

Selective Absorption of Swelling Rubber in Hot and Warm Asphalt Binder Fractions

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ABSTRACT

The use of waste tire rubber as asphalt modifier has been a practice-ready technology. However, the interaction among components within asphalt rubber (AR) and warm asphalt rubber (WAR) is still unclear. During the blending process, the swelling rubber releases polymer agents in asphalt and absorbs components from both asphalt and warm mix asphalt (WMA) additive simultaneously. The component interaction significantly influences the final rheological properties. A comprehensive understanding of the selective absorption of crumb rubber during the blending process provides references to optimize the material and procedure design of rubberized asphalt. To this end, one AR and two WARs were prepared with three mixing durations. The liquid phases and crumb rubber particles were separated. The separated swelling rubber particles were then processed by the staged extraction

method to divide the asphalt-rubber interacting area from outside to inside into four layers. The absorption preference of swelling rubber and its influence on rheological properties were investigated by chemical and rheological tests. Test results showed that asphalt fractions with smaller molecular weight were absorbed into deeper layers of swelling rubber. By contrast, crumb rubber was found to be reluctant to absorb the fractions with C-O bond during the mixing process. In addition, the Fischer Tropsch (FT) wax showed a negligible influence on the absorption preference, while the effect of surfactant on absorption preference was significant. Finally, the relationship between absorption preference and rheological properties was established. It was found that the absorption preference of crumb rubber is beneficial to the rutting resistance of rubberized asphalt.

Key Words: Swelling Rubber, Absorption Preference, Chemical Analysis, Rheological Analysis, Staged Extraction

1 Introduction

With the rapid rise of vehicles and highway mileage, the amount of waste tyres has increased year by year all over the world [1]. Known as “black pollution”, the degradation of waste tyres could be more difficult than that of plastic pollution (white pollution). On the other hand, the abundant waste tyres are precious polymer resources. To turn waste into useful material again, one prevailing measure is to grind waste tyres into crumb rubber and used as the modifier for asphalt paving materials. Wet process-Asphalt rubber (AR) is produced by mixing crumb rubber modifier (CRM) into raw asphalt at high temperature for 30-90 mins, while the dosage of CRM should be more than 15% weight of the raw binder [2]. The re-use of waste rubber grants AR superior high-temperature, intermediate-

1 temperature, and low-temperature performances compared to their corresponding raw
2 asphalt [3-5].

3 Although the incorporation of CRM brings enhanced performances, it increases the
4 viscosity of raw asphalt, resulting in the bad workability of AR. Thus, higher blending and
5 paving temperatures are required for the construction of AR pavement. The elevated energy
6 consumption and construction emission result in serious environmental problems and limit
7 the wide application of AR [6]. To alleviate the environmental concern of AR, the warm
8 mix asphalt (WMA) technology has been incorporated to produce warm asphalt rubber
9 (WAR) [7]. WMA technology allows rubberized asphalt material to be produced at a 15-
10 30 °C lower temperature by decreasing the binder viscosity, producing asphalt foaming or
11 reducing the friction between binder and aggregates [8-11].

12 The production of AR and WAR does not refer to simply mixing and dispersing CRM into
13 hot and warm asphalt binder fractions. Complicated interaction could happen between
14 CRM, raw asphalt and WMA additive during the wet process. The outer part of CRM
15 dissolves with mixing time, releasing natural rubber, synthetic rubber and other
16 components into asphalt binder. Meanwhile, the bulk of CRM particles enlarges by
17 absorbing light components of asphalt binder, forming a high viscosity semisolid
18 continuous phase system around the elastic rubber core. The swelling rubber plays an
19 important role in the enhanced performance of rubberized asphalt. Ghavibazoo [12]
20 indicated that the swelling rubber reduces the free space between particles and stiffens the
21 binder. Wang [13] found out that the enhanced rutting and fatigue performances of
22 rubberized asphalt binder are majorly contributed by the particle effect of CRM.

1 Figure 1 shows the schematic of the AR/WAR working system. During the mixing process
2 of raw asphalt, CRM and WMA additives, certain components within hot or warm asphalt
3 binder fractions are absorbed from the liquid phase into the rubber-asphalt interacting area,
4 which influences the rheological properties of AR and WAR binders. So far, the
5 rheological properties of WAR have been well evaluated and researchers have been trying
6 to characterize the interaction between rubber and asphalt by using different methods. The
7 scanning electron microscopy (SEM) was used to spectate the size change of CRM before
8 and after mixing [14]. The gel permeation chromatography (GPC) was used to evaluate the
9 components and molecular weight variations of asphalt binder [13,15,16]. The thermal
10 gravity (TG) analysis was used to analyze the component loss after reaction [17,18].
11 Although the degradation of rubber and the modification of asphalt fraction in AR/WAR
12 have been well acknowledged, limited research has been conducted to investigate the
13 composition of asphalt-rubber interacting area. To study the role of swelling rubber in the
14 work system of AR/WAR, a more comprehensive understanding about the absorption
15 preference of swelling rubber during its interaction with asphalt fractions and how it is
16 affected by WMA additives is needed.

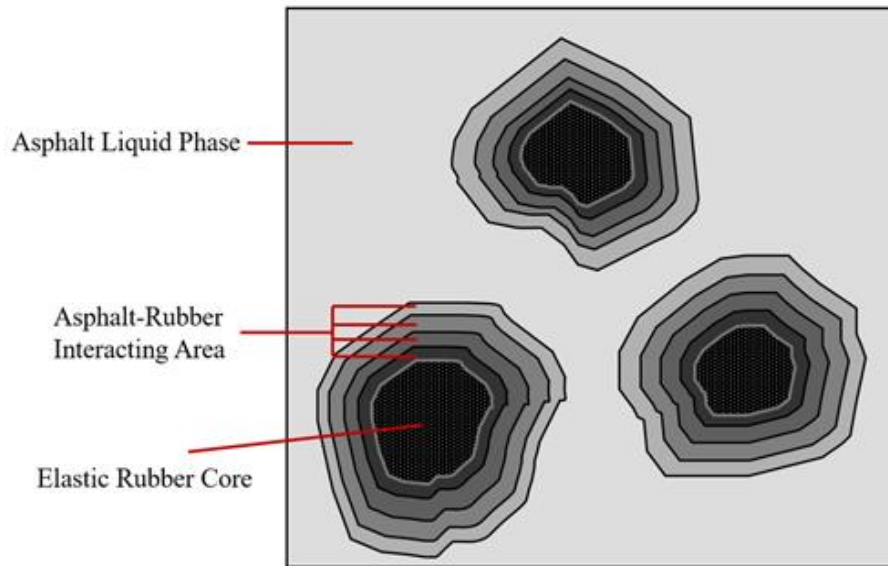


FIGURE 1 Schematic of AR/WAR work system

This study aims to characterize the selective absorption of swelling rubber within hot and warm asphalt binder fractions. AR and two kinds of WAR (with organic and chemical WMA additives) were produced by three different mixing durations. The swelling rubber particles after interaction were obtained by filtrating away the liquid phase binder. The reclaimed swelling rubber were then processed by an improved staged extraction method to divide the asphalt-rubber interacting area from outside to inside into 4 layers. Afterward, 4 layers of extractions and liquid phases were tested by GPC and Fourier transform infrared spectroscopy (FTIR) to determine the molecular weight and functional group distributions of the components absorbed by swelling rubber. Finally, the relationship between the rheological properties and absorption preference was analyzed. The findings of this paper are expected to provide a deeper insight into the interaction mechanism between swelling rubber and asphalt fractions in AR/WAR, and thus contribute to the optimization of material and blending condition design of rubberized asphalt.

