing time resulted in low complex modulus and blending degree. Meanwhile, the maximum complex modulus and blending degree occurred when the mixing time was around 120s. The maximum complex modulus and blending degree can be achieved by a longer mixing time at relatively low temperatures concerning the basalt aggregate. However, the minimum complex modulus and blending degree occurred when the temperature was lower than 120℃.

4.5.2 Meso-scale homogeneity of recycled asphalt mixtures

The above section demonstrated that the prerequisite for the microcosmic uniformity of recycled asphalt mixtures is to achieve a certain uniformity at the mesoscale. For this reason, this section investigated the mesoscale homogeneity of recycled asphalt mixtures. In specific, the FTIR tests were used to identify the diffusion samples collected from different tracking aggregates. According to Equation 4.7 and Equation 4.8, indicators *Iso* and *Ico* can be calculated, respectively. For each mixing condition, five parallel samples were measured. Table 4.6 presents the calculated average values and *CoVs*.

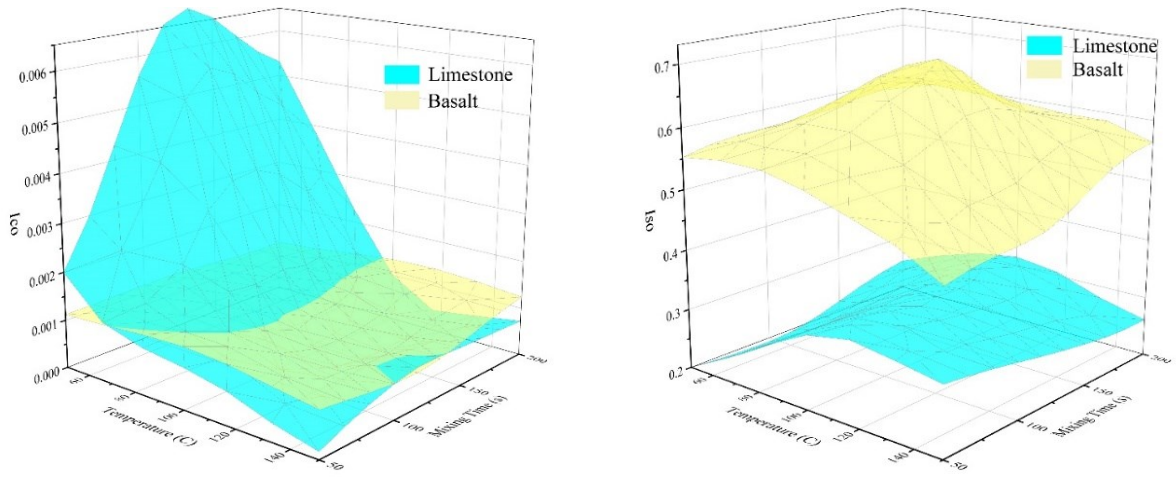
It can be concluded from Table 4.6 that the mixing condition had a critical influence on the chemical compositions of diffusion samples. The highest *CoV* (92.39%) of *Ico* was observed at 110°C and 60s. As for the *Iso*, the critical mixing condition regarding the highest *CoV* (25.54%) also happened at the 110°C and 60s. Referring to Figure 4.7, it can be found that the blending degree at 110°C and 60s was the lowest, which claimed the tight relationship between migration and diffusion of bitumen.

Table 4.6 The average values and CoVs of Ico and Iso

		Limestone				Basalt			
		Ico		*Iso*		*Ico*		*Iso*	
T(°C)	*t*(s)	Mean	*CoV*	Mean	*CoV*	Mean	*CoV*	Mean	*CoV*
60	60	0.0017	**68.16%**	0.2187	**15.56%**	0.0011	**34.29%**	0.5696	**7.85%**
	120	0.0064	**21.20%**	0.2138	**9.97%**	0.0012	**34.56%**	0.581	**2.98%**
	180	0.0047	**37.85%**	0.2629	**12.69%**	0.0011	**16.43%**	0.6127	**1.56%**
110	60	0.001	**92.39%**	0.3392	**25.54%**	0.0012	**39.08%**	0.5441	**9.04%**
	120	0.0001	**44.88%**	0.3232	**11.53%**	0.001	**72.43%**	0.7243	**5.00%**
	180	0.0002	**47.05%**	0.3233	**11.74%**	0.0013	**19.14%**	0.589	**4.58%**
135	60	0.0004	**53.34%**	0.3214	**21.58%**	0.001	**48.46%**	0.5093	**8.22%**
	120	0.0008	**11.68%**	0.2959	**9.47%**	0.0007	**55.09%**	0.5212	**7.86%**
	180	0.0007	**6.26%**	0.2732	**8.68%**	0.0012	**30.82%**	0.5953	**3.58%**

Concerning the influence of aggregate types, it can be found that the overall *CoVs* for basalt were lower than that for limestone. Therefore, the aggregate type affects not only the micro-scale homogeneity but also the mesoscale homogeneity. Unfortunately, the primary mechanism of how the aggregate influences the *CoVs* requires further experimental evidence.

Figure 4.8 shows the average values of *Ico* and *Iso* for limestone and basalt, respectively. It is worth noting that *Ico*'s average value measured from limestone was more significant than the one measured from basalt. Meanwhile, the average value of *Iso* for basalt was significantly larger than that for limestone. This discrepancy was on account of the aggregate’s selection absorption. Due to the interaction between aggregate and bitumen, the conformational distribution of chemical compositions was different. Therefore, the concentration of sulfoxide group or carbon oxide group was not uniform at the molecular scale. This phenomenon was ascribed to the complicated compositions of diffusion samples. Besides, the interaction between aggregate and bitumen might contribute to the inhomogeneous distribution of sulfoxide group or carbon oxide group (Gao *et al.*, 2018, 2019) .

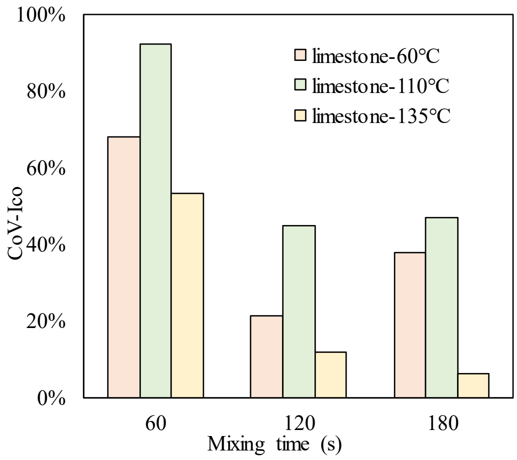


(a) *Ico* (b) *Iso*

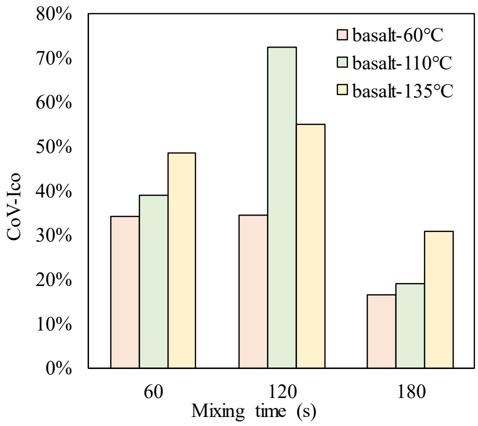
Figure 4.8 Average values of Ico and Iso for limestone and basalt

Regarding the influence of mixing conditions, it is interesting to observe that the tendency of surfaces for limestone and basalt was opposite. The *Ico* of limestone showed a decreasing tendency with mixing temperature, while in the case of basalt, the *Ico* increased with the temperature. At the mixing time of the 60s, the *Ico* of limestone reached its maximum value. However, the minimum value of *Ico* for basalt took place at the mixing time of the 60s. A similar conclusion can be achieved for the indicator *Iso*.

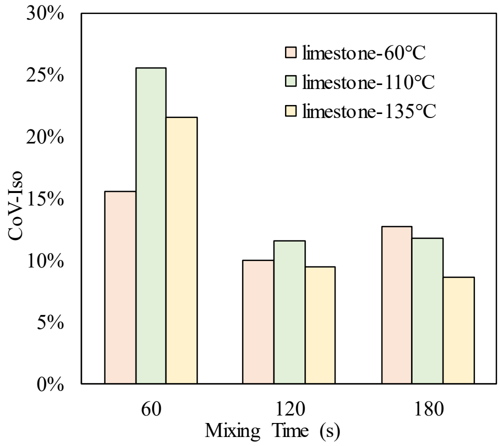
The *CoV* was adopted to evaluate the influence of mixing conditions on the mesoscale homogeneity, as shown in Figure 4.9. It can be seen that the homogeneity evaluation based on *Ico* showed significant variation compared with that based on Iso. In other words, the homogeneity evaluation would vary with the selection of evaluation indicators. Using the *Iso* to evaluate recycled asphalt mixtures' homogeneity concluded that the variation would not beyond 30%. Whereas for the *Ico*, the variation could reach high above 90%, representing an inhomogeneous state. There are two reasons probably explaining the above issue. As can be seen in Table 4.6, the calculated *Ico* was relatively more minor than the *Iso*. Therefore, large *CoV* can be attributed to mathematical concerns. The second reason can be ascribed to the non-uniform coating of binders. According to Figure 4.6, the proportions of new bitumen and aged bitumen in diffusion samples were different. Therefore, the amount of detected characteristic groups also showed differently.



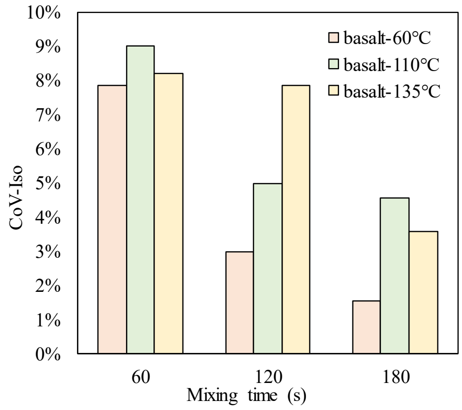
(a) limestone-*Ico*



(b) Basalt-*Ico*



(c) limestone-*Iso*



(d) Basalt-*Iso*

Figure 4.9 Calculated CoVs of different mixing conditions

Apart from the *Ico* for basalt aggregates, at a mixing time of the 60s, the worst homogeneity state happened when the mixing temperature was 110°C. The reason can be concluded as follows: at low temperature (60°C), the aged bitumen was not flowable, and thus, the migration behavior was mainly attributed to the new bitumen coating outside the RAP materials. As the temperature increased to 110°C, the aged bitumen started to flow. Nevertheless, insufficient flowability ability induced complicated migration behaviours. Consequently, the diffusion samples varied significantly. Once the temperature continued increasing, both new bitumen and aged bitumen owned sufficient viscosity, resulting in a relatively homogenous bitumen film thickness.

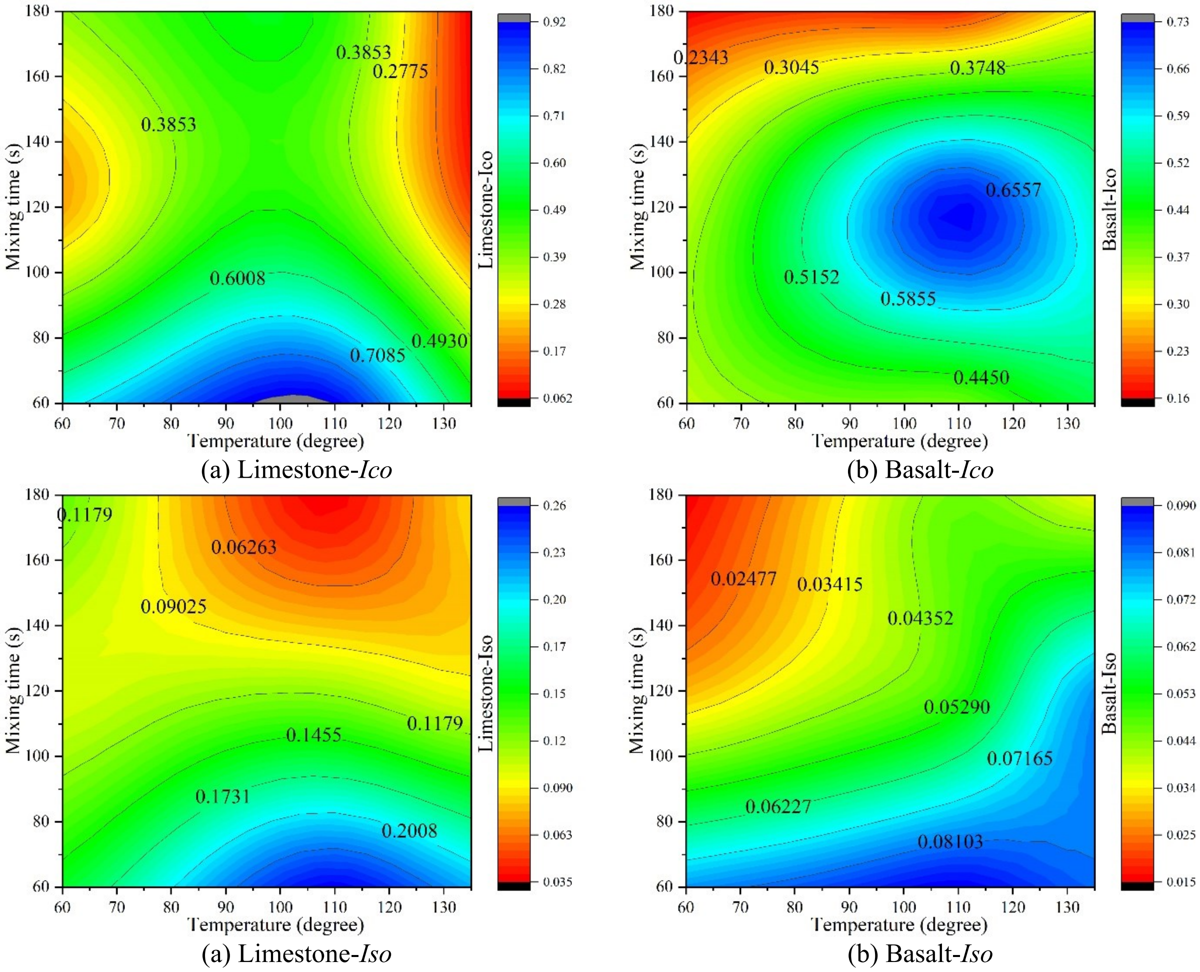


Figure 4.10 Contour plots: the influence of mixing conditions on Ico and Iso

On the other hand, it can be observed that the mixing time, in general, had a positive impact on the variation of the diffusion sample. However, when the mixing time increased, the bonus from extending the mixing time was limited when the temperature was relatively low. In particular, at low-temperature 60℃, the *CoV*s increased although the mixing time increased, which could be ascribed to the re-clustering phenomenon during the mixing process.

Similarly, the contour plots concerning the *CoV* patterns as a function of mixing time and temperature were also plotted, as shown in Figure 4.10. These patterns indicated that the evaluation of homogeneity was dependent on the aggregate type and selected indicators. Besides, that the worst mixing temperature was around 110℃, was demonstrated. The influence of mixing time on the homogeneity showed a close relationship with the mixing temperature and a positive role in an overall perspective.

4.6 Conclusions

This study performed an investigation focusing on the micro- and mesoscale homogeneity of laboratory-produced asphalt mixtures considering the thermal-non-equilibrium environment. Although there is a gap between the laboratory experiments and in-situ measurements, the primary mechanism concerning the blending can be concluded, which could be a crucial reference to the practice. Based on the results, some key findings were summarized as follows.

(1) The micro-scale homogeneity (diffusion) of asphalt mixtures was tightly associated with the mesoscale homogeneity of asphalt mixtures. In particular, the binder migration induced varying binder film conditions, causing a significant non-uniformity of asphalt mixtures at a micro-scale.
(2) The mixing temperature was the decisive factor that influences the migration and diffusion of binders. However, extending the mixing time did not mean increasing the homogeneity of asphalt mixtures due to the re-clustering phenomena in the mixing process.
(3) The estimation of homogeneity of asphalt mixtures was dependent on the selected indicator. Therefore, merely one indicator cannot fully reflect the homogeneity of asphalt mixtures.
(4) Generally, the mixing time had a positive impact on the homogeneity of asphalt mixtures at the mesoscale. However, the worst homogeneity state was observed at the mixing temperature of 110°C.

5 Micro-scale investigation of aging gradient within bitumen film around air-binder interface

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Individual contributions:

Quan Liu conceptualized research idea, designed the experiments, completed the simulation, conducted data analysis, contributed to writing and editing. Jiantao Wu and Linlin Xie carried out the experiments. Zeyu Zhang and Xinyuan Ma contributed to the draft proofread. Markus Oeser contributed to the supervision and final manuscript check.

5 Micro-scale investigation of aging gradient within bitumen film around air-binder interface

5.1 Abstract

The aging issue of bitumen is one of the most concerned topics for the bituminous pavement duration. Currently, the laboratory accelerates the aging by applying high temperature and pressure. However, an extremely thin state of bitumen in a real asphalt mixture could induce the interference of aging that happened at two interfaces, namely the air-bitumen interface and the bitumen-aggregate interface. Hence, it is of great importance to explore more deeply about what is happening on the air-bitumen interface. This study performed experimental research on the aging gradient of bitumen during the TFOT test, together with the molecular simulation. To that end, Thin Film Oven Tests (TFOTs) on bitumen with different aging durations (0, 1, 5, 10, 20 hours) were conducted and further, the microscopic aging gradient along with the aging depths (11 layers in total) was investigated. The Dynamic Shear Rheometer (DSR) and Fourier Transform Infrared Spectroscopy (FTIR) tests were performed to characterize the aged bitumen samples. From the molecular perspective, this study adopted the molecular dynamic simulation of oxygen and bitumen. The results indicated that the aging of bitumen induced the increase of complex modulus and the generation of chemical functional groups. Experimental data demonstrated the microscopic aging gradient, and the effective depth of thermal oxidation could be within 1000 μm due to the limited oxygen diffusion. The results of molecular dynamics simulation showed consistent conclusions with the experimental results. This research revealed the complicated aging mechanism from the molecular scale and provided further research with fundamental findings.

5.2 Introduction

Asphalt pavements, due to its superior servicing performance and relatively low cost, have been recognized and adopted for more than a century (Wang *et al.*, 2018; Wu *et al.*, 2021). Bituminous binders, accounting for around 4% by mass in asphalt mixtures, contribute considerably to the pavement resistance to the wheel loading and environmental actions. However, the aging issue of bitumen is still one of the major concerns for the duration of asphaltic pavements (Airey and Choi, 2002). Due to the exposure and/or high temperature, the bitumen will deteriorate, inducing the low cracking resistance and adhesion failure (Yang *et al.*, 2018). When the bitumen is excessively aged, the asphalt mixture will become brittle, and its ability to support traffic-induced stresses and strains may significantly reduce, which can easily cause some cracking damage to the bound layer of a pavement. Excessive hardening can also weaken the adhesion between the bitumen and aggregate, resulting in loss of materials at the surface layer.

Traxler (Traxler, 1936) identified 15 different factors that may affect the chemical, rheological, and adhesion characteristics of bitumen. Some of these effects were proved with experimental data, and some were not. Further studies have confirmed that aging is generally ascribed for the loss of oily components (by volatility and/or absorption by porous aggregates), thermal oxidation, steric hardening, and photo oxidation(Petersen, 2000b; Soenen, Lu and Laukkanen, 2016). The loss of volatile components mainly occurs during the construction period because of the high temperature. The thermal oxidation is responsible for the whole pavement life and, accordingly, composed of short-term and long-term aging. Other explanations also contribute to aging, such as the steric hardening due to the molecular structuring and actinic light, especially for the ultraviolet radiation (D. Wang *et al.*, 2019). It should be emphasized that, in terms of the effects of mineral aggregates on bitumen aging, the studies of Petersen's group have shown that it is not only the exudation part of bitumen aging that the aggregate shows its significance, but the petrographic nature of aggregates may also have added effects on the aging of bitumen, i.e., catalysis of bitumen oxidation and adsorption of bitumen polar components (Petersen, Barbour and Dorrence, 1974; Petersen, Ensley and Barbour, 1974; Huang *et al.*, 2002).

Based on the above statements, Wu (Wu, 2009) concluded that most composition-related bitumen aging happens on two interfaces: the air-bitumen interface and the bitumen-aggregate interface, as shown in 0. It is noticeable that aging occurred in the bitumen-aggregate interface consists of two competitive mechanisms, namely absorption of oily fractions and adsorption of polar fractions. The absorption of oily fractions accelerates the aging hardening while the adsorption of polar fractions, to some extent, may soften the effective bitumen. A lot of work has been done by Guo et al. (Guo *et al.*, 2016, 2017; Guo, Bhasin and Tan, 2017) considering the bitumen-aggregate interaction. In authors' opinion, as the bitumen film in a real asphalt mixture is extremely thin, the different aging mechanisms that happen on the two interfaces (as shown in Figure1) will definitely affect each other. Therefore, it is of great importance to explore more deeply about what is happening on the air-bitumen interface.

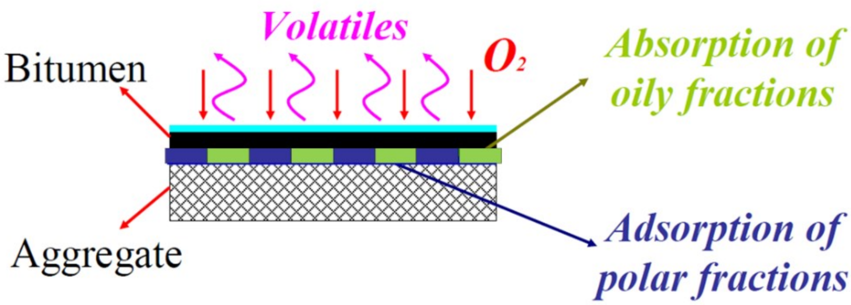


Figure 5.1 Major factors affecting bitumen aging

Over the year, studies regarding the simulation of bitumen aging in the laboratory have never come to an end. Many innovative aging investigation methods have been developed to stepwise reveal the mechanism of the realistic aging condition. Al-Qadi research group developed an accelerated aging method for compacted asphalt mixtures called TEcnico Accelerated aGEing (TEAGE) (Crucho *et al.*, 2018). The TEAGE research demonstrated the aging gradient through specimens' depth of asphalt mixtures. When it comes to the micro-scale for bitumen binder, the bitumen film thickness is around 10μm, and the two aging interfaces shown in 0, as stated above, will consequentially engender aging interference in such a thin state. Aiming to study the aging interference phenomena within the bitumen, this study focuses on the air-bitumen interface aging from the micro-scale perspective. It is plausible to assume that, although in the very thin state when performing the aging simulation, the phase gradient induced by aging might occur. Two additional pieces of evidence could support this assumption. In the TFOT, the bitumen forms a film thickness of 3.2mm in the plate for 5 hours at 163°C (D1754, 2002). While the film thickness decreases to around 100 μm and corresponding simulation time reduces to 85 minutes for the Rolling Thin Film Oven Test (RTFOT) (ASTM, 2004). Thicker binder film will bring about the concern that the aging could be limited to a very thin surface on the bitumen sample without any agitation and rotation. Therefore, a realistic aging process should not comply with the acceleration method in the laboratory. Many attempts have been made aiming to develop a more realistic aging simulation. Farrar et al. (Farrar *et al.*, 2012) suggested a short- and long- term aging test with a binder film of 300 μm. It was demonstrated that the developed aging test is comparable to the RTFO and RTFO/PAV in terms of the rheological measurement. More importantly, a sufficient amount of bitumen can be obtained for the following characterizations. Das et al. (Das, Kringos and Birgisson, 2014) adopted the atomic force microscopy (AFM) and differential scanning calorimetry (DSC) to feature the thin film surface aging of bitumen. The AFM results implied that a thin film formed at the bitumen surface, which interfered with the observation of microstructures.

Furthermore, experiments claimed that UV radiation induced more surface aging than thermal oxidation. Wu et al. (Wu *et al.*, 2008) investigated the ultraviolet (UV) and thermal aging of pure bitumen by fabricating bitumen film with different thicknesses. The results indicated that the UV radiation aging played a dominant role in the bitumen aging when the binder film was smaller than 100 μm. The studies above revealed the fundamental mechanisms of bitumen aging, especially for the bitumen surface. In addition, these achievements implied that even within the range extremely close to the bitumen-air interface, aging gradient might still exist and therefore, it was considered by authors that quantifying this gradient would of certain help to our understanding of bitumen-mineral interaction and the real rheology situation of the binder films (6-10 μm) in asphalt mixtures.

This paper contained an experimental investigation of the aging gradient inside the bitumen when conducting the TFOT test, together with a corresponding molecular simulation study. A multi-staged stratified elution was adopted to obtain bitumen samples at different depths. This study applied the Dynamic Shear Rheometer (DSR), and Fourier Transform Infrared Spectroscopy (FTIR) tests to identify the aging gradient. Specifically, the DSR test characterized the variation of mechanical performance due to the phase gradient of aging, while the FTIR test differentiated the chemical compositions. The aging duration varied from 1 hour to 20 hours, aiming to feature the evolution of the aging gradient. Besides, the molecular simulation was proceeded to understand the interaction between bitumen and oxygen based on a 12-component molecular model. This study may contribute to the research designing the aging acceleration method and help better understanding the deterioration of asphalt pavements in the field.

5.3 Materials and Test Program

5.3.1 Materials and the Aging method

This study adopted an unmodified bitumen with a penetration grade of 60/80. Table 5.1 lists the conventional properties for the used bitumen. The aging device utilized the Thin Film Oven Test (TFOT) to simulate the thermal oxidation of bitumen in the mixing and paving process. For the investigated purpose, this study followed the specification ASTM D1754. It conforms to the 50g bitumen melted bitumen in a 140mm diameter steel plate. Subsequently, four plates were positioned in the oven at 163˚C with a rotation speed of 5 rpm. Unlike the specification, the simulation duration varied with 1, 2, 5, and 20 hours.

Table 5.1 Conventional properties of unmodified bitumen

Test Items	bitumen	Standard test methods
Penetration (25 ˚C, 100g, 5s)/0.1mm	74.8	ASTM D5 (Drews, 2008)
Ductility (15˚C)/cm	117	ASTM D113 (ASTM International, 2017)
Softening point/ ˚C	53.1	ASTM D36 (ASTM International, 2014)
Viscosity (60 ˚C)/Pa s	195	ASTM D4402 (ASTM, 2006)

5.3.2 Research Program

Figure 5.2 illustrates the research framework of this study. The micro-scale investigation of the aging gradient in bitumen consisted of two parts, which were laboratory investigation and molecular simulation, respectively. In the laboratory investigation, bitumen samples firstly experienced the aging acceleration for a predetermined time (1 hour, 5hours, 10 hours, and 20 hours) at 163℃. After the aging treatment, the plate cooled down in the ambient environment for 24 hours. Subsequently, as seen in Figure 5.3, every 30s, 100 ml trichloroethylene was used to dissolve the surface bitumen on the plate. With the repeated elution, a total of 11 layers of bitumen were obtained. The FTIR and DST tests were performed to identify the difference among the aging bitumen samples of 11 layers.

Typically, the DSR test requires several grams of bitumen, and around 200mg bitumen is required for the FTIR test (Farrar *et al.*, 2012). Therefore, four parallel aging tests (a standard test) were performed at one time to collect sufficient bitumen samples for the test. On the other hand, the extraction of bitumen via the conventional approach became difficult. Thus, this study adopted a compromised method for the extraction, referring to previous research (Wu *et al.*, 2008). Specifically, the solution was poured into a silica container. In what follows, the container was kept in the 60℃ until the trichloroethylene completely evaporated. During the process, the weight of the total container was monitored as the signal. Finally, a very thin bitumen layer was deposited on the surface of a silica container. Due to the weak adhesion between silica materials and bitumen, the bitumen sample can be easily collected. The collected bitumen was mixed at 120℃ to reach a homogenous state before the DSR and FTIR measurements.

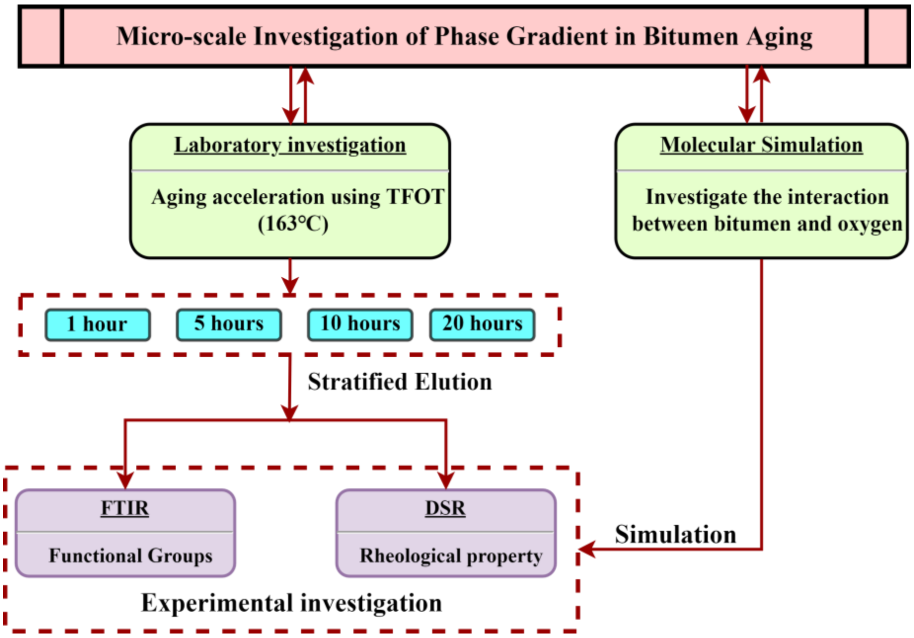


Figure 5.2 The flow chart in this study

FTIR Test: In this study, the Attenuated Total Reflection (ATR) mode was used to obtain the infrared spectra since the ATR technique enables the sample to be measured almost without preparation. Around 200mg solid bitumen was sampled by a tweezer. The wavenumber scan range is from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}. The interpretation of measurement results adopted a semi-quantitative infrared analysis (Ruau, Landais and Gardette, 1997). Specifically, the oxygenated function quantities are determined based on the following structural indices. The carbonyl area is defined between 1660 and 1753 cm^{-1}, the sulfoxide is defined between 1047 and 995 cm^{-1}. It is assumed that groups at 1460 cm^{-1} and 1375 cm^{-1} are not significantly changed by oxidation of binders. The baseline for the calculation referred to the literature (Marsac *et al.*, 2014). The positive area above the baseline was taken into account for the calculation.

DSR Test: Frequency sweep was conducted to characterize the rheological performance of bitumen within the linear viscoelastic (LVE) range (Yang *et al.*, 2019). The frequencies ranged from 0.1 to 10Hz, with temperatures varying from 10 to 50°C (with 10°C intervals). Parallel plates were adopted with a diameter of 8mm and a gap size of 2mm. The complex modulus master curves were constructed based on the Time-Temperature Superposition Principle (TTSP) with a reference temperature of 30°C.