2 Experimental Program

2.1 Materials and sample preparation

Raw asphalt with a penetration grade of 60-70 was used. As for the CRM, the production method and particle size of CRM relate to its surface area contacted with asphalt binder and its filling volume, which mainly affect its interaction speed with asphalt fractions as well as the rheological properties of modified binder [19, 20]. On the other hand, the main chemical compositions of different types of tyres are almost the same, including natural rubber, synthetic rubber and carbon black, etc [21]. This study mainly focuses on characterizing the absorption preference of swelling rubber by investigating the chemical composition within the interacting area of asphalt, rubber and different WMA additives, so the source of rubber should have limited influence on the test results. Therefore, only 40-mesh CRM produced through the ambient ground was used and the dosage is 20% weight of the raw binder for each production. One organic Fischer Tropsch (FT) wax and one chemical surfactant were used as WMA additives. The FT wax is composed of long-chain carbon wax, which can melt into liquid at mixing temperature so that the fluidity of asphalt binder can be improved [22]. The chemical surfactant is consisting of fatty amine derivatives and alkylamines, which facilitates the coating by reducing the friction between aggregate and binder [9,10]. Table 1 describes the basic properties and dosages of FT wax and surfactant. In each mixing, the raw asphalt, CRM and WMA additive were directly blending together by a high shear mixer with 6,000 rpm. To obtain different absorption and dissolution levels of rubber, three different mixing durations were used for each kind of binder, i.e. 30, 60 and 90 minutes. Besides, AR was mixing at 176 °C and WARs were mixing at 160 °C. The AR mixed with FT wax and chemical surfactant were labelled as

ARW and ARC, respectively. The preparation parameters of AR/WAR used in this study were selected based on previous researches, which provided satisfied rheological properties [9, 13, 23].

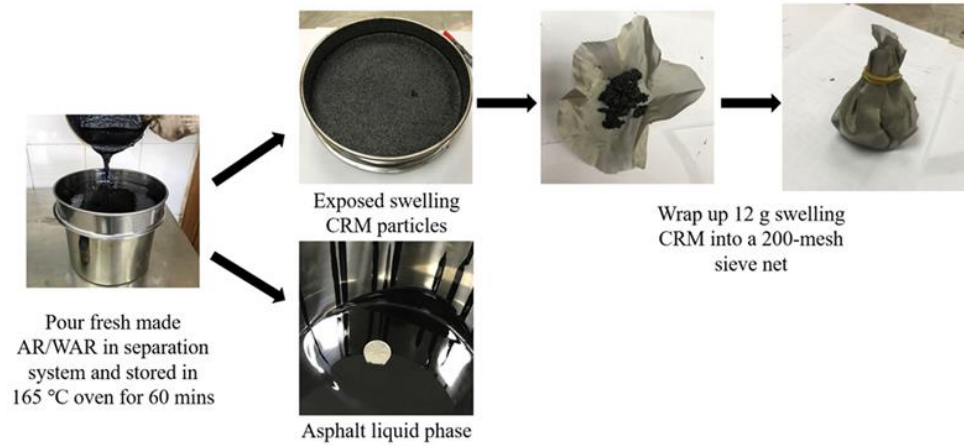
TABLE 1 Properties of WMA additives

Properties	FT wax	Surfactant
Ingredients	saturated hydrocarbons	fatty amine derivatives, alkylamines
Dosage	3wt% of AR binder	5wt% of AR binder
State	solid	liquid
Color	milk white	amber
Odor	none	amine-like
Density	0.622 g/cm ³	1.0-1.1 g/cm ³
PH value	N/A	9-10
Melting point	105-110 °C	N/A
Boiling point	N/A	150-170 °C
Water solubility	insoluble	partially soluble

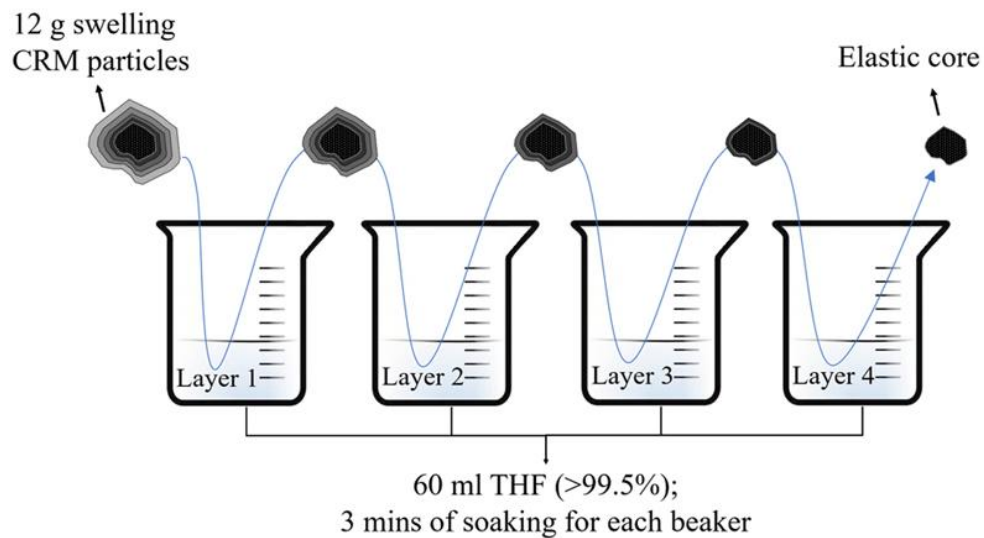
2.2 The separation of swelling CRM and asphalt liquid phase

Before the staged extraction, the swelling CRM particles need to be separated from the liquid phase asphalt. A self-designed separating device was used, whose details can be found in a previous study [13]. Figure 2a shows the separating process. First, 3 kinds of AR and 6 kinds of WAR binders were produced by high shear mixing. The fresh-made binder was then poured onto a sieve of 200-mesh, which was placed on a metal container. Subsequently, the whole separating device was stored in an oven of 165 °C for one hour. To protect the sample from direct contact to hot air in oven, the sieve was covered by a cap during the separating process. Under high temperature, the asphalt liquid phase slowly flew through the sieve pore and dropped into the metal container, while the swelling CRM particles were exposed on the sieve where no asphalt liquid phase can be visually detected. Therefore, the swelling CRM particles could be ready for the staged extraction method.