Concerning the molecular simulation, this part constructed the amorphous cell models for four fractions and a two-layer molecular model composed of bitumen and oxygen. The individual amorphous cell model characterizes the diffusion behavior for each fraction. As for the two-layer model, the interaction between oxygen and bitumen can be observed through the molecular dynamic simulation. The results in this section aimed to support the analysis in the experimental investigation. Further details regarding the simulation process are introduced in the following section.

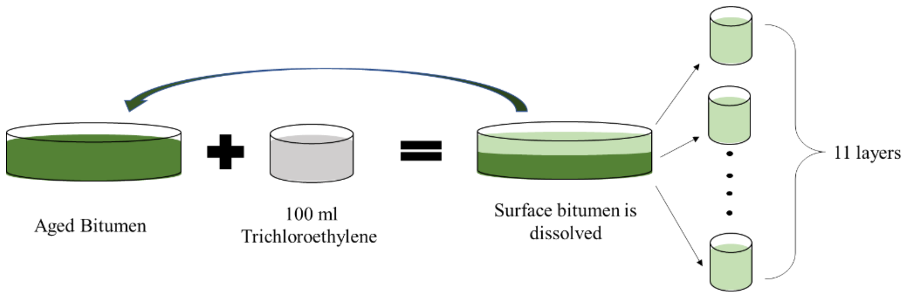


Figure 5.3 Schematic of multi-staged stratified elution

5.4 Molecular Simulation Methods

There is a need to understand thermal aging from the molecular perspective. As mentioned above, thermal aging was ascribed to two main mechanisms, the loss of volatile components and thermal oxidation. In the molecule, volatilization occurs when molecules move into the air due to drastic molecular motion. It is associated with motion energy and diffusion rate. As for thermal oxidation, the bitumen component changes through bond formation and breakage. The distribution of bitumen fraction significantly affects the possibility of oxidation. Therefore, the separated components, namely saturate, aromatic, resin, and asphaltene, were investigated by comparing their internal diffusion rates. Subsequently, a two-layer model between consisted of oxygen and bitumen was constructed to observe the conformation structures, especially near the bitumen-oxygen interface.

5.4.1 Molecule modeling

According to existing studies, the bitumen model of AAA-1, a typical bitumen used in the Strategic Highway Research Program (SHRP), was adopted (Xu and Wang, 2017a). Figure 5.4 shows the quantities of molecules in the AAA-1 bitumen systems and corresponding molecule schematics. As shown in Figure 5.4, the bitumen model of AAA-1 consists of 12 components, representing four fractions in the bitumen binder.

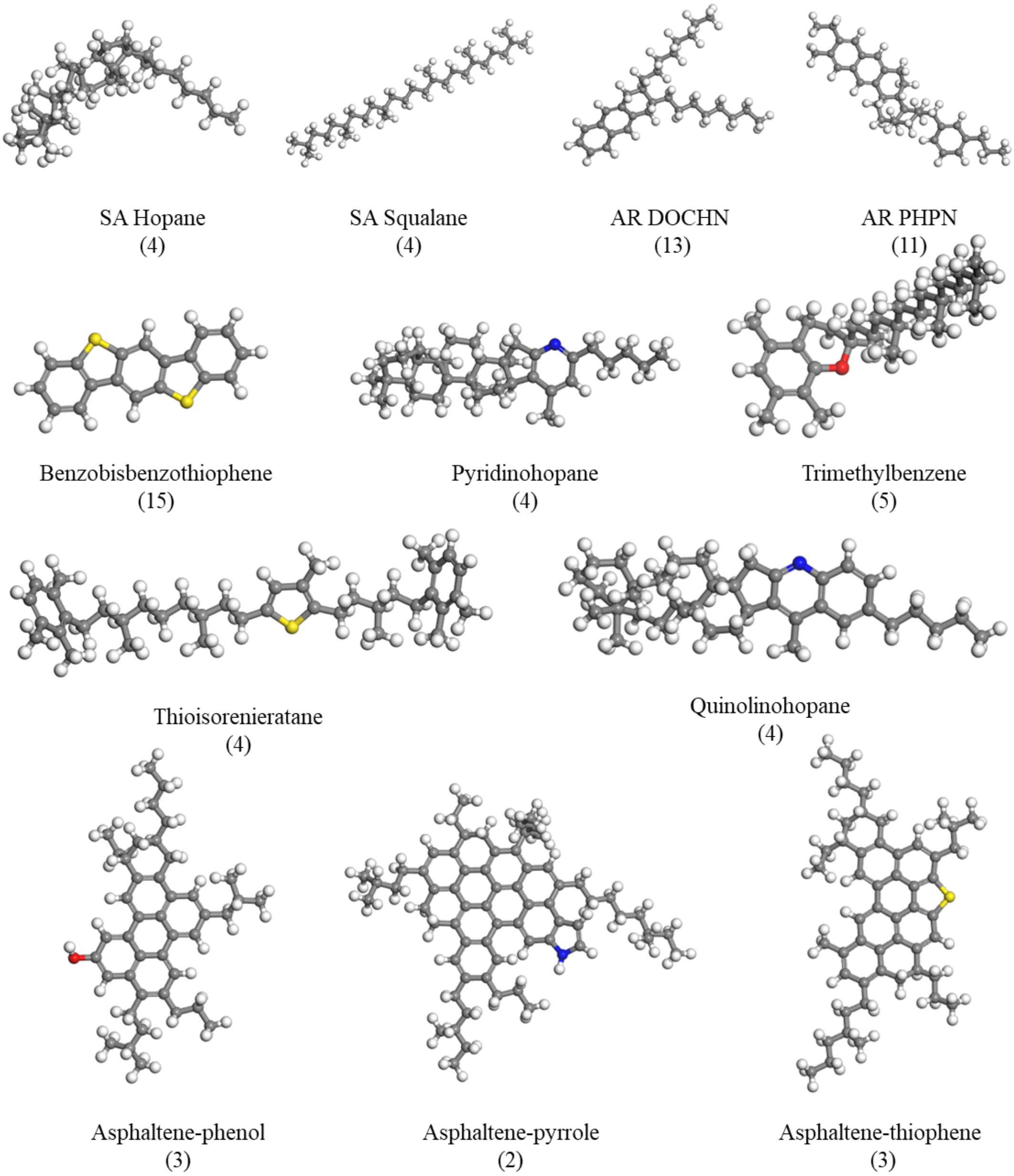
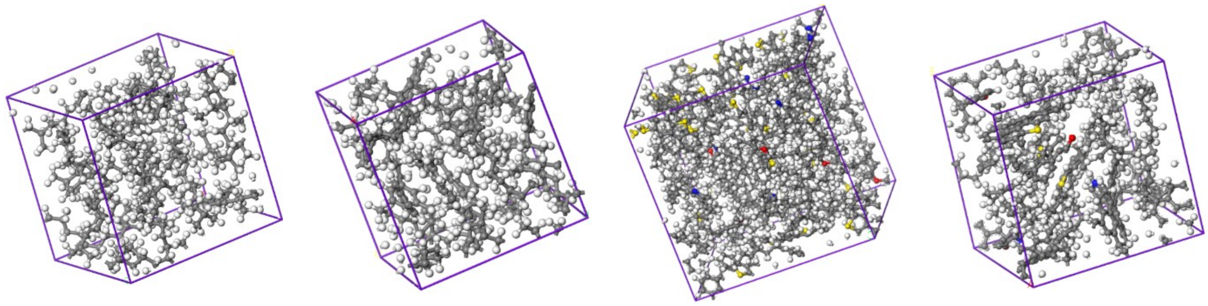


Figure 5.4 The molecules in the AAA-1 bitumen systems (Qu, Wang, et al., 2018)

To separately investigate the diffusion and motion ability of bitumen compositions at the predetermined temperature (163℃), each fraction of bitumen was constructed in the Amorphous Cell, as shown in Figure 5.5, the oxygen-bitumen layer model was constructed as shown in Figure 5.6. When constructing the layer model, an additional 80-angstrom vacuum layer was added to void the boundary effect (Xu and Wang, 2016). Later on, the molecular dynamics simulation was executed.



(a) Saturate (b) Aromatic (c) Resin (d) Asphaltene

Figure 5.5 Amorphous cell models for four fractions

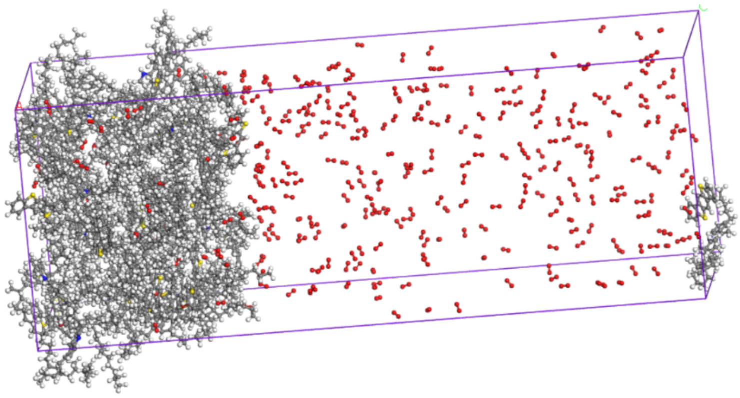


Figure 5.6 A two-layer model for bitumen and oxygen

5.4.2 Simulation protocols

For all the investigated models, the model was subjected to geometry optimization for 5000 iterations followed by Isothermal-isobaric (NPT) ensemble running for 100ps to achieve an equilibrium density. Later on, the canonical ensemble (NVT) was carried out for 200ps. The force field used the COMPASS II (condensed-phase optimized molecular potentials for atomistic simulation studies). The targeted temperature and pressure of the system were maintained with the Nose-Hoover-Langevin (NHL) thermostat and Andersen-barostat, respectively. The simulation temperature was set at 163°C.

The motion behavior of molecules can be described by the means square displacement analysis, and hence, the diffusion coefficient of particles can be estimated. It can be calculated from the statistical analysis of the particle positions, as illustrated in the following equation (Luo, Guo and Tan, 2018).

$$MSD(\Delta t) = \frac{1}{T - \Delta t}\int_0^{T-\Delta t} [r(t - \Delta t) - r(t)]^2 dt = \langle [r(t - \Delta t) - r(t)]^2 \rangle \qquad \text{Equation 5.1}$$

The diffusion coefficient *D* is defined as follows (Luo, Guo and Tan, 2018).

$$D = \frac{1}{6}\lim_{\Delta t \to \infty} \frac{dMSD}{d\Delta t} \qquad \text{Equation 5.2}$$

The concentration profile computes the profile of atom density within evenly spaced slices. To run this calculation, a specific direction is divided into several bins, and the related atoms were counted. The relative concentration of a set of atoms in a slab is as follows (Xu and Wang, 2018b):

$$\text{Relative } [\text{set}]_{\text{slab}} = [\text{set}]_{\text{slab}} / [\text{set}]_{\text{bulk}} \qquad \text{Equation 5.3}$$

$[\text{set}]_{\text{slab}}$ = (no. atoms in slab)/ (volume of slab)

$[\text{set}]_{\text{bulk}}$ = (total no. atoms in system)/ (volume of system)

The relative concentration is a dimensionless quantity. A value of 2 means that there are twice the number of atoms in the slab that if all atoms were distributed homogeneously across the system

5.5 Results and Discussion

5.5.1 Effect of aging on bitumen from the chemical perspective

The oxidation aging of bitumen will generate specific functional groups such as carbonyl and sulfoxide. Therefore, the infrared spectroscopy technique can be used to identify the oxidation of bitumen. In this study, bitumen samples with different aging times were subjected to infrared spectroscopy measurement. Unfortunately, the 5- and 10-hour aged bitumen samples were contaminated. As a result, this section only discussed the effect of aging on chemical compositions by comparing the pure and 20-hour aged bitumen. Figure 5.7 presents the FTIR results of virgin and 20-hour aged bitumen. Accordingly, two oxidation indices, namely Ico and Iso, were calculated to determine the oxidation level, as shown in Table 5.2. It can be seen that the Ico increased considerably after the oxidation aging. It demonstrated that after the 20-hour aging process, the oxygen chemically reacted with bitumen components, inducing the increase of *Ico*.

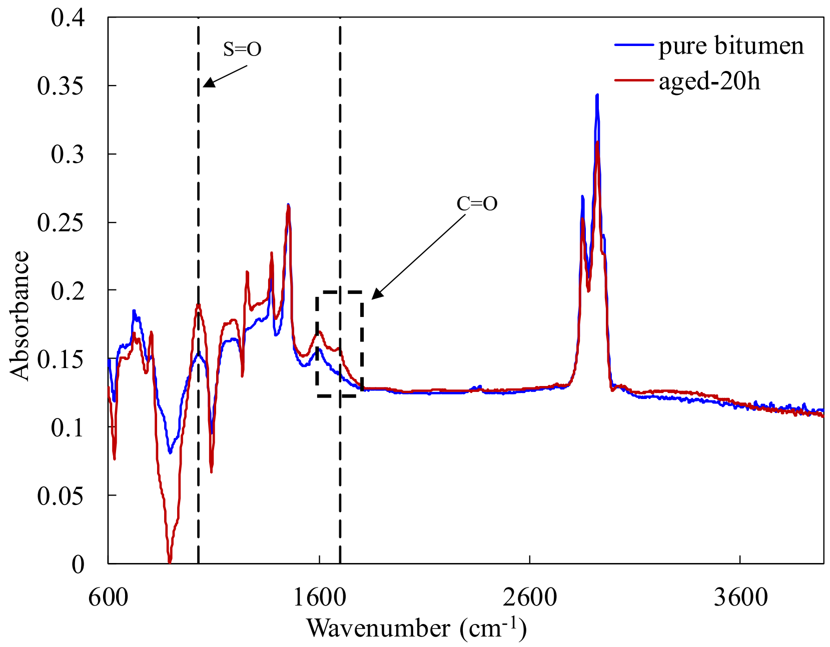


Figure 5.7 FTIR results for virgin and aged bitumen

The changes of sulfoxide before and after the aging also presented an increased tendency. However, it can be noticed that the Iso (from 0.018 to 0.031) evolved relatively less than the *Ico* (from 0.022 to 0.043). Both indices proved that the oxygen diffused into the bitumen and subsequently oxidized the bitumen components.

Table 5.2 ICO and ISO for virgin and 20-hour aged bitumen

Sample	Ico	Iso
Virgin bitumen	0.022	0.018
Aged bitumen 20h	0.043	0.031

5.5.2 Effect of aging on bitumen from the rheological perspective

The variation of complex moduli with the aging time was investigated, as shown in Figure 5.8. A clear upward tendency indicated that the complex moduli of bitumen increased as the aging duration increased, especially at the beginning of the aging process or when the aging time increased to 20 hours. The short-term aging of bitumen is usually ascribed to the oxidation and the loss of volatile components during the asphalt mixture construction (Airey and Choi, 2002). Thus, the increase of modulus could be due to the coupling effect of oxidation and volatile loss in this study.

As shown in Figure 5.8, the modulus of bitumen underwent a considerable increase within the first 1 hour. During the aging between one to ten hours, the increased rate of modulus slowed down. However, after the aging of 10 hours, the modulus increase showed a significant rate again. The change in the increased rate of modulus depended on the aging process in the microscopic. It can be speculated that the diffusion of oxygen into the bitumen is a kind of aggressive process which requires a particular time. This issue has been discussed in plenty of literature that focused on aging kinetics (Kai-Fu *et al.*, 2001; Yan, 2005; Petersen and Glaser, 2011; Glaser *et al.*, 2013).