- 1 Besides, the liquid phases were labelled as L-(AR/ARW/ARC) and saved for rheological
- 2 and chemical tests.



(a) Separation of liquid phase and swelling rubber



(b) Staged extraction of the asphalt-rubber interacting area

3

4 **FIGURE 2 The separating of swelling rubber and the staged extraction method**

5 **2.3 Staged Extraction**

6 The staged extraction method designed by Huang [24] was once utilized to quantify the

7 binder homogeneity of recycled asphalt and virgin asphalt. In his study, the RAP

aggregates were put into a copper basket and then immersed into 4 beakers of trichloroethylene (TCE) in turn. It was assumed that each immersion could wash down one “layer” of components that attached to the RAP aggregates. Considering the absorption behavior of crumb rubber in AR/WAR binder, the staged extraction method should be helpful for removing the layers in the asphalt-rubber interacting area. Figure 2b indicates the schematic of the staged extraction method used in this study. 12 g of swelling CRM particles were immersed into 4 beakers of tetrahydrofuran (THF) (60 ml) in order. The duration of each soaking was 3 minutes. After each soaking, one layer of components in the asphalt-rubber interacting area was supposed to be removed and dissolved in the solvent. To bring out the staged extraction method in this study, some adjustments were needed according to the physical properties of crumb rubber. A 200-mesh sieve net was used to wrap up the 12 g swelling CRM particles like a “dumpling” and the top of the “dumpling” was tied by a rubber band. By doing so, the transfer of swelling rubber particles from beaker to beaker could be easier without losing them. Subsequently, 4 beakers were filled with 60 ml of THF, respectively. A clamp was used to soak the swelling rubber into the beaker and stir it to enhance the dissolution. Therefore, each beaker of solvent represented one layer of components that absorbed by the swelling rubber.

2.4 Testing Program

This study aims to evaluate the role of swelling rubber in the work system of AR/WARs in a more comprehensive way. First, two chemical tests, namely GPC test and FTIR test, were conducted on liquid phases and staged extraction layers to estimate the absorption preference of swelling rubber towards different molecular sizes or certain functional groups. Then the rheological properties of AR/WARs and their liquid phases were compared.

1 Finally, the relationship between the absorption behaviours of swelling rubber and the
2 rheological properties of AR/WARs was investigated.

3 ***2.4.1 GPC test***

4 GPC tests were conducted to measure the molecular weight distribution of each sample.
5 An Agilent 1260 GPC, which used THF solvent as its mobile phase, was the instrument
6 applied in this study. Two chromatographic columns were equipped, namely PLgel 3 μ m
7 Mixed-E and PLgel 5 μ m 10³Å. The temperature of the two columns was set as 30 °C. The
8 set flow rate was 1 mL/min, and the injection volume was 20 μ L. Since THF was used in
9 the staged extraction method, the solvent containing extracted components in each beaker
10 can be directly tested by the GPC test, while liquid phase samples were dissolved in THF
11 before the GPC test. The concentration of each sample was about 1.0 mg sample per mL
12 of THF. Before the injection, all samples were filtered through a 0.2 μ m filter. During the
13 GPC test, the molecules were driven by the THF eluent towards the porous gel particles.
14 Only the molecules whose diameter was smaller than the pore diameter could enter the gel
15 pore channel, while the large molecules could pass through the gap between gel particles
16 and take the lead. Therefore, the molecules came out of the column in order from large size
17 to small size. Meantime, the concentration of the expelled molecules was recorded as
18 chromatogram by a Refractive Index Differential (RID) detector.

19 To analyze the molecular weight distribution, one common method used in asphalt binder
20 chemistry is to divide the chromatogram into several slices and integrate each of them.
21 Therefore, the distribution of molecular weight can be represented by the area ratio
22 (Area%), which refers to the area of each slice divided by the total area. It is also a method
23 of normalization, helping to eliminate the error generated from the concentration difference

of injected solution [25]. The absorption preference of swelling rubber among molecules of different sizes could be characterized by comparing the Area% of each molecular size (MS) level.

2.4.2 FTIR test

In this study, a VERTEX 70 FTIR Spectrometer with a resolution of 4 cm^{-1} and a scan number of 16 was used to detect the chemical bonds in asphalt binder. The functional groups between the wavenumber range of $400\text{--}4000\text{ cm}^{-1}$ were scanned. Before the test, retoo evaporation was conducted to reclaim the staged extraction components from the THF solvent. The staged extraction THF solvent was poured into a vial and then heated by a $70\text{ }^{\circ}\text{C}$ water bath until no liquid can be seen in the vial. Subsequently, the vial was stored in a vacuum oven at $80\text{ }^{\circ}\text{C}$ for 8 hours to remove any remaining THF solvent or water, eliminating its influence on the test results. The FTIR test began with evenly spreading the sample onto a potassium bromide (KBr) plate, and then the KBr plate was placed into the sample chamber to launch the spectral scanning.

In the FTIR test, peak intensities are susceptible to the concentration of sample. To eliminate this disturbance, the FTIR spectra are usually normalized before analysis. The results can be processed by deriving the peak values of specific absorbance band or calculating the integral areas within certain wavenumber ranges. Hokfo et al. [26] suggested that using normalized spectra and absolute baseline at an absorbance value of 0 for integration provides more consistent results. Based on this method, FTIR can be adopted as a quantitative method in asphalt chemistry to characterize the changes in functional groups. The carbonyl band ($\text{C}=\text{O}$) around $1,700\text{ cm}^{-1}$ and sulfoxide band ($\text{S}=\text{O}$) around $1,000\text{ cm}^{-1}$ are two common indicators of oxidation. Among these two bands, the

1 carbonyl band is considered to be more reliable in rating the aging level of asphalt binder
 2 [27]. The oxidation level can be represented by the area ratio of carbonyl band and C-C
 3 band (1,455 cm⁻¹), because the saturated C-C band is relatively stable through the aging
 4 process but C=O bond will increase due to addition of oxygen [28]. The calculation of the
 5 carbonyl index can be illustrated by Equation 1:

$$6 \quad \text{Carbonyl index} = \frac{\text{Area}_{1700}}{\text{Area}_{1455}} = \frac{\int_{1675}^{1724} f(w) dw}{\int_{1400}^{1500} f(w) dw} \quad (1)$$

7 where Area_{1700} and Area_{1455} represent the integrated area within the wavenumber ranges of
 8 1724-1675 cm⁻¹ and 1500-1400 cm⁻¹, respectively; w is the wavenumber (cm⁻¹); and $f(w)$
 9 is the normalized absorbance at w .