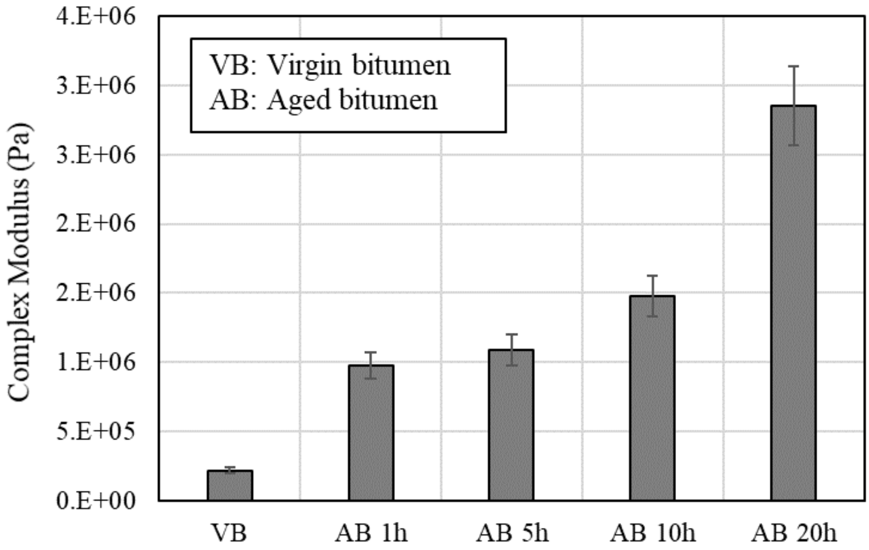


Figure 5.8 Complex moduli for virgin and aged bitumen at 20°C, 1Hz

5.5.3 Aging gradient along with the depth

Evidence showed that short-term aging includes two individual processes, which are volatilization and thermal oxidation. Another conclusion achieved from the above section claimed that oxygen diffusion is a progressive process. In this case, it is reasonable to assume that, though the thin film oven test proceeds with the bitumen film thickness around three millimetres, the aging gradient, along with the depth from the micro-perspective, does exist. Aiming to figure out this issue, samples located in varying depths were obtained through the multi-staged stratified elution method. Table 5.3 illustrates the layer samples for bitumen binders aging with different durations. For each aged bitumen, 11 layers are supposed to be extracted. However, some layer samples are not acceptable for the analysis due to some practical mistakes, as seen in Table 5.3.

Table 5.3 The multi-staged stratified elution results

Layer	aged-1h		aged-5h		aged-10h		aged-20h	
	Mass (g)	Thickness (µm)	Mass (g)	Thickness (µm)	Mass (g)	Thickness (µm)	Mass (g)	Thickness (µm)
1	1.20	77.95	2.50	162.40	2.40	155.91	1.50	97.44
2	1.70	110.43	1.60	103.94	1.80	116.93	1.30	84.45
3	1.60	103.94	1.60	103.94	1.80	116.93	1.50	97.44
4	1.60	103.94	1.60	103.94	1.60	103.94	1.70	110.43
5	1.60	103.94	1.70	110.43	1.70	110.43	1.50	97.44
6	1.80	116.93	1.70	110.43	1.80	116.93	1.60	103.94
7	-		1.80	116.93	1.90	123.43	1.30	84.45
8	-		1.50	97.44	1.70	110.43	1.50	97.44
9	-		-		1.80	116.93	1.30	84.45
10	-		-		1.50	97.44	1.50	97.44
11	-		-		-		1.70	110.43

Figure 5.9 presents the master curves of complex modulus for different aged bitumen. In order to achieve a clear comparison and better presentation, the top six-layer samples were presented. As shown in Figure 5.9, samples located in different depths show varying rheological properties. It demonstrated that, from the micro-scale, the aging degree of bitumen was dependent on the position when conducting the thin film oven test. In general, the bitumen sample on the surface performed the most elastic property reflecting by the relative phase angle. Besides, the surface sample also showed the highest complex modulus. It is not difficult to explain as the surface is where the light molecules escaped from the bitumen. Bitumen sample on the surface directly in contact with the air, and the concentration of oxygen on the surface should be the highest, inducing the most serve thermal oxidation.

On the other hand, the phenomena of aging gradient became more and more evident. Therefore, it can be speculated that the increase of aging time will enhance the aging gradient. It has a practical meaning. To some extent, the current laboratory aging acceleration method is an average concept of aging. Many researchers have realized this problem, and therefore, the rolling thin film oven test was developed as the alternative for a thin-film oven test. However, according to the analysis in this study, the film thickness of bitumen for the RTOFT is around 85µm. It is not clear whether such a thin state can achieve homogenous aging. Hence, it is vital to study the aging gradient along with the depth from the micro perspective.

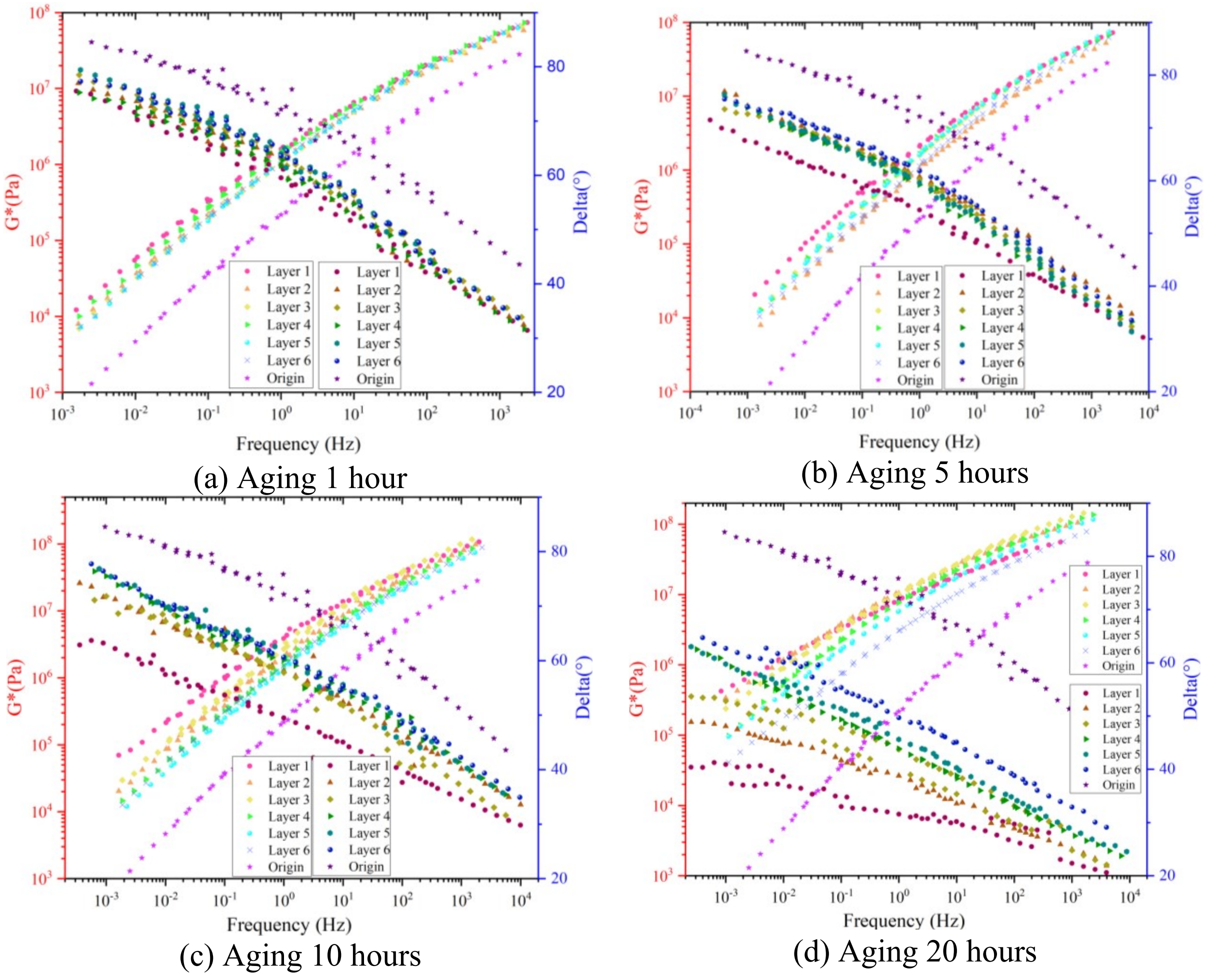


Figure 5.9 Master curves of aged bitumen for the top six layers

According to the basic definition of the aging index, as shown in Equation 5.4 (D. Wang *et al.*, 2019), this study calculated the aging indexes for each layer and their related depths.

$$aging\ index = \frac{G^*_{after\ aging}}{G^*_{before\ aging}} \qquad \text{Equation 5.4}$$

The numerator means the complex modulus of bitumen after aging for a particular time, and the denominator indicates the complex modulus of unaged bitumen. The G^* refers to the complex modulus measured at 20°C, 1Hz.

Figure 5.10 shows the aging index varying with the depth for different aged bitumen samples. It is very interesting to observe that there is no consistent tendency for the aging index to change with depth. It indicated that, after the aging acceleration, the aging distribution of the aging degree is not homogenous inside the sample, at least with the depth. It is ascribed to the non-uniform distribution of oxidation and also the non-uniform colloidal structures from the micro-scale. At a depth of 1000μm, bitumen samples showed a comparative aging degree even if the aging duration varied with each other. Therefore, it can be speculated that, at a specific depth, the loss of light mass contributed to the primary aging mechanism as the oxygen no longer diffused into such depth.

On the other hand, the aging mechanism of bitumen samples near the surface was supposed to be a complicated coupling action of thermal oxidation and volatiles loss. In terms of the aging duration, aging time over 20 hours induced a considerable aging degree compared with aging samples less than 10 hours. Therefore, the aging degree of bitumen does not comply with the linear rules. Nevertheless, it should be stressed that the exact rule for the aging index requires more reproducible experiments. The possibility that the erratic behavior of the aging index is due to experimental variation cannot be denied. Only in this case, a convincing conclusion could be made. Besides, the relationship between aging degree and time belongs to the research of aging kinetic, which is not the primary concern herein, therefore, no more discussion on this issue.

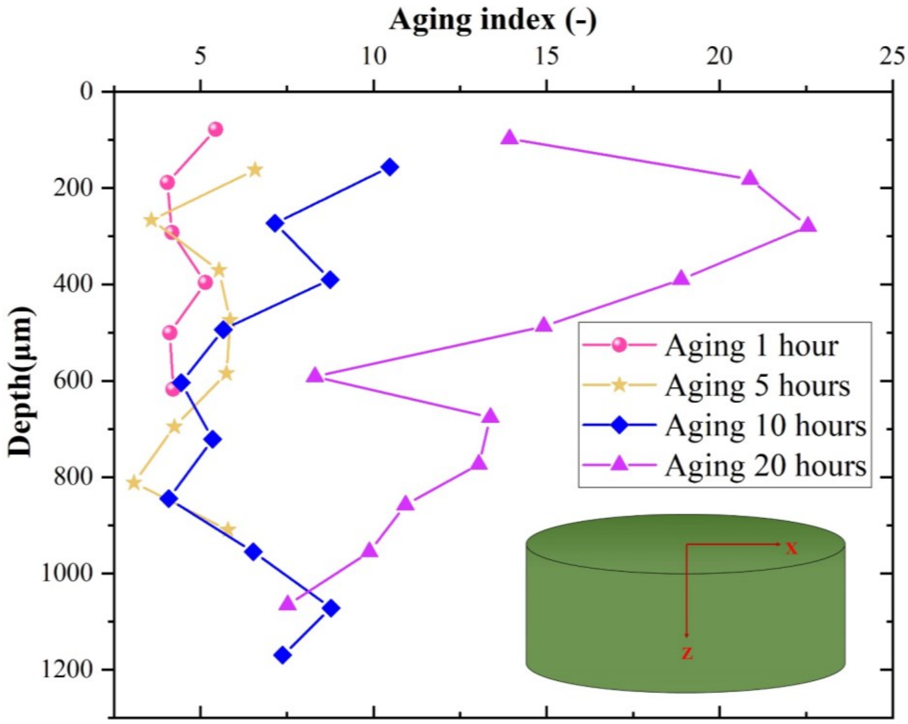


Figure 5.10 The change of aging index with the depth

5.5.4 Interaction between oxygen and bitumen

Figure 5.11 presents the relative concentration file of oxygen in the amorphous model. The concentrations of oxygen along the X and Y directions are almost the same due to the periodic boundary. As for the Z direction, the bottom of the bitumen layer was defined as the start point (zero distance). It can be seen that the oxygen concentration kept a relatively low value, with the range from 0 to 25 angstroms. The considerable decrease observed from 0 to 8 angstroms was ascribed to the boundary effect of simulation. It illustrated that the very few oxygen molecules located in this range. Starting from the 25 angstroms, the oxygen concentration increased with the distance until 40 angstroms, following the linear rule. According to the simulation results, it can be concluded that the oxygen diffused into the bitumen conformed to the linear relationship with the diffusion depth. When the distance beyond 40 angstroms, the oxygen concentration maintained a stable and high value, indicating the oxygen layer in the amorphous cell model.

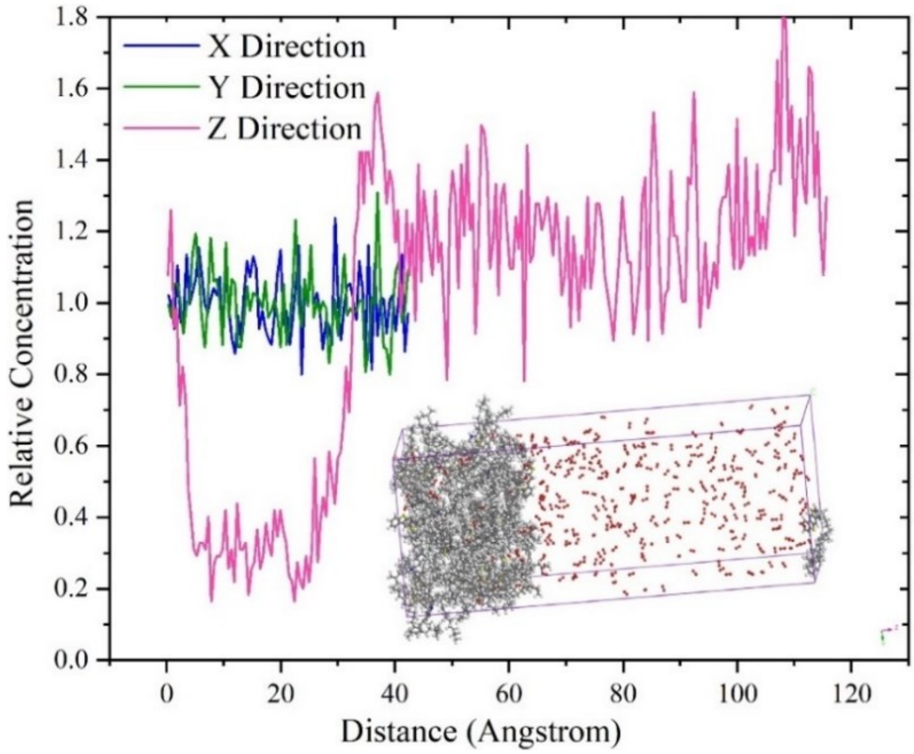


Figure 5.11 The concentration file for the oxygen in the amorphous model

The relative concentration file of oxygen conclusively demonstrated the reason for aging gradients. From the perspective of thermal oxidation, the aging gradient could exist on account of the oxygen distribution.