10 Additionally, Tang et al. [29] used the ratio of band areas around 965 cm⁻¹ and 810 cm⁻¹,
 11 which was defined as Active Polymer Index (API), to represent the content of polymer
 12 released by vulcanized rubber. In this study, a similar indicator, Polymer Absorption Index
 13 (PAI), was used to characterize the amount of polymer absorbed into the asphalt-rubber
 14 interacting area. The integrated area within the wavenumber range of 1,290⁻¹,235 cm⁻¹
 15 (Area_{1270}) was divided by that of 840-785 cm⁻¹ (Area_{810}) for analysis, as shown in the
 16 following equation:

$$17 \quad \text{PAI} = \frac{\text{Area}_{1270}}{\text{Area}_{810}} = \frac{\int_{1235}^{1290} f(w) dw}{\int_{785}^{840} f(w) dw} \quad (2)$$

18 where Area_{1270} & Area_{810} are the normalized integrated areas within the wavenumber
 19 ranges of 1290-1235 cm⁻¹ and 840-785 cm⁻¹.

20 **2.4.3 Rheological Analysis (MSCR and LAS tests)**

21 The rheological tests were carried out by a dynamic shear rheometer (DSR) of Malvern
 22 Kinexus Lab+. The rutting resistance was evaluated by the Multiple Stress Creep Recovery

(MSCR) test. 2 mm gap between the parallel 25 mm-diameter test plates was used for the binders containing swelling rubber (AR, ARW and ARC), so the errors brought by rubber particles touching the test plates can be reduced [12, 30]. By contrast, 1 mm gap was used for the asphalt liquid phase (Pen60/70, L-AR, L-ARW and L-ARC). The MSCR test was conducted by applying a one-second creep load to the sample and then removing the load to let the sample recover for 9 seconds. Starting with the stress level of 0.1 kPa, this creep/recovery cycle was repeated 10 times. Afterward, the stress level was increased to 3.2 kPa and another 10 creep/recovery cycles were applied. All the samples were aged by a rolling thin film oven (RTFO) before the test. The test temperature was set to 60 °C. The non-recoverable creep compliance (J_{nr}) was used as a rutting potential index [31], which can be calculated by the following equation:

$$J_{nr} = \frac{\varepsilon_{nr}}{\sigma} \quad (3)$$

where ε_{nr} is the nonrecoverable strain; σ is the stress level, 0.1/3.2 kPa.

It has been proved that the Linear Amplitude Sweep (LAS) test is more reliable than the $G^*\sin\delta$ test in estimating the fatigue resistance of modified asphalt [32]. 8 mm-diameter plates with a 2mm gap and an experimental temperature of 25 °C were adopted. The samples were aged by the RTFO and Pressure Aging Vessel (PAV) tests before the test. In LAS tests, a frequency sweep test was first conducted by a 0.1% strain-controlled load with a frequency range of 0.2-30 Hz. The value α representing the rheological property of the sample can be obtained by using the following equation:

$$\log G'(\omega) = \frac{1}{\alpha} (\log \omega) + b \quad (4)$$

where ω is phase angle (°); $G'(\omega)$ is storage modulus; α and b are fitting coefficients.

Subsequently, the amplitude sweep test was carried out by using oscillatory load cycles with a frequency of 10 Hz to increase the strain from 0 to 30%. The viscoelastic continuum damage (VECD) analysis was then conducted by combining the results from both frequency sweep and amplitude sweep tests. Finally, the fatigue resistance of the sample can be represented by the number of cycles to failure (N_f), as shown in the following Equation:

$$N_f = A(\gamma)^B \quad (5)$$

where A is VECD model coefficient; $B = 2\alpha$; γ is the applied binder strain (2.5% and 5%).

3 Results and Discussion

3.1 Molecular weight distribution (GPC evaluation)

In this study, the molecular size (MS) was categorized into 7 levels. Table 2 lists the corresponding range of each MS level and the molecular weight distribution of raw asphalt, FT wax and surfactant. It can be seen that the molecular composition of surfactant is more evenly distributed within the molecular size less than 1000 g/mol, while that of FT wax is mainly concentrated in MS5 (2500-1000 g/mol). According to the MS level and MS range summarized in Table 2, the Area% of liquid phases and staged extractions were calculated.

TABLE 2 Molecular weight distribution of raw asphalt and WMA additives

Molecular size (MS) level	Molecular size range (g/mol)	Molecular weight distribution (Area%)		
		Raw asphalt	FT wax	Surfactant
MS1	> 20000	0.85	0	0
MS2	20000 - 10000	2.12	0	0
MS3	10000 - 5000	8.69	0.03	0.08
MS4	5000 - 2500	11.84	2.15	0.36
MS5	2500 - 1000	26.87	88.76	24.13
MS6	1000 - 500	25.10	8.10	38.61
MS7	< 500	20.89	0.96	36.82

1 Figure 3a presents the GPC chromatograms of staged extraction layers from AR of 60-
2 minute mixing duration. As a contrast, the curve of L-AR was also drawn. Obvious change
3 can be observed between the liquid phase and staged extraction layers, referring to their
4 different molecular weight distributions. The liquid phase has a higher curve during 10-14
5 mins but a lower peak at 15.7 mins compared with layer 1-4. It indicates that mixing CRM
6 into virgin asphalt caused a higher large molecule content, but the rubber did not absorb
7 the components from asphalt fraction uniformly. Instead, certain absorption preference
8 existed among components of different molecular sizes during the swelling process of
9 rubber. Figure 4a&4b compares how Percent MS1-MS3 and Percent MS5-MS6 varied in
10 AR from the liquid phase to staged extraction layers. From the outside to inside, Percent
11 MS1-MS3 gradually decreased. By contrast, Percent MS5-MS6 in staged extraction layers
12 were apparently larger than that in the liquid phase. It indicates that the swelling rubber
13 were inclined to absorb components of smaller molecular size. Meanwhile, mixing duration
14 had a more obvious impact on Percent MS1-MS3. AR of 60-minute had more Percent
15 MS1-MS3 than the other mixing duration, both in liquid phase and asphalt-rubber
16 interacting area. This is because when mixing time was inadequate, only a limited portion
17 of large rubber molecules were released into asphalt binder, but excessive mixing time
18 might also lead to the further decomposition of rubber molecules. Besides, the Percent MS4
19 and Percent MS7 of the liquid phase and staged extractions were very similar.

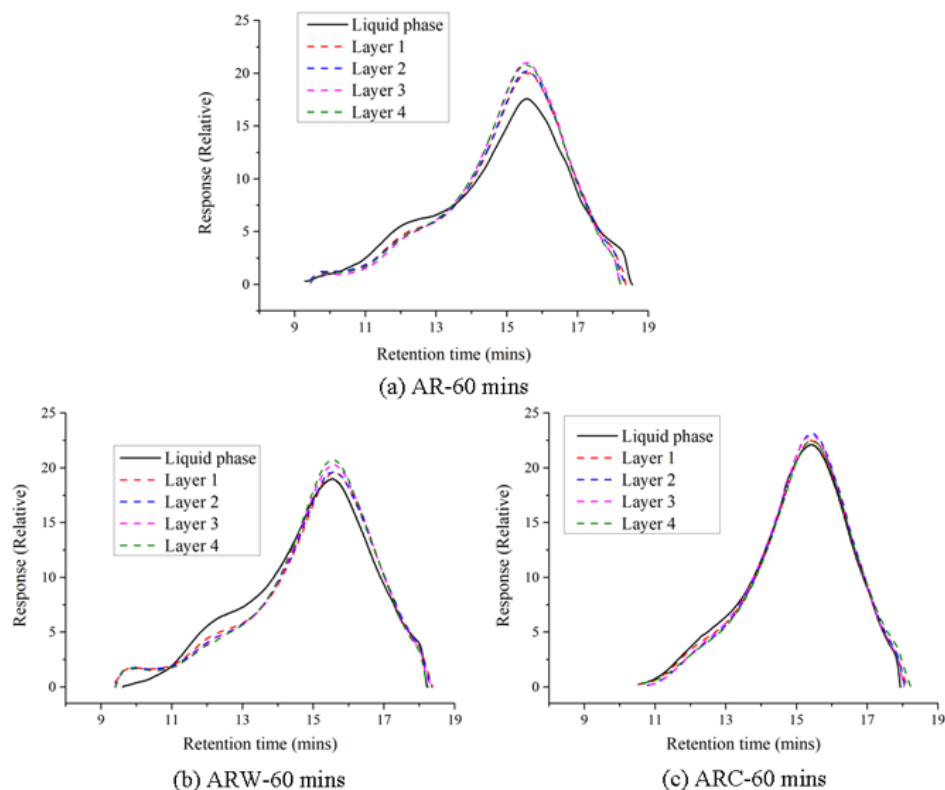


FIGURE 3 Comparison of molecular weight distribution of liquid phase and staged extraction layers

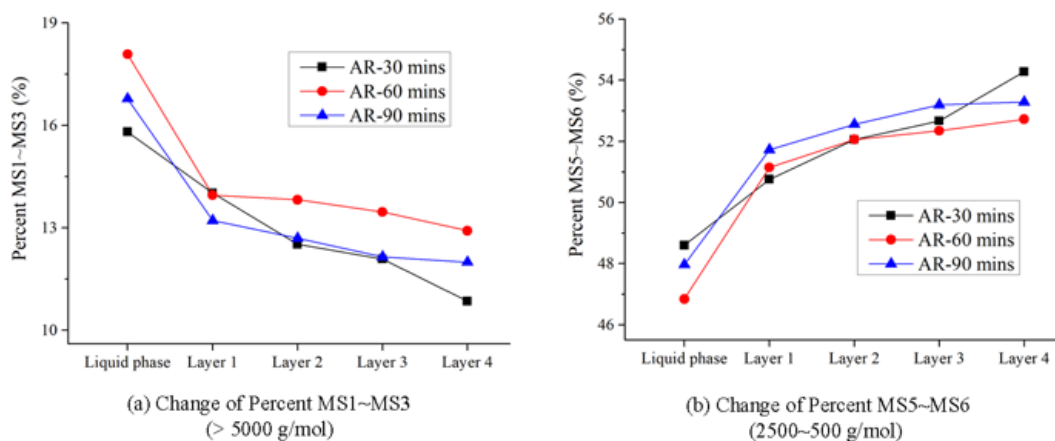


FIGURE 4 Comparison of absorption between different molecular sizes in AR

It can be seen in Figure 3b that the difference between the liquid phase and staged extraction layers in ARW is still detectable. However, it was unexpected that staged extraction layers of ARW had a stronger response than the liquid phase before 11 mins in

1 ARW. One possible explanation is that the incorporation of FT wax created a tendency for
2 molecules larger than 20000 g/mol (MS1) to get into the asphalt-rubber interacting area.
3 Therefore, the decrease of percent MS1 in the liquid phase of AR after adding FT wax may
4 be partially due to the absorption of swelling rubber. Although the Percent MS1 was
5 affected, Figure 5 shows that in ARW the Percent MS2-MS4 decreased sharply and Percent
6 MS6-MS7 increased obviously from the liquid phase to Layer 1, indicating that the
7 absorption preference towards smaller molecules of swelling rubber was still obvious after
8 the addition of FT wax. As for the ARC, Figure 3c shows that the curve of liquid phase is
9 very similar to those of the staged extraction layers. These tiny differences referred to
10 inconspicuous absorption preference, so the swelling rubber could more evenly absorb the
11 substances from asphalt fractions. Additionally, the elution time of ARC was about 10.5
12 mins, which was one minute later than that of AR and ARW. It was because the addition
13 of surfactant significantly decreased the large molecules content by promoting the
14 dissolution of rubber molecules [13]. As a result, the Percent MS1 of ARC were all less
15 than 0.5%. Besides, ARC had a higher peak at 15 mins than AR and ARW. This augment
16 might derive from the components of surfactant and the decomposed rubber molecules.
17 Figure 6 demonstrates that the decreasing trend and amplitude of Percent MS2-MS4 in
18 ARC were smaller than those in AR and ARW, because the large molecule content in
19 asphalt fraction was significantly decreased by the incorporation of surfactant.
20 Consequently, the increasing trend of Percent MS5-MS6 was also alleviated in ARC,
21 which confirms the more evenly absorption of swelling rubber.