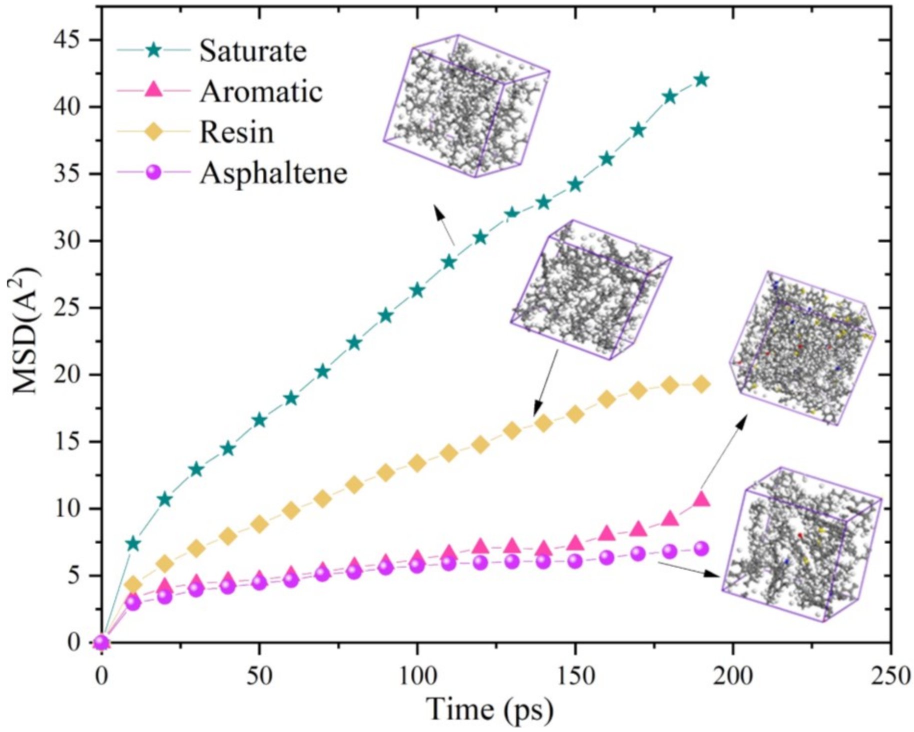


Figure 5.12 The MSDs for different fractions based on MD simulation

Aiming to understand the volatilization of light mass from the molecular scale, the molecular dynamics simulation for four fractions in the bitumen was carried out. It should be noticed that the stability of bitumen not only relied on the material property for each fraction but also the interactions among them. Unfortunately, it is difficult to consider the interaction as vague colloidal structures. Therefore, this study merely investigated the motion property of individual fractions with molecular dynamics simulation. Figure 5.12 gives the results of mean square displacement for four fractions of bitumen. As seen from the figure, saturate fraction performed the maximum MSD while the asphaltene owned the lowest MSD. It indicated that at the temperature of 163C, the motion of the saturate was the most significant; in other words, the saturate possessed the highest motion energy. As a result, the molecules of the saturate have the highest possibility of escaping from the bitumen. Similarly, analysis, the asphaltene is the most stable fraction in the bitumen.

Figure 5.13 summarizes the diffusion coefficient according to Equation 5.2. The diffusion coefficient of a given group was calculated independently, considering that the molecules diffuse among the same type of molecules. It can be seen that the saturate has the highest diffusion coefficient, and the asphaltene owns the lowest. Concerning the aromatic and resin, the diffusion coefficient of resin is higher than aromatic. As mentioned before, the structural effect was not considered when conducting the molecular dynamic simulation. The classical colloidal structure of bitumen can be described as follows: bitumen was early described as a colloidal dispersion of asphaltenes micelles in the maltenes. The resins that are the polar components of the maltenes were thought to stabilize the asphaltene micelles (Lesueur, 2009). Accordingly, combining the material and structure effect, the stability of four fractures should be Asphaltene > Resin > Aromatic > Saturate. This sequence is widely accepted, and in this study, it was confirmed once again.

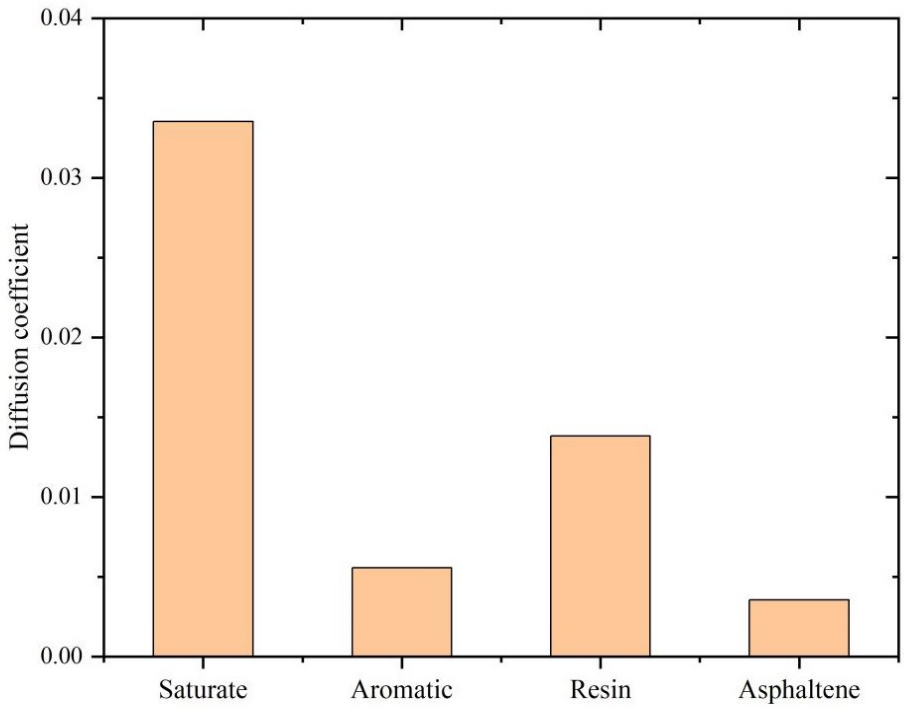


Figure 5.13 The calculated diffusion coefficient based on the MSDs

5.6 Conclusions

This study performed an investigation on the aging gradient of bitumen along with the depth when conducting the Thin Film Oven Test. It aims to reveal the micro-scale variation of the bitumen aging process. It can help understand the aging mechanism and provide a reference regarding the bitumen aging at an extremely thin state. Some critical findings were concluded.

(1) During the aging process, bitumen will generate the carbonyl and sulfur oxide groups aggressively due to thermal oxidation.
(2) From a microscopic view, the aging gradient does exist along with the depth. According to the result in this study, the effective depth of thermal oxidation could be 1000μm on account of the oxygen diffusion depth.

(3) The molecular simulation demonstrated the concentration gradient of oxygen in the bitumen, which is consistent with the experimental observation.

(4) The short-term aging is ascribed to the thermal oxidation and volatilization of light mass (mainly saturate). The stability of four fractions in the bitumen depends on the fraction property and the colloidal structure. For both perspectives, the stability of asphaltene is higher than the saturate.

6 Investigation on Diffusion Interface between New and Aged Bitumen Using Molecular Dynamics Simulation

<u>This work has been submitted to:</u>

Quan Liu, Jiantao Wu, Markus Oeser. Investigation on Diffusion Interface between New and Aged Bitumen Using Molecular Dynamics Simulation. Materials and Structures (Under review).

<u>Individual contributions:</u>

Quan Liu conceptualized research idea, completed the simulation, conducted data analysis, contributed to writing and editing. Jiantao Wu contributed to the proofread of manuscript. Markus Oeser contributed to the supervision and final manuscript check.

6 Investigation on Diffusion Interface between New and Aged Bitumen Using Molecular Dynamics Simulation

6.1 Abstract

Recycled asphalt pavements (RAP) have been extensively used for pavement constructions. However, the incorporation of reclaimed asphalt materials brings up new challenges compared with conventional asphalt mixtures. Among these, the performance recovery of RAP binders attracts the interest of many researchers. This study provides an insight into the molecular-scale diffusion between new and aged bitumen. Compared with previous studies, this study was particularly concerned with the diffusion interface. In addition, the influence of temperatures and aggregate on the diffusion process was discussed in detail. To this end, a two-layer model and a three-layer model were constructed, followed by the molecular dynamic simulations at 298.15K, 383.15K, 403.15K, and 423.15K, respectively. The concentration profiles derived from simulation results were used to trace the diffusion process. Visualization of diffusion patterns as a function of simulation time was also conducted for better understanding of diffusion process. The results indicated that the diffusion process between new and aged bitumen was a long-term process; however, the diffusion interface can be formed quickly. Due to the polar interaction, aggregate remarkably accelerated the diffusion process between new and aged bitumen. Moreover, the blend of new and aged bitumen can be observed, which did not occur in the two-layer model. Microvoids might form at 403.15K, which obstacle the diffusion process. However, this phenomenon can be eliminated by the temperature increase.

6.2 Introduction

Reclaimed asphalt pavement (RAP) can be considered an efficient construction methodology for material reuse and environmental benefit (McDaniel and Michael Anderson, 2001). However, current practice indicates that asphalt mixtures with a high RAP quantity (beyond 50%) are not recommended, as the quality of produced recycled asphalt mixtures cannot be well controlled (Newcomb, Ray Brown and Epps, 2007). The incorporation of RAP in pavement construction encounters varying challenges, attracting many researchers working on the recycled asphalt mixtures (Karlsson and Isacsson, 2006).

To a great extent, the properties of asphalt mixtures with RAP are associated with the blending efficiency of recycled asphalt mixtures (Mucinis, Sivilevicius and Oginskas, 2009). The blending efficiency refers to the structural uniformity of recycled asphalt mixtures and the chemical uniformity of binders concerning the diffusion between new bitumen (rejuvenators) and aged bitumen (Mucinis, Sivilevicius and Oginskas, 2009). In the mixing process, the agglomeration of small-size particles in RAP induces many clusters with a relatively high RAP amount, which prevents the formation of homogenous asphalt structures and the diffusion of binders. Wu et al. (Wu *et al.*, 2018b) studied the effect of mixing temperature and time on the homogeneity of recycled asphalt mixtures. The results demonstrated the cyclic 'crush-cluster-crush' process existed in the blending. In terms of the chemical uniformity, so-called diffusion, many studies have been carried out to characterize this diffusion phenomenon during production. Previously, in 1983, Lee et al. (Lee, Terrel and Mahoney, 1983) designed the resilient modulus test on samples mixed at different conditions to reflect the mixing efficiency. However, in this research, the structural and chemical uniformities were not distinguished. Karlsson and Isacsson (R Karlsson and Isacsson, 2003) proposed using well-defined substances as markers to monitor the diffusion process in bitumen. For this purpose, two-layer samples consisting of diffusant and bitumen were prepared and then subjected to the FTIR-ATR (Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance) measurements. It was claimed that using the proper substance could effectively trace the diffusion process in bitumen. However, it is challenging to select the suitable substance, and more importantly, many influencing factors were still vague, which induced the variation between the results predicted by the Einstein-Stokes Equation and the actual measurements. By far, the extraction and recovery of bitumen were widely used to evaluate the blending efficiency. The staged extraction and recovery were intended to obtain the diffusion samples from the outer to inner layers of the bitumen film (Huang *et al.*, 2005a).

In recent years, the diffusion characteristics of rejuvenators in aged bitumen have been studied with many innovative methodologies. Xiao et al. (Xiao *et al.*, 2017) performed the study using image thresholding and Gas Chromatography-Mass Spectrometer (GC-MS) tracer analysis. The results showed that the image threshold analysis and tracer method could visualize the diffusion process intuitively. Wang et al. (F. Wang *et al.*, 2019) conducted three bitumen tests to study rejuvenators' diffusion in emulsified bitumen. The results demonstrated that the proposed indexes were capable of qualifying the diffusion rate of different rejuvenators.

Nevertheless, the above studies' results only experimentally feature the diffusion degree during the mixing of asphalt mixture with RAP materials. Essentially, the diffusion process is a macroscopic phenomenon driven by molecular motions. Therefore, understanding the diffusion between rejuvenators/new bitumen and aged bitumen at the molecular scale is necessary. In the past decades, molecular dynamic simulation was popularized in the study of bituminous materials since some reasonable molecular models of bitumen were proposed. For this reason, molecular dynamics simulation has been introduced to study the diffusion process. Xu et al. (Xu and Wang, 2018a) constructed a three-layer model consisted of rejuvenator, new bitumen, and aged bitumen to study the diffusion and interaction mechanism. In this study, the radial distribution functions (RDF), mean square displacement (MSD), and inter-diffusion coefficients were used to characterize the nanoaggregate and translation mobility.

Furthermore, in another study, a two-layer model only composed of the rejuvenator and RAP binders was built (Xu, Wang and Sun, 2018). Subsequently, the rejuvenators' effect on the molecular interaction of saturate, aromatic, resin, and asphaltene (SARA) fractions was investigated. Using the molecular dynamics simulation, Cui et al. (Cui *et al.*, 2020) studied the effect of physical conditions on the rejuvenators' diffusion behavior in aged bitumen. The coupled effect of water and temperature were mainly discussed in the results. Xu et al. (Xu *et al.*, 2019) also performed the molecular dynamics simulation to study bitumen rejuvenators' diffusion. The results claimed that, apart from the thermal motion, the molecular forces also drive the diffusion process. Besides, it was reported that the temperature was the decisive factor determining the motion of aged bitumen at the molecular scale.

An interesting finding concluded from the above studies was that, at the molecular scale, the rejuvenator layer and aged bitumen layer penetrated with each other limitedly, although the simulation duration reached ten nanosecond, as seen in (Xu and Wang, 2018a; Xu, Wang and Sun, 2018; Xu *et al.*, 2019). On the other hand, the multi-layer bitumen structure was claimed from many experimental studies (Huang *et al.*, 2005a; Zhao, Huang and Shu, 2015; Vassaux *et al.*, 2019). From this perspective, the diffusion process between rejuvenator and aged bitumen should be classified into the field of interfacial study. Accordingly, this study used the molecular dynamics simulation to study the interface between new and aged bitumen. The interface formation and molecular motion near the interface were mainly focused. Also, the temperature and aggregate influence on the interface formation between new bitumen and aged bitumen were discussed.

6.3 Aims and Scope

This section illustrated the aims and scope of this study. As indicated by the introduction, many valuable molecular dynamics simulation achievements have been reported concerning the diffusion mechanism between rejuvenators/virgin bitumen and aged bitumen. Under the research framework of multi-scale homogeneity of recycled asphalt mixtures, this study aims to apply the molecular dynamics simulation method to investigate the homogeneity of recycled asphalt mixtures at the molecular scale, namely the diffusion process. To this end, a two-layer model of virgin and aged bitumen and a three-layer model that included the aggregate layer were respectively constructed. Unlike previous studies, this study focused on the formation of diffusion interface between virgin and aged bitumen. Also, the influence of aggregate on the interface diffusion was discussed. Figure 6.1 shows the fundamental research flow chart used in this study. Following the literature review, feasible molecular models for the virgin bitumen, aged bitumen, and aggregate were selected. After that, diffusion models with and without the aggregate were constructed. Once the diffusion models were constructed, primary structural optimization and equilibrium process was carried to reach a stable system before running the molecular dynamics simulation at different temperatures. After simulation, the concentration profiles at varying running times were calculated to feature the interfacial formation process. In addition, a visualized presentation of the early-stage evolution of diffusion was showed. Based on these two aspects, some key findings were then concluded, and corresponding recommendations.

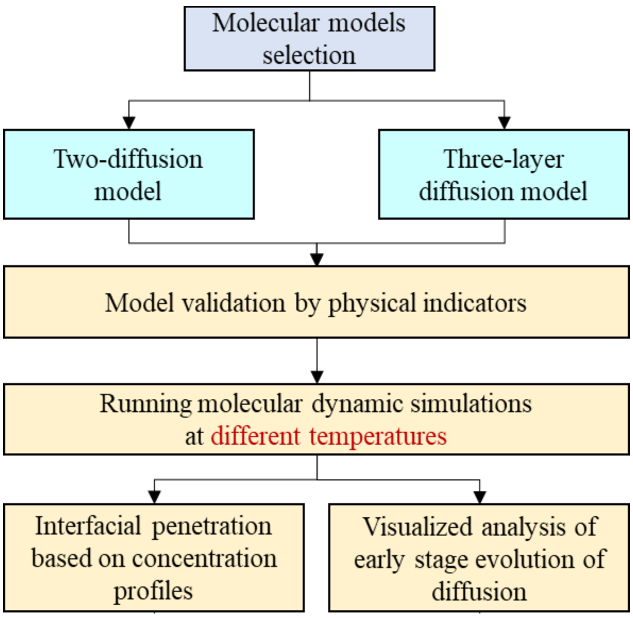


Figure 6.1 The research flow chart in this study

6.4 Molecular Models and Simulation Details

6.4.1 Construction of molecular models

According to the literature, the molecular models of virgin bitumen adopted the classical 12-component model proposed by Greenfield (Li and Greenfield, 2014). As for aged bitumen, Qu et al. (Qu, Liu, *et al.*, 2018) and Xu et al. (Xu and Wang, 2017b) constructed the aged bitumen model by manually replace sulfur elements with the oxygen elements in the conventional bitumen model. The aggregate was primarily composed of silica. Therefore, a silica crystal model was used to represent the aggregate. Detailed information of molecular models for each composition is shown in Table 6.1 and Table 6.2. Corresponding models were constructed in Figure 6.2.

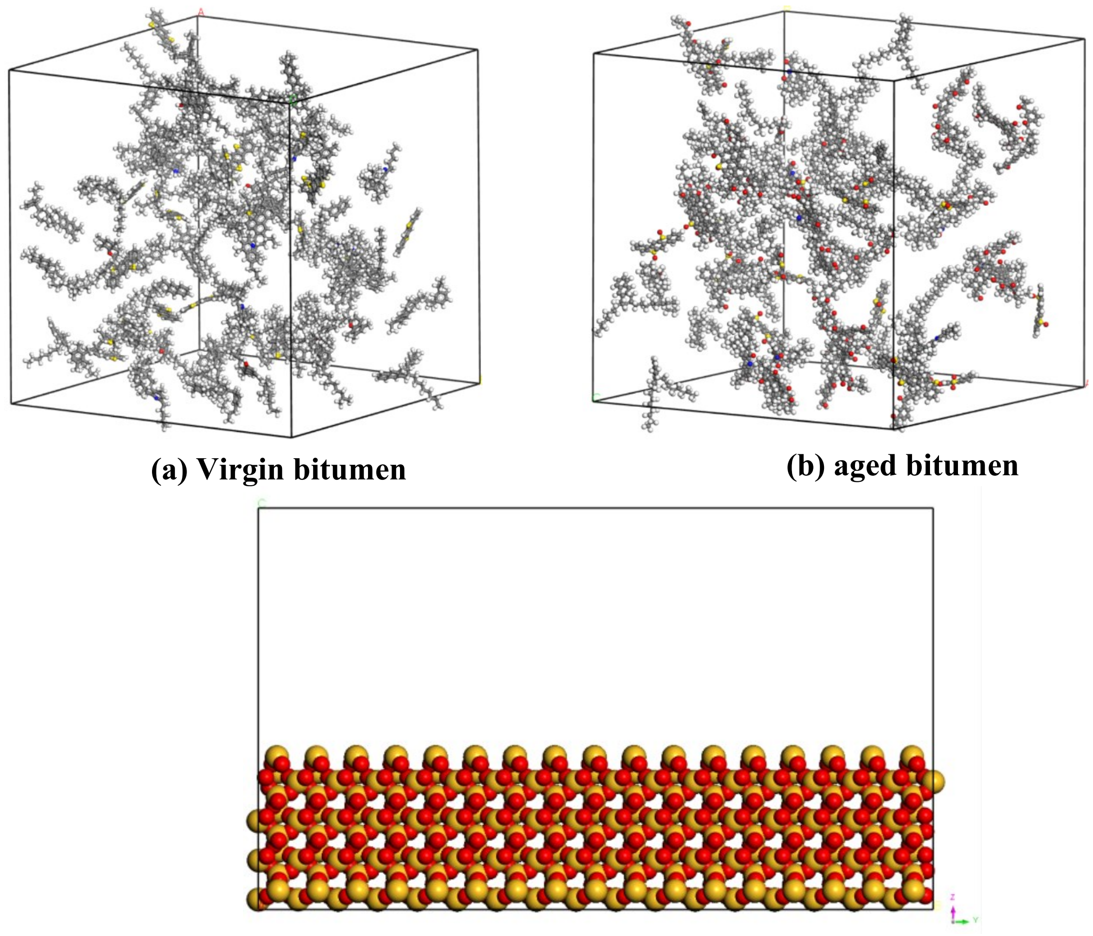
The Amorphous cell module was used to merge all components into a cubic cell at the target temperature. Following this, a 10000-step geometry optimization process was applied to relax the whole structure. Moreover, the dynamic process in the NVT ensemble was proceeded for 300ps to equilibrate the model to obtain a reasonable conformational structure. Considering the construction of the layer model, the construction of virgin or aged models all adopted the confined model, which means the atoms cannot move through the cubic in the Z direction. As for the construction of aggregate, the silica layer was established using the supercells to extend the fundamental element in the XY plane. By adding a 0 Å vacuum slab, the aggregate model can transfer from two dimensions to three-dimension. For other details regarding the model, construction referred to the literature (Ma *et al.*, 2021). Consequently, three models were constructed respectively, as shown in Figure 6.2.

Table 6.1 Molecular structure information of virgin bitumen (Qu et al., 2018)

Fraction	Molecular structure	Chemical formula		Number
		virgin	aged	
Asphaltene	Asphaltene-phenol	$C_{42}H_{54}O$	$C_{42}H_{46}O_5$	3
	Asphaltene-pyrrole	$C_{66}H_{81}N$	$C_{66}H_{67}NO_7$	2
	Asphaltene-thiophene	$C_{51}H_{62}S$	$C_{51}H_{54}O_5S$	3
Saturate	Squalane	$C_{30}H_{62}$	$C_{30}H_{62}$	4
	Hopane	$C_{35}H_{62}$	$C_{35}H_{62}$	4
Aromatic	PHPN	$C_{35}H_{44}$	$C_{35}H_{36}O_4$	11
	DOCHN	$C_{30}H_{46}$	$C_{30}H_{46}$	13
Resin	Quinolinohopane	$C_{40}H_{59}N$	$C_{40}H_{56}NO_2$	4
	Thioisorenieratane	$C_{40}H_{60}S$	$C_{40}H_{56}O_2S$	4
	Benzobisbenzothiophene	$C_{18}H_{10}S_2$	$C_{18}H_{10}O_2S_2$	15
	Pyridinohopane	$C_{36}H_{57}N$	$C_{36}H_{53}NO_2$	4
	Trimethylbenzeneoxane	$C_{29}H_{50}O$	$C_{29}H_{48}O_2$	5

Table 6.2 Parameters of the mineral model (Ma et al., 2021)

Parameters	SiO_2	
Lattice constant	a=b= 4.909996 Å,c= 5.402 Å α=β=90°, γ=120°	
Supercell size	39.280×39.280×31.783 $Å^3$	
Element	Si	O
Force field type	si4o	o_si
Charge	1.000 e	-0.500 e



(a) Virgin bitumen

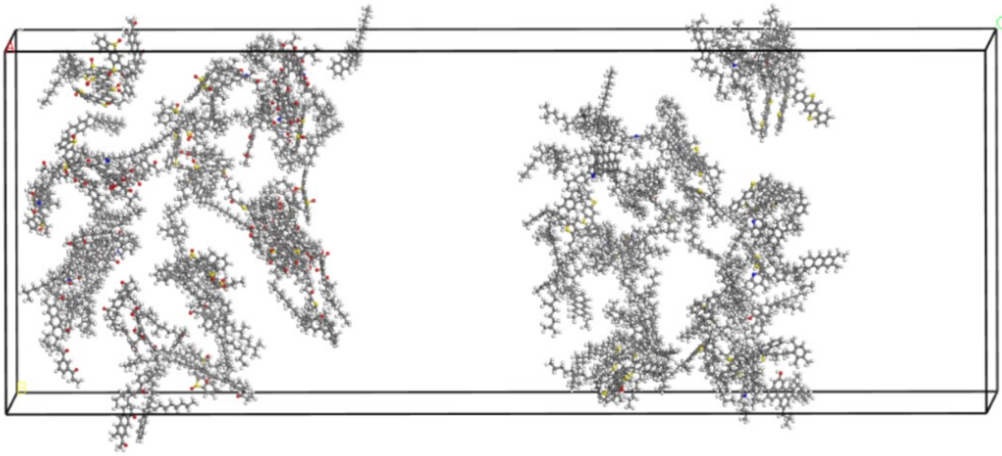
(b) aged bitumen

(c) aggregate

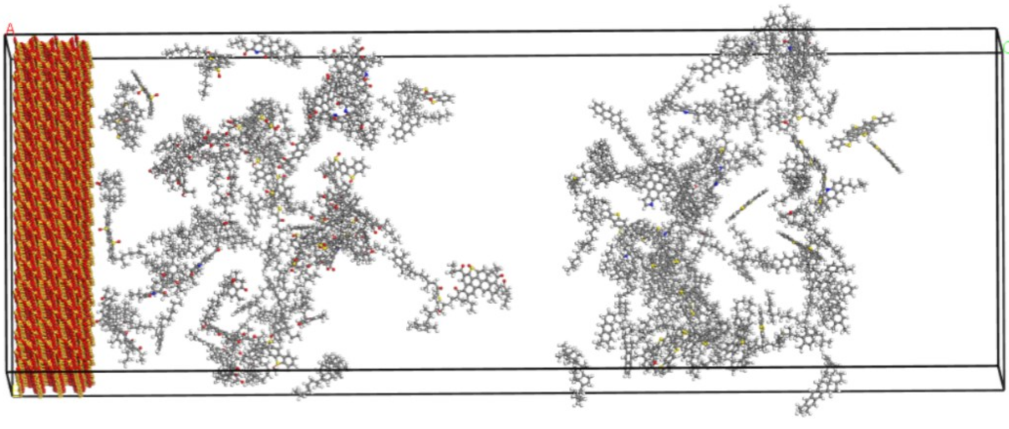
Figure 6.2 Molecular models (a) virgin bitumen (b) aged bitumen (c) aggregate

Diffusion models were then generated by assembling concerning compositions into a layer structure, as shown in Figure 6.3. The entire structure's equilibrium was carried out by literally conducting the structural optimization (10000 steps), Anneal dynamics (5 cycles from 300K to 500K).

Equilibrated models were run for 200ps for the dynamic simulation process. This study mainly concentrated on the formation of virgin-aged bitumen interface. A detailed explanation was provided to demonstrate that the 200ps simulation duration was acceptable for this study's specific research purpose in the result and discussion part. This study's global settings were described as follows: the force field adopted the COMPASS II (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies II) force field. The Ewald method and atom-based method were applied to calculate the electrostatic energy and Van der Waals energy. To adjust the system temperature and pressure, the Nosé-Hoover thermostat and Andersen constant pressure were adopted. Besides, the cut-off distance and time steps were 12.5 Å and one fs, respectively.



(a) two-layer model



(b) three-layer model

Figure 6.3 Constructed diffusion models with and without aggregate

6.4.2 Concentration profiles

Concentration profiles described a relative concentration variable for each variable and are used to determine inter-diffusion flux (Dayananda, 1983). By analyzing the dynamic properties of simulation results, each layer's concentration profiles can be calculated for each layer. Based on this, the intersect area of concentration profiles indicates the diffusion degree between two components. For calculating the concentration profile, the layer is divided into several bins along a specific direction. In what follows, the atom density in each slab is counted. The concentration profile can be calculated referring to Chapter 5.

6.5 Results and Discussion

6.5.1 Validation of molecular dynamic simulation

Due to the scale effect concerning the simulation size and time, the simulation results are tough to be validated. Although previous studies used thermodynamic properties such as density, surface energy, viscosity, and cohesive energy density to demonstrate the study's reasonability, significant variation caused by the scale effect is still unsolved (Xu and Wang, 2017a). This study did not devote to verify the constructed model since all the models of each component were used extensively in the literature (Li and Greenfield, 2014; Xu and Wang, 2016, 2017a; Hou *et al.*, 2017). Alternatively, it is necessary to examine whether the entire structure is equilibrated based on primary physical parameters' convergent curves.

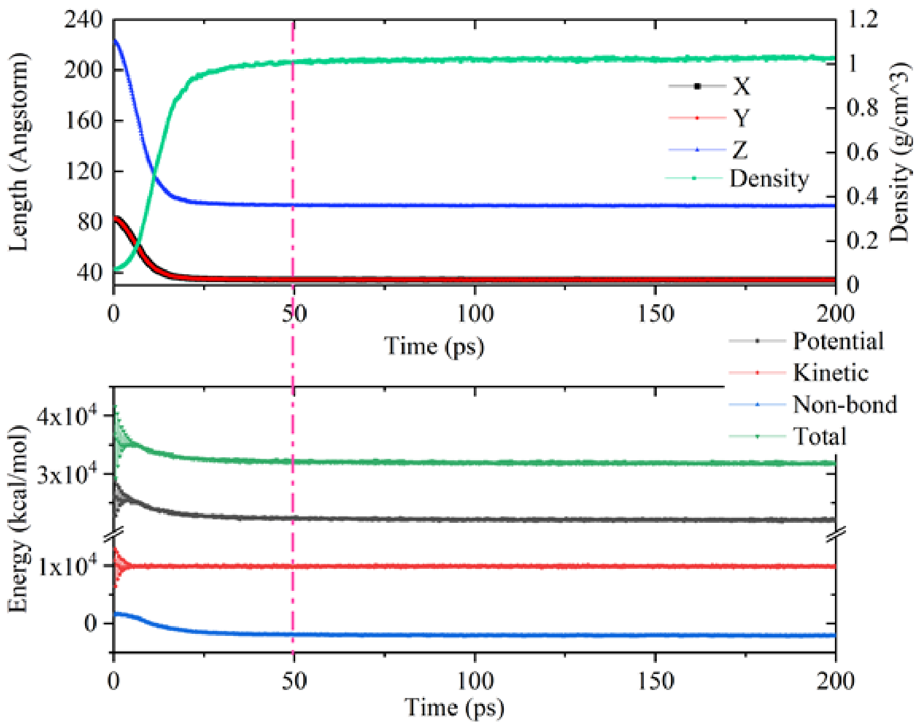
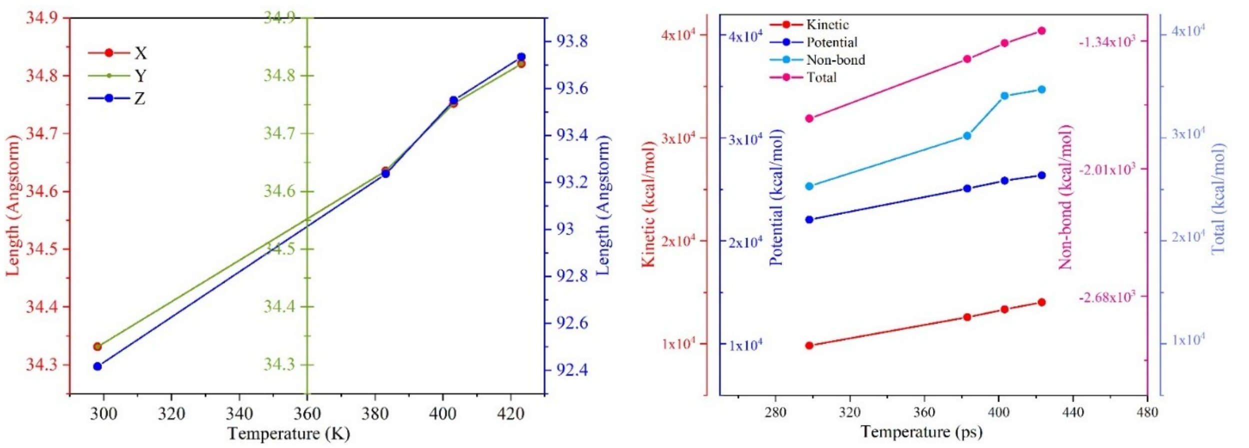


Figure 6.4 Primary indicators as a function of time for two-layer model (298.15K)

Figure 6.4 presents the cell parameters, density, and energy components as a function of simulation time, respectively. It can be observed that all physical parameters reached a platform after 50ps simulation, indicating an equilibrated state of the whole structure. In addition, the final density of the whole structure was around 1.02 at 298.15K, which was comparable to the experimental result. It was worth noting that only the two-layer results at 298.15K were presented herein. The increase of temperature can accelerate the molecular motion and, therefore, reaching the equilibrated at an earlier time. The three-layer, the incorporated silica layer, was a crystal structure layer that can reach the equilibrated state more quickly than amorphous structures. In conclusion, the simulation time of 200ps was sufficient for this study.