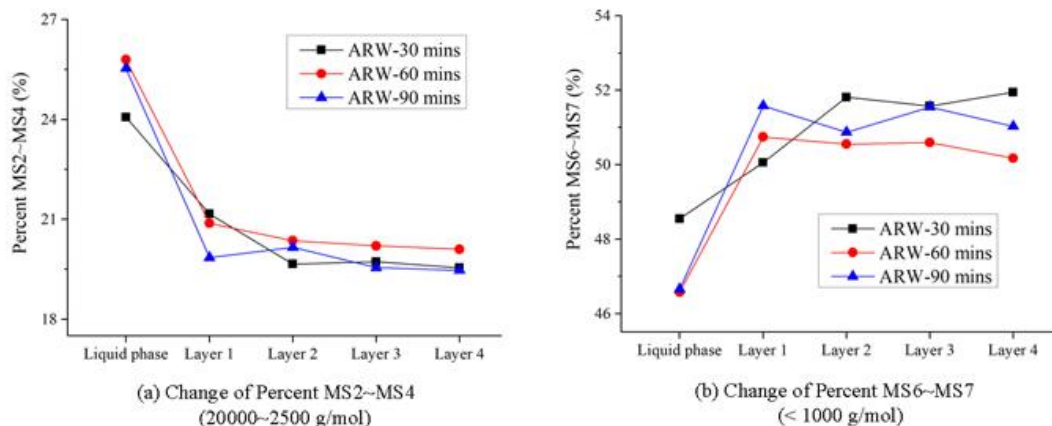


FIGURE 5 Comparison of absorption between different molecular sizes in ARW

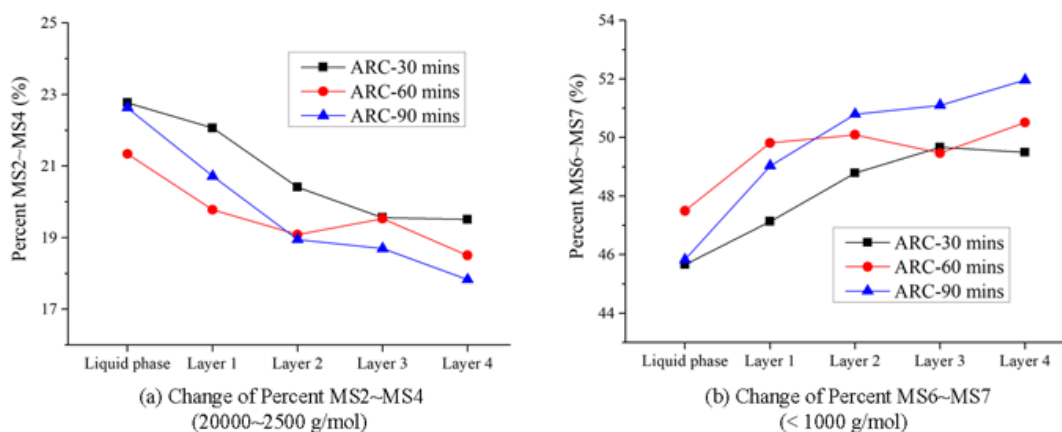


FIGURE 6 Comparison of absorption between different molecular sizes in ARC

3.2 Functional group distribution (FTIR evaluation)

The FTIR spectra of base binder, liquid phases of AR and WARs were drawn to evaluate the change of functional group after the mixing process. Meanwhile, Pen60/70s after short-term aging in RTFO and long-term aging in pressure aging vessel (PAV) were also tested by FTIR as a comparison to the oxidation degree happened during the production of AR and WARs. As shown in Figure 7, carbonyl peak shows up at 1700 cm^{-1} in RTFO aged and PAV aged Pen60/70 compared to the unaged status. Besides, no obvious peak can be detected around 1700 cm^{-1} in L-AR and L-WARs. The increase of carbonyl band indicated

1 the occurrence of oxidation during the aging process where the oxygen was introduced into
2 the unsaturated carbon chain [33]. Table 3 shows the calculated carbonyl index of different
3 samples. It is noted that the carbonyl index of PAV aged Pen60/70 (26.50) is obviously
4 larger than that of RTFO aged Pen60/70 (10.92). By further comparing the carbonyl
5 indexes of L-AR, L-ARW and Pen60/70, it can be deduced that only minor oxidation
6 generated during the mixing of rubber and asphalt. However, Figure 7 shows that a peak
7 was generated at 1270 cm^{-1} in L-AR attributed to the asymmetric stretching of C-O single
8 bond [34,35]. The C-O stretching around $1260\text{-}1270\text{ cm}^{-1}$ is the indicia for ester compounds,
9 which was reported to occur during the oxidative process of elastomer like rubber [36].
10 Furthermore, none of Pen60/70 in different aging statuses shows the sign of C-O peak.
11 Thus, it can be inferred that certain oxidation has taken place on rubber during the high-
12 temperature mixing with asphalt, and the produced oxidative polymers containing C-O
13 single bond were released into asphalt binder. The addition of C-O bond may contribute to
14 why L-AR has higher large molecule content. On the other hand, L-ARW showed a similar
15 spectrum to L-AR, which means the incorporation of FT wax did not affect the generation
16 of the C-O bond. Relatively, L-ARC had no sign of C-O single bond or C=O bond,
17 corresponding to the fact that surfactant could decrease the large molecule content of AR.
18 Therefore, one possible explanation is that mixing surfactant probably promoted the
19 dissolution of such polymers, which restrained the formation of the C-O peak in asphalt
20 fraction. It should be noted that the large carbonyl indexes of ARC did not represent a
21 serious oxidation degree, since the calculation was affected by the strong band at about
22 1655 cm^{-1} , which was caused by the fatty acid esters or lipids components in surfactant
23 [23].