6.5.2 The influence of temperature on the physical parameters of the model

Figure 6.5 shows the influence of temperature on the model's physical parameters, including the cell parameters and energy components. As the increase of temperature, the constructed two-layer model increased, as seen in the increase of length in three directions. In addition, it can be found that the relationship between temperature and volume approximated to a linear relation.



(a) Cell parameters **(b) Energy components**

Figure 6.5 The influence of temperature on physical parameters (two-layer model)

In terms of the energy change, it can be found that the increased temperature induced the increase of kinetic energy, potential energy, and total energy. The potential energy and kinetic energy were linearly associated with the temperature. Since the coordinate adopted the same scale for the other three types of energy, the increase of potential energy and kinetic energy was identical. It should be noticed that the non-bond energy was shown in a negative value. Therefore, the increase of value indicated the decrease of absolute value. When the temperature increased, the molecular motions turned out to be more intensive. As a result, the non-bond energy caused by the molecular interaction was reduced.

6.5.3 Diffusion of the binary mixture without aggregate

Figure 6.6 presents a visualization of layer diffusion for the two-layer model. The dark blue one referred to the constructed aged bitumen, while the green one represented the virgin bitumen. The diffusion direction was from the aged bitumen to virgin bitumen, which conformed to the Fick law that the diffusion was mainly driven by the concentration gradient, provided that the concentration of aged bitumen was higher than that of virgin bitumen. After 20ps simulation, the interface between virgin bitumen and aged bitumen almost formed. According to Figure 6.6 (b), after the 10ps simulation, the aromatic components started to migrate to virgin bitumen. It illustrated that diffusion between virgin and aged bitumen firstly occurred with the migration of aromatic components. It is attributed to the relatively low molecular mass. Saturate component, although with the lowest molecular mass, almost had not polarity. The interaction between aromatic rings in the aromatic component could probably induce the migration of the aromatic component in the first place. However, it is interesting to observe that further diffusion seems terminated as seen marked virgin and aged bitumen no longer changed their positions.

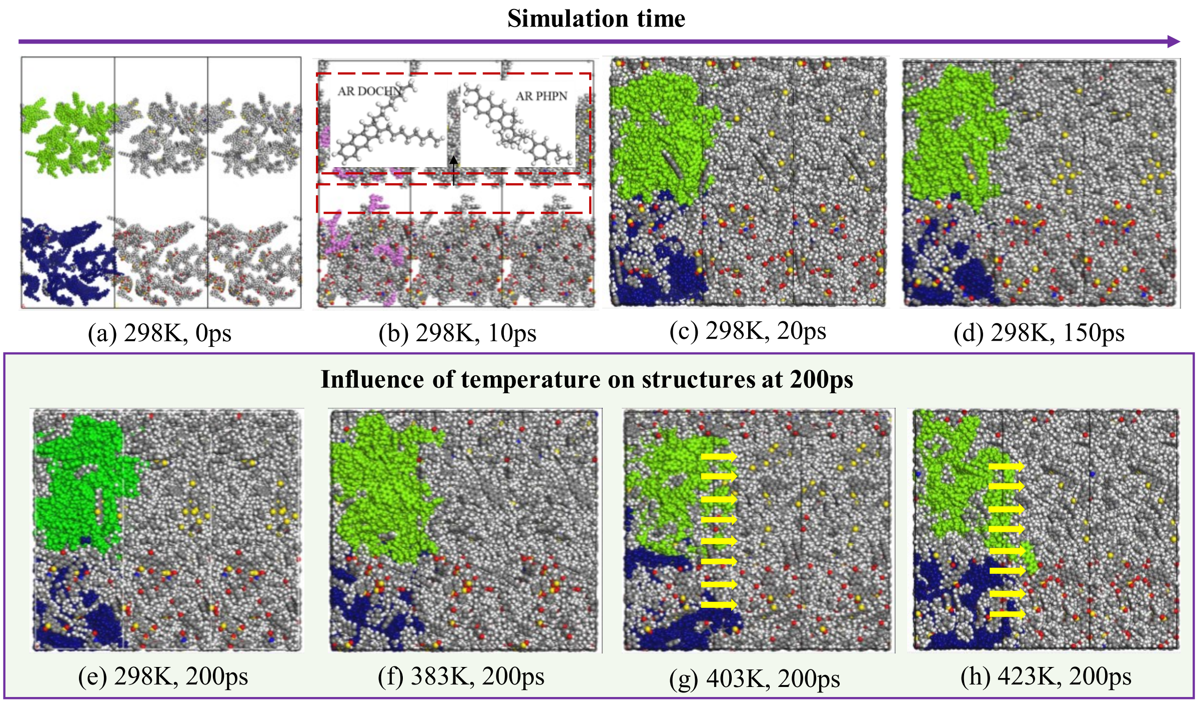


Figure 6.6 Evolution of diffusion between virgin and aged bitumen

Nevertheless, it can be concluded that the diffusion interface could be established in a short time. Whereas the diffusion process was remarkably long compared with the formation of the interface. Figure 6.6 (e) to (h), the influence of temperature on two-layer structures at 200ps was visualized. It can be seen that, although the temperature increased to 423.15K, the blend of virgin and aged bitumen was still not occurred. However, another interesting phenomenon was that, when the simulation temperatures were 403.15K and 423.15K, the molecular motion was no longer constrained in the concentration gradient direction and observed in the translational direction. The increase of simulation temperature intensified the motion of molecules, and therefore, the translational motion happened. This phenomenon indicated that the driven force off diffusion was mainly dominated by the concentration gradient when the temperature was low. At the same time, sufficient temperature could essentially accelerate the diffusion process by intensifying the molecular motion. In this study, this temperature was regarded as 403.15K, namely 130°C.

The concentration profiles at 0ps, 75ps, 150ps and 200ps were extracted from the simulation trajectory profile considering different temperatures, as shown in Figure 6.7. In general, the concentration profiles quantitatively demonstrated the conclusions obtained from Figure 6.6 that the incomplete diffusion process was simulated with 200ps, and the diffusion orientation was from aged bitumen to virgin bitumen. In addition, the concentration of profiles for virgin and aged bitumen were shown obviously with three peaks. At the simulation time of 0ps, the four concentration profiles for the two-layer were identical. However, when the diffusion interface was formed, significant three peaks were not observed. It illustrated that when the virgin bitumen and aged bitumen are contacted with each other, the structure of virgin bitumen or aged bitumen will suffer a reassembly of molecules before the molecular migration through the diffusion interface started. One thing that should be clarified that, due to the periodical boundary, the concentration profile of virgin reappeared when the distance beyond 75 Angstroms.

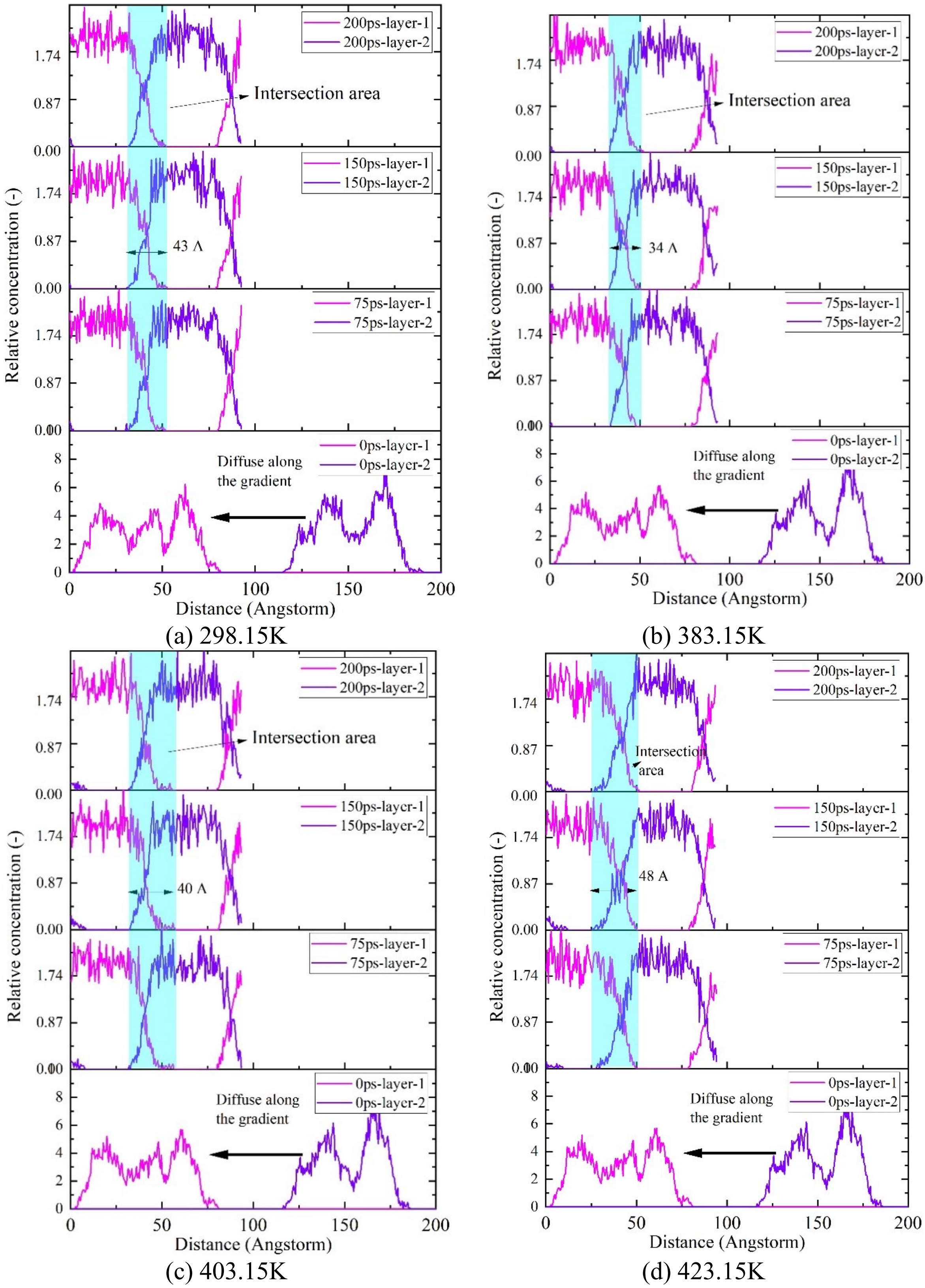


Figure 6.7 Concentration profiles at various temperatures (two-layer)

At a specific temperature, the intersection area marked in the figure was unchanged, which claimed that the blend of virgin and aged bitumen was a progressive process that requires remarkable duration, although the temperature was increased to 423.15K. The intersection areas of the two-layer model at different simulation temperatures were calculated and noted in Figure 6.7. It can be seen that the intersection distance decreased from 43 Angstroms to 34 Angstroms when the temperature increased from 298.15K to 383.15K. Until the temperature increased from 403.15K to 423.15K, the intersection distance increased to 48 Angstroms. This phenomenon was abnormal due to that the high temperature should positively influence the diffusion process. The plausible reason to explain this phenomenon could attribute to the self-assembly simultaneously happened with the diffusion process. As a result, the self-assembly enlarged the distance between virgin and aged bitumen.

6.5.4 Diffusion of the binary mixture with aggregate

Figure 6.8 compares the structures of the three-layer model after running 200ps simulation at different temperatures. The aggregate layer's incorporation significantly altered the conformational structure of virgin and aged bitumen when comparing Figure 6.6 and Figure 6.8. At 298.15K, as mentioned above, the primary driven force for the molecular migration was the concentration gradient. Due to periodical boundary settings, the virgin bitumen layer was closer to the aggregate layer in the extended boundary. Hence, most of the molecules adhered to the upper aggregate layer. In this case, the diffusion process represented another diffusion condition in the actual mixing process, as shown in Figure 6.8. Aged bitumen would coat on the surface of new asphalt mixtures. Notably, it can be seen that the blend degree of virgin bitumen and aged bitumen was higher than that observed in two-layer models. It was demonstrated that the presence of aggregate layer positively contributed to the diffusion process between virgin and aged bitumen by attracting more polar molecules in asphalt binder. In addition, it can be observed at 298.15K that the molecular cluster occurred at the lower aggregate layer, which further demonstrated the attraction force of the aggregate layer on bitumen.

As the temperature increased, the diffusion direction changed from virgin bitumen to aged bitumen. The adhesion between aggregate and bitumen was enhanced. The aged bitumen cannot easily escape from the surface aggregate layer. As a result, the blend of virgin and aged bitumen mainly happens in the lower aggregate layer's surface. Regardless of which aggregate surface the blend takes place; a relatively high blend degree can be intuitively observed. Therefore, the incorporation of the aggregate layer can accelerate the diffusion process. It should be clarified that part of aged bitumen also existed on the upper aggregate layer's surface. The reason is that, at a relatively high temperature, the random molecular motion was intensified between the aggregate layers, inducing some polar molecules in aged bitumen to migrate to the upper aggregate surface. On the other hand, the translational migration also occurred in the three-layer model. In particular, the critical temperature inducing the translational migration was reduced to 298.15K.