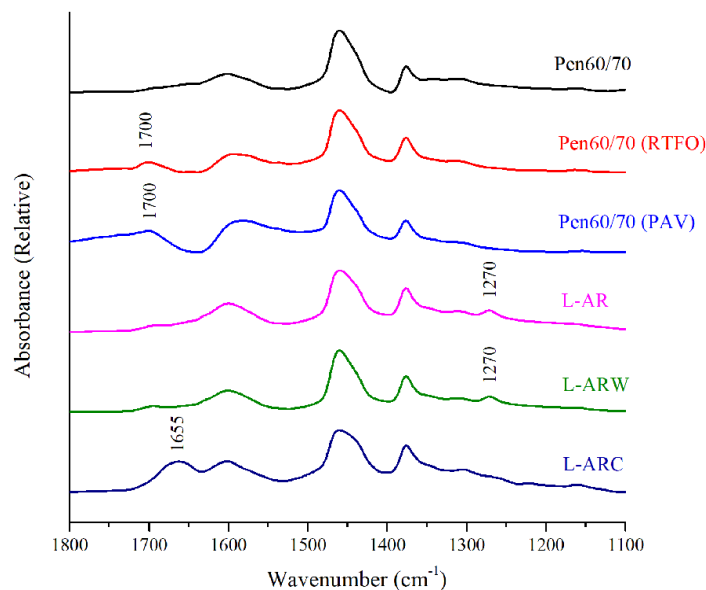


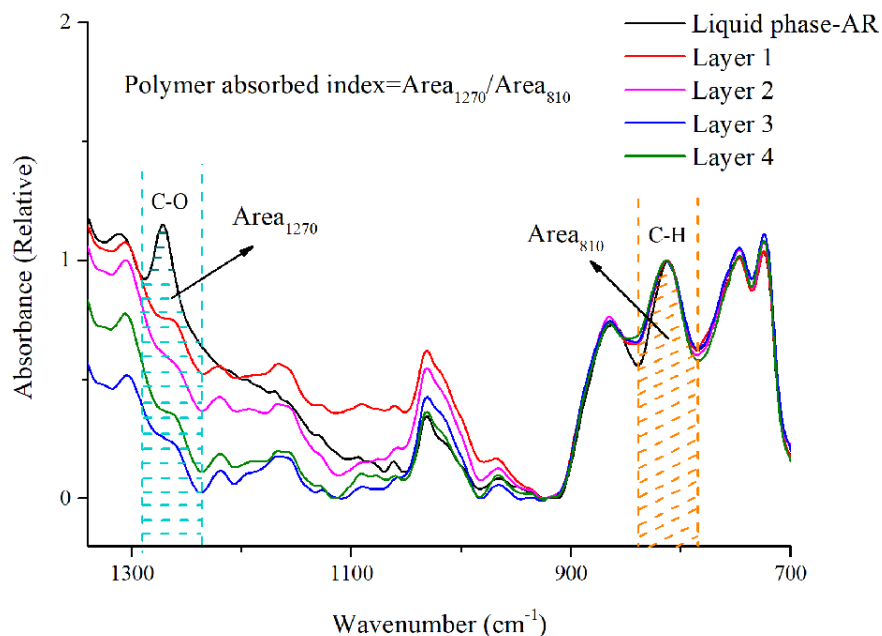
FIGURE 7 FTIR spectra of Pen60/70 (different aging statuses), L-AR, L-ARW and L-ARC (Each absorbance is vertical shifted for comparison)

TABLE 3 Carbonyl index of each sample

Binder type	Carbonyl index (%)					
	Blending time			Aging status		
	30 min	60 min	90 min	Unaged	RTFO	PAV
Pen60/70	N/A	N/A	N/A	5.10	10.92	26.50
AR	5.79	7.05	11.45	N/A		
ARW	5.52	7.17	8.40			
ARC	20.22	16.03	11.47			

The GPC results above found out that rubber has a less absorption preference towards large molecules. To validate this assumption, the PAI index (Equation 1) was adopted to characterize the content of large molecule polymer absorbed into the asphalt-rubber interacting area. Figure 8 shows the band areas between 1290-1235 cm^{-1} and 840-785 cm^{-1} used in the calculation of PAI. The Peak at 810 cm^{-1} was attributed by the C-H out of plane bending of aromatics, whose Area₈₁₀ was found to be very stable and has also been used as reference peak in the quantitative study of high-cured CRM asphalt and SBS modified asphalt [37]. It can be seen that the C-O peak was prominent in L-AR but quite

- 1 obscure in staged extraction layers, which indicated that the polymers containing C-O bond
- 2 were not completely absorbed into asphalt-rubber interacting area.



3

4 **FIGURE 8 Illustration of the calculation of PAI**

5 A decreasing trend of PAI can be seen in Figure 9a, describing the repellency of the rubber

6 to the absorption of such polymers containing C-O bond. Meanwhile, the PAI in liquid

7 phase increased with the mixing time, which means longer mixing duration generated more

8 polymers containing C-O bond in the asphalt fractions. Figure 9b shows the PAI also

9 decreases in ARW from liquid phase to staged extraction layers, so mixing FT wax into

10 AR did not affect the absorption of such polymers. The reduction of PAI in AR and ARW

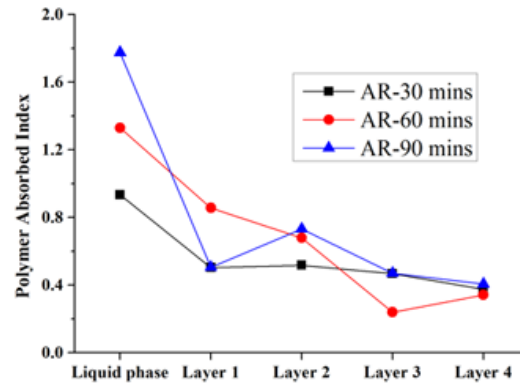
11 might correspond to the decreasing trend of absorbed large molecule content shown in GPC

12 results. Besides, the different mixing durations didn't change the absorption preference of

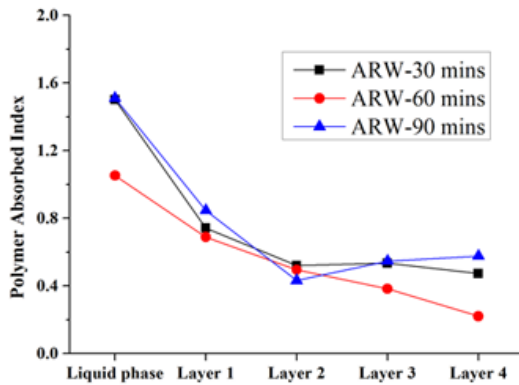
13 swelling rubber. Finally, Figure 9c shows an unstable change trend of PAI in ARC, because

14 the incorporation of surfactant restrained the formation of C-O bond in asphalt fraction.

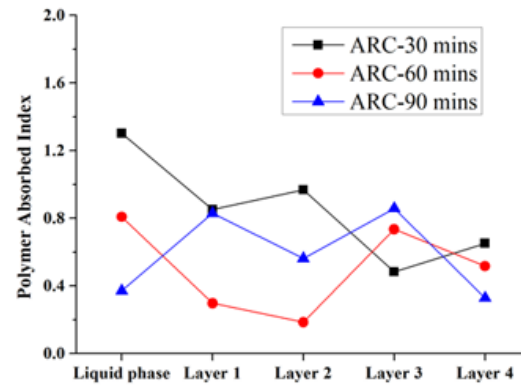
- 1 Therefore, the absorption reluctance of swelling rubber towards polymers containing C-O
- 2 bond disappeared, resulting in a more uniform absorption.