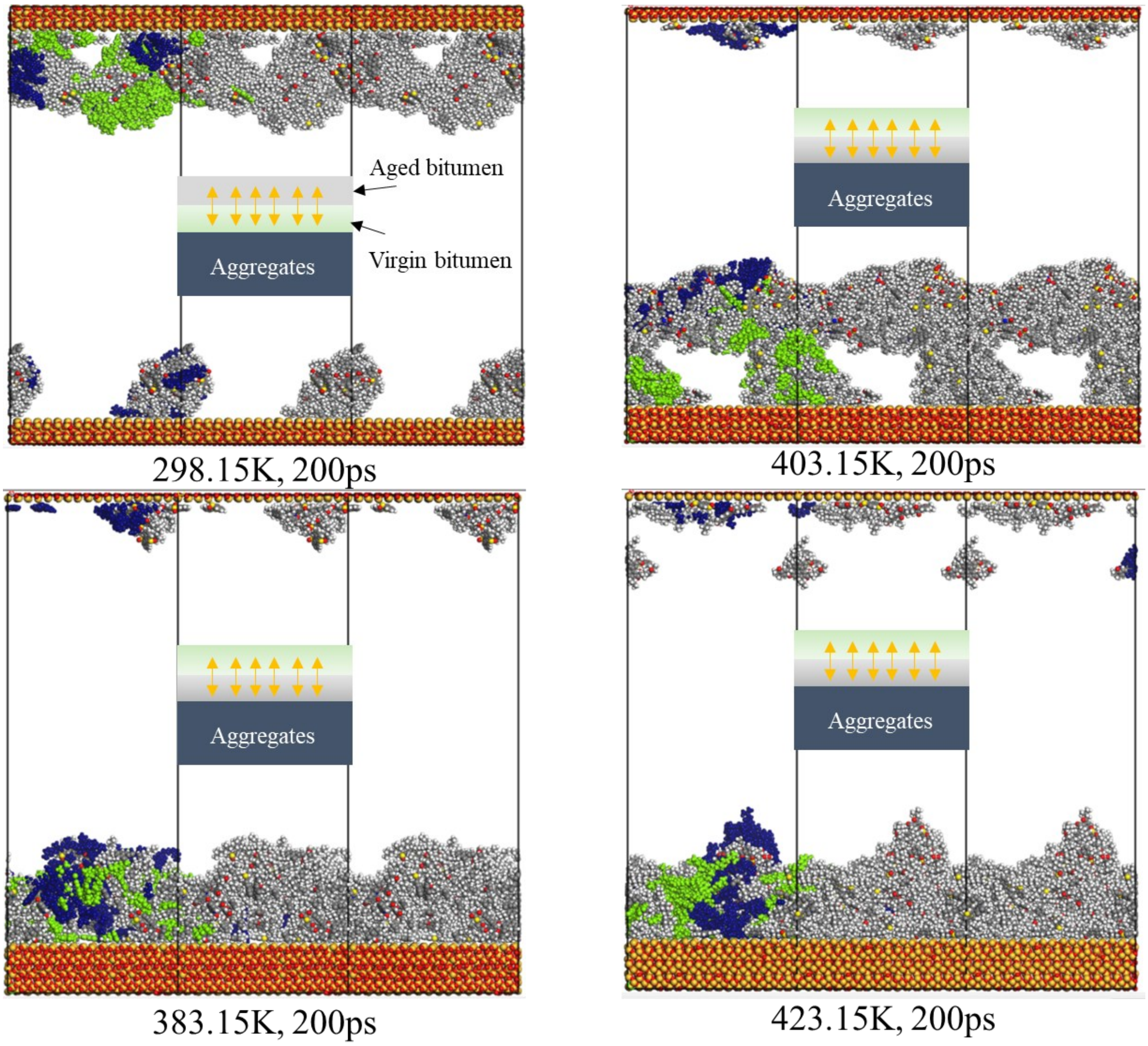
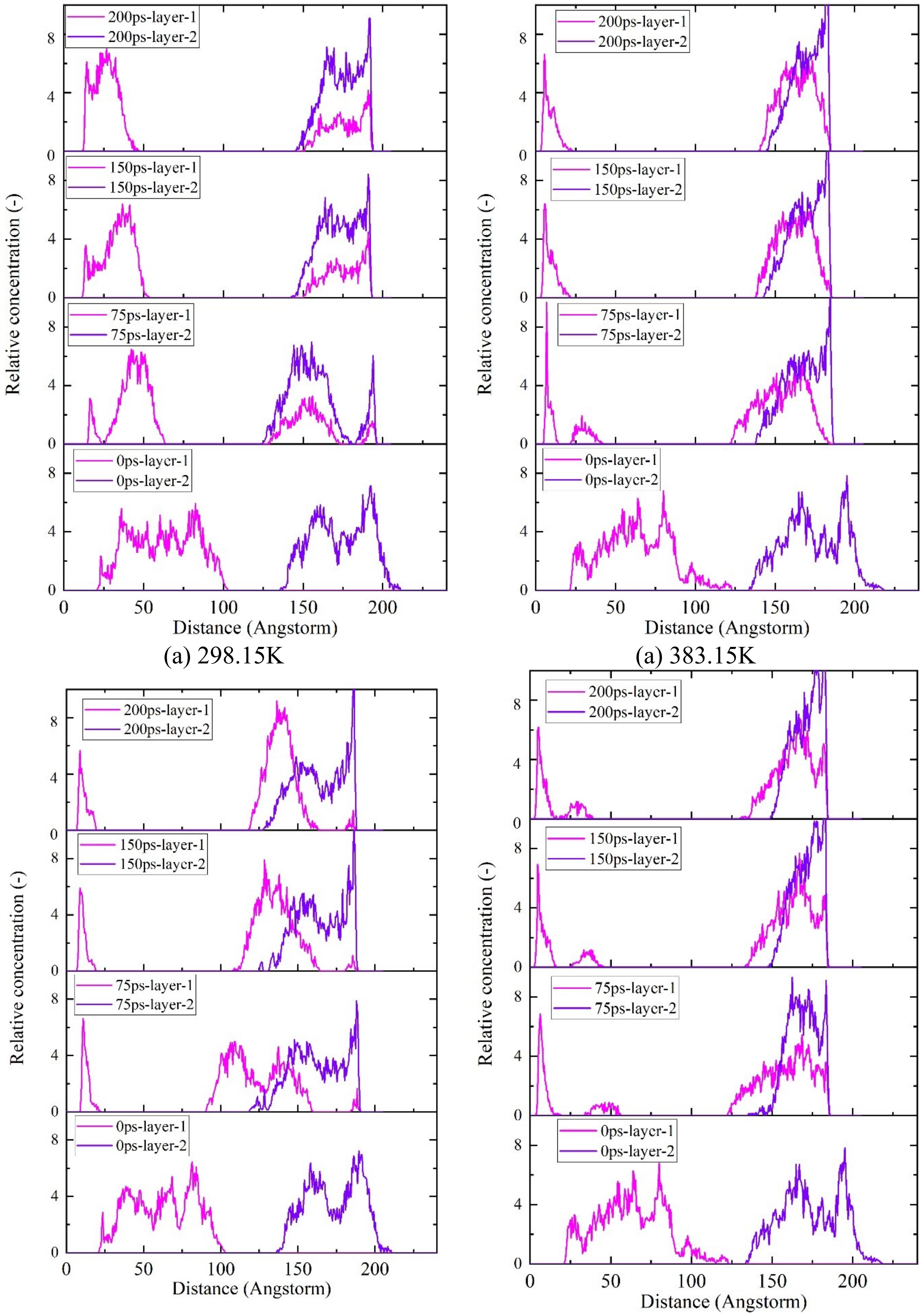


Figure 6.8 Evolution of diffusion between virgin and aged bitumen

Figure 6.9 shows the concentration profiles derived for the three-layer model. It can be found that for all temperatures, the migration direction mainly happened from virgin to aged bitumen, which was ascribed to the constrain of aggregated to aged bitumen layer. The partial component migrated far away from the aged bitumen shown in Figure 6.9. This phenomenon was on account of the setting of the periodical boundary. In this study, the concentration profiles shown in the right part were a major concern. Accordingly, it can be found that the virgin bitumen migrated into aged bitumen at 75ps. After that, when the simulation time reached 150ps, it was found that the concentration profiles for both virgin bitumen and aged bitumen changed, which indicated a conformational reassembly occurred during the simulation process. Comparing the results at 150ps and 200ps, the concentration profiles were identical, claiming a relatively equilibrated state of structures.

Concerning the influence of temperature, it can be found that at 298.15K after 200ps simulation, the proportion of virgin bitumen in the blend was lower than that of aged bitumen. When the temperature increased to 383.15K, the proportions of virgin and aged bitumen in the blend were comparable. However, at the temperature of 403.15K, the blend degree abnormally decreased. Referring to Figure 6.8, micro-void in the structure formed, which further diffuses virgin and aged bitumen. The microvoids were also reported in another research (Xu *et al.*, 2019); however, this study did not clearly illustrate microvoids formation. A plausible assumption to explain this can attribute to the assembly of polar molecules forming a ring that prevents other molecules. According to Figure 6.9 (d), these formed microvoids were a temporary transition state. Once the temperature continued to increase, the intensified molecule motion would break the equilibrium state, and thus microvoids disappeared.



(a) 298.15K (a) 383.15K

(c) 403.15K (d) 423.15K

Figure 6.9 Concentration profiles at various temperatures (three-layer)

6.6 Conclusions

Under the concept of molecular-scale homogeneity for asphalt mixtures with RAP, the interface between new and aged bitumen was investigated using the molecular dynamics simulation method to understand the molecular scale's diffusion process better. For this reason, a two-layer model including new and aged bitumen was constructed, and the dynamic simulation was run at four different temperatures. The incorporation of the aggregate layer was also added to study the influence of aggregate on the diffusion between binders. Accordingly, some key findings were concluded as below:

(1) The increase of temperature enlarged the constructed models' volume, following a positively linear relationship. In terms of the energy, the kinetic energy, potential energy increased while the non-bond energy decreased as the intensified molecular motions.

(2) The interface between new bitumen and aged can be quickly achieved due to resin components' migration. However, the diffusion process was considerably slow compared with the formation of the interface.

(3) The aggregate layer, through adhering the polar molecules in bitumen binders, can accelerate the diffusion process between new and aged bitumen, and the mix of new and aged bitumen can be explicitly observed.

(4) In the three-layer model, microvoids were formed, which hindered the further diffusion process. However, these microvoids can be eliminated by increasing the temperature.

7 Conclusion and Recommendations

The conclusions and recommendations that resulted from the research described in this thesis are presented. A more elaborate description can be found in the respective chapter.

7.1 Conclusions

Main conclusions with regards to the goal of this thesis are given below:

Macro-scale

(1) The asphalt mixtures with RAP produced in different mixing times and mixing temperatures showed significant varied mechanical performance. The asphalt mixtures were produced in a thermal-equilibrium environment, the variation caused by migration or diffusion of binders can be eliminated as little as possible. Therefore, the distinct mechanical performance indicated a variation of macro-homogeneity of asphalt mixtures.

(2) A long mixing time benefited the formation of homogenous state, in particular for the breaking of clusters in RAP materials. As the mixing time increased, the macro-homogeneity of asphalt mixture experienced from ‘momentary homogeneity’ state to ‘real homogeneity’ state.

(3) A high mixing temperature played a negative role in the distribution of materials, claimed as that the increase of temperature would obstacle the breaking of clusters and prolong the state shift toward a ‘real homogeneity’ state. On the other hand, the increase of temperature increased the flow ability of binders, including the RAP binder and new bitumen. As a result, the migration behavior of components would be altered. Moreover, high temperature induced high diffusion rate between RAP binder and new bitumen, which correspondingly affected the mechanical performance of asphalt mixture produced with RAP.

Meso-scale:

(1) In terms of the migration and diffusion, the mixing temperature played a more important role in the formation of final asphalt mixtures containing RAP materials by considerably changing the viscosity of binders.

(2) During the mixing process, it can be usually divided into two stages. In the first stage, the migration of new bitumen or RAP binder basically reached an equilibrium state. In what follows, the diffusion played a dominate role before the loose mixture subjected to the compaction.

(3) This study proposed the Asymmetric Gaussian Model to describe the blending rate with mixing time. In specific, two stages during the mixing process were defined as the migration-dominated and diffusion-dominated stages. The migration-dominated stage was mainly affected by the temperature and mixing work, while the diffusion-dominated stage reacts to the temperature and bitumen properties.

Micro-scale:

(1) The diffusion between RAP binder and new bitumen was tightly associated with the meso-scale homogeneity of asphalt mixtures (migration of binders). In another word, the diffusion occurred only if the RAP binder and new bitumen interacted.

(2) The mixing temperature, to some extent, determined the diffusion between RAP binder and new bitumen. The micro-scale of asphalt mixture was very complicated. Currently used indicators such as blending efficiency was not sufficient to achieve a comprehensive estimation. Therefore, merely one indicator cannot fully reflect the homogeneity of asphalt mixtures.

Molecular-scale:

(1) During the aging process, bitumen will generate the carbonyl and sulfur oxide groups progressively due to thermal oxidation. From a microscopic view, the aging gradient does exist along with the depth. Short-term aging is ascribed to the thermal oxidation and volatilization of light mass (mainly saturate). The stability of four fractions in the bitumen depends on the fraction property and the colloidal structure. For both perspectives, the stability of asphaltene is higher than the saturate.

(2) The interface between virgin bitumen and aged can be quickly achieved due to resin components' migration. However, the diffusion process was considerably slow compared with the formation of the interface. The aggregate layer, by adhering to the polar molecules in bitumen binders, can accelerate the diffusion process between virgin and aged bitumen. The mix of virgin and aged bitumen can be explicitly observed.

7.2 Outlook

From the experience obtained from this study, the following topics appear important for further research:

Topics 1: Quantitative characterization of sample morphology from two-dimension (2D) to three-dimension (3D)

This topic aims to incorporate the topology theories in the analysis of sample morphology. It is required to use some topological indicators to estimate the macro-homogeneity of asphalt mixtures. In addition, according to the experience in this study. The dimension reduction from 3D to 2D would loss some important structural information, making the morphology of asphalt mixture untraceable. In future work, using non-destructive methodology like CT scanning to obtain detailed 3D information could be a promising method.

Topics 2: The development of Multi-scale Synchro-adjust Methodology (MSM) towards a near-perfect homogenous asphalt mixture

This study reported that the mechanisms of homogeneity evolution were essentially varied in different scales. Therefore, it is a challenging work to design a mixing procedure particular for the one containing RAP materials to synchronized multi-scale homogeneity. In this case, the asphalt mixtures with RAP would not be significantly affected by the mixing procedure, which benefits the research consistency conducted by different researchers.

Topics 3: The use of computer-aided methods in the design of asphalt mixtures containing RAP from begin to the end

The presence of RAP clusters and the materials variation induced a complicated mixing mechanism of asphalt mixture. No doubt that such complicated material composition will cause significant uncertainty especially for the experimental investigation. As the development of computer-aided methods, the use of simulation method to alternate the experiments become more and more attractive. In future work, it is strongly recommended to use more simulation method study the asphalt mixtures with RAP materials, following are some immature ideas：

(1) Finite element method for the study of asphalt mechanical performance

(2) Discrete Element Method for the study of mixing and compaction process
(3) Coarse-grained method for the study of clusters and the collision occurred in the mixing process
(4) Molecular dynamic method for the study of diffusion between RAP binder and new bitumen

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Appendix

Declaration by Doctoral Candidate of Own Contribution to Publication-based dissertation with Three or More Authors

I hereby confirm, that Quan Liu contributed to the study as stated below:

Article:

Wu, Jiantao, Quan Liu*, Shuai Yang, Markus Oeser, and Cadnel Ago. "Study of migration and diffusion during the mixing process of asphalt mixtures with RAP." Road Materials and Pavement Design (2020): 1-16.

Author Contributions:

Quan Liu and Jiantao Wu conceptualized research idea and designed the experiments. Quan Liu also contributed to the experiment completion, data analysis, manuscript writing and editing. Shuai Yang contributed to the assistance of experiments. Cadnel Ago contributed to the proof-read of manuscript. Markus Oeser contributed to the supervision and final manuscript check.

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Quan Liu conceptualized research idea, completed the experiments, conducted data analysis, contributed to writing and editing. Jiantao Wu contributed to the proofread of manuscript. Markus Oeser contributed to the supervision and final manuscript check.

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Author Contributions:

Quan Liu conceptualized research idea, designed the experiments, completed the simulation, conducted data analysis, contributed to writing and editing. Jiantao Wu and Linlin Xie carried out the experiments. Zeyu Zhang and Xinyuan Ma contributed to the draft proofread. Markus Oeser contributed to the supervision and final manuscript check.

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