(a) AR



(b) ARW



(c) ARC

3

4 **FIGURE 9 The variation of PAI from liquid phase to staged extraction layers**

5 **3.3 Analysis on the relationship between absorption preference and rheological**

6 **properties**

7 Figure 10a shows the J_{nr} of AR/WARs and their liquid phases at the stress level of 3.2 kPa.

8 The lower the J_{nr} , the better the rutting resistance. It can be seen that the J_{nr} of AR was

9 much smaller than that of the Pen60/70, representing a great improvement in rutting

10 resistance of base asphalt after mixed with CRM. By contrast, the J_{nr} of L-AR was larger

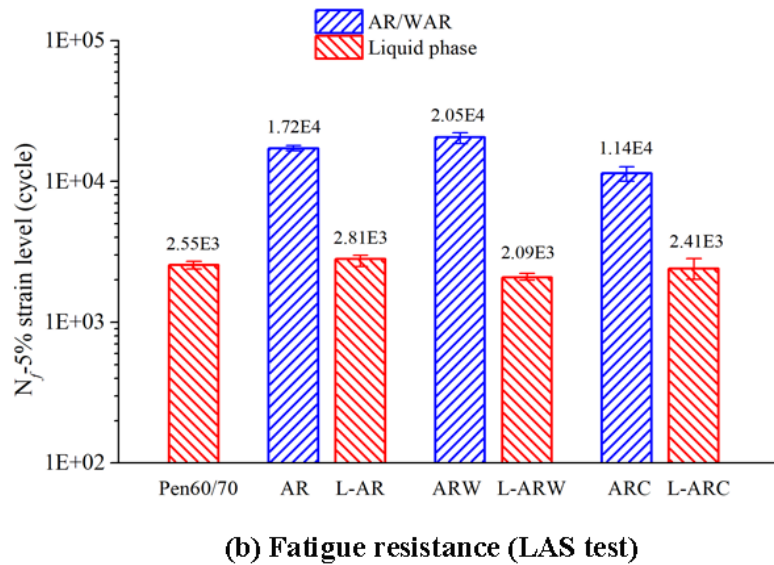
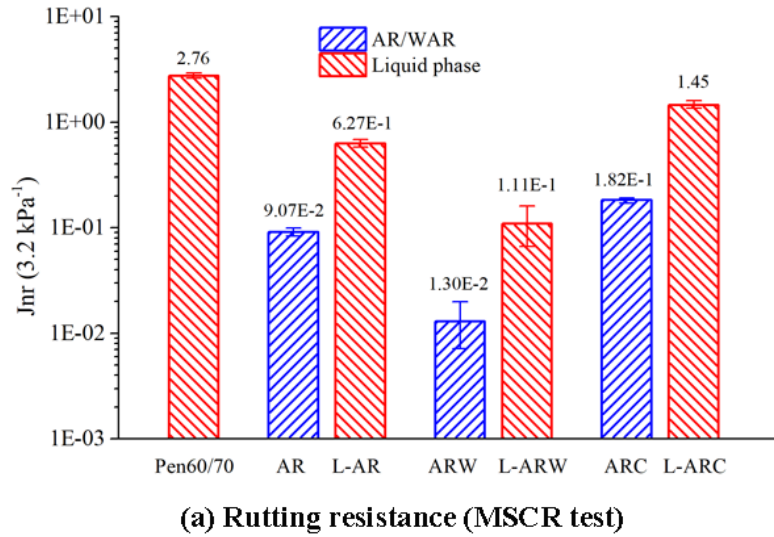
11 than that of AR but smaller than Pen60/70. Such difference should be discussed from two

12 different angles: (i) the removal of swelling rubber caused the reduction of rutting

1 resistance, because the swelling rubber acting as resilient filler could enhance the binder
2 modulus at high temperature; (ii) L-AR still exhibited better rutting resistance than
3 Pen60/70, since part of CRM components were dissolved into the asphalt fraction, which
4 modifies the base asphalt like SBS [38]. Combined with the findings from chemical tests,
5 a deduction could be made that the generation of polymers containing C-O bond partially
6 increased the large molecule content in asphalt fraction. Meanwhile, the swelling rubber
7 had stronger absorption preference towards the smaller size molecules, so more large
8 molecules were retained in asphalt fraction. The change in molecular weight distribution
9 of asphalt binder fraction led to stronger viscosity and rutting resistance of L-AR.
10 Therefore, a more viscous asphalt fraction could interact with swelling rubber to endow
11 the whole working system of AR with greater tenacity and stiffness, further improving its
12 rutting resistance.

13 Additionally, Figure 10a shows that ARW and L-ARW exhibited better high-temperature
14 performance than AR and L-AR, respectively. On the one hand, chemical tests indicated
15 that adding FT wax didn't affect the generation of polymers with C-O bond or the
16 absorption preference of swelling rubber. On the other hand, FT wax is known as a kind of
17 anti-rutting agent [39]. Therefore, not only the interaction between asphalt fraction and
18 swelling rubber, but also the physical property of FT wax contributed to a better rutting
19 resistance. By comparison, the J_{nr} of L-ARC is slightly smaller than that of Pen60/70 but
20 larger than that of L-AR and L-ARW. The decline in the high-temperature performance of
21 L-ARC may be due to the loss of the large molecule polymers when chemical surfactant
22 was added. With reduced large molecule content, the swelling rubber could absorb the
23 asphalt fraction more evenly. Thus, the swelling behavior of swelling rubber could not

- 1 affect the molecular weight distribution of asphalt liquid phase, resulting in the worse
- 2 rutting resistance of ARC compared to AR.



- 3
- 4 **FIGURE 10 Comparison of rheological properties between AR/WARs and their**
- 5 **liquid phases**
- 6 The fatigue resistance of AR/WARs and their liquid phases are presented by N_f at 5% strain
- 7 level in Figure 10b. A larger N_f value represents a longer fatigue life. When the swelling
- 8 rubbers were separated, the N_f of Pen60/70, L-AR, L-ARW and L-ARC were very close to
- 9 each other. It indicates the dissolution of CRM and WMA additives didn't improve the

fatigue resistance. Therefore, the relationship between the fatigue performance and chemical test results of liquid phases was difficult to find. However, it can be found out that the N_f of binder containing swelling rubber (AR, ARW, ARC) are much larger. The enhanced fatigue resistance of AR/WARs was mainly contributed by the filling effect of swelling rubber. Further studies should be conducted to analyze how the absorption behaviors of swelling rubber affect its filling effect.

4 Findings and Recommendations

In this study, the swelling rubber in AR and two kinds of WAR were first separated from their asphalt liquid phase, then processed by an improved staged extraction method to divide the rubber-asphalt interacting area into four layers. The selective absorption of swelling rubber and its influence on the rheological properties were investigated by a series of chemical and rheological methods. The following findings can be concluded:

- The GPC tests reflected that the components with small molecular weight were easier to be absorbed into the rubber-asphalt interacting area than those of large molecular weight.
- The FTIR results showed that certain oxidation occurred on rubber during the mixing process, which released polymers with C-O peak in asphalt binder fraction. The polymer absorbed index indicated that swelling rubber had limited absorption preference for such polymers.
- The incorporation of FT wax had a negligible influence on the absorption preference of swelling rubber. However, chemical surfactant significantly decreased the large molecule content and prevented the formation of C-O bond, so the absorption of swelling rubber was more evenly in ARC.

- The absorption preference contributed to a better interaction between swelling rubber and asphalt binder fraction, which positively affected the rutting resistance. However, the relationship between absorption preference and fatigue resistance was hard to build in this study.

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