

1 Thermal analysis on the component interaction of asphalt 2 binders modified with crumb rubber and warm mix additives

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4 **ABSTRACT:** This study investigated the interaction among different components of
5 asphalt binders collectively modified with crumb rubber and warm mix additives through
6 thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC) testing.
7 The modified binders were divided into two parts for analysis purpose, namely the
8 extracted crumb rubber modifier (CRM) by removing all asphalt components and the
9 separated asphalt system by removing insoluble CRM particles. The main findings of this
10 study include that: (1) the interaction between CRM and base asphalt was a component
11 exchange process, i.e., natural rubber and styrene-butadiene rubber were released from
12 CRM and blended with asphalt molecules; (2) wax-based warm mix additives penetrated
13 into CRM during the mixing process; and (3) the incorporation of warm mix additives,
14 especially the wax-based additives, promoted the component exchange between rubber and
15 asphalt.

16 **Keywords:** Thermal analysis; Interaction mechanism; Asphalt rubber; Warm mix additive

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17 1. INTRODUCTION

18 Recycling waste tyre rubber into asphalt pavement is a sustainable technology that not only
19 enhances the engineering performance but also reduces tyre-road noise of asphalt pavement
20 (1, 2, 3). The performance of the waste tyre rubber or crumb rubber modifier (CRM)
21 modified asphalt is affected by various factors, such as base asphalt properties, mixing
22 conditions, rubber size and rubber content. Those asphalt binders modified with no less
23 than 15% of crumb rubber are usually named asphalt rubber (AR) (4). Many studies have
24 reported that AR provides better rutting, cracking and fatigue resistance than its
25 corresponding base asphalt (2, 5), mainly due to the effect of rubber on reducing the
26 temperature dependence of binder viscosity. However, due to the high viscous behavior,
27 AR mixtures have to be paved at higher temperature than conventional mixtures, resulting
28 in higher energy consumption and compromised working environment (5, 6).

29 Recently, various warm-mix asphalt (WMA) additives have been developed and applied to
30 improve the workability of high-viscosity asphalt binders like AR (7, 8, 9). WMA additives
31 can be generally classified into three categories: foaming additives, organic additives and
32 chemical additives. Foaming additives improve the workability of asphalt binder by causing
33 volume expansion of asphalt, while organic additives and chemical additives achieve this
34 goal by decreasing the viscosity of asphalt and acting as a surfactant at the asphalt-
35 aggregate interface, respectively (8, 10). The incorporation of WMA additives, especially
36 organic and chemical additives, affects the rheological properties of asphalt binder, since
37 the additives may physically or chemically interact with the components in asphalt binder.
38 For AR binders, the situation becomes more complicated as WMA additives may also
39 affect the interaction between base asphalt and CRM.

40 Numerous studies have been conducted to investigate the effects of various non-foaming
41 WMA additives on AR binder's rheological properties (7, 11, 12). However, very few of
42 them have looked into the interaction mechanism of different components within warm AR
43 binders, which explains the rheological behaviors of warm AR binders. To help fill this gap,
44 this study aims to investigate the interaction among WMA additives, crumb rubber and
45 base asphalt through analyzing their thermal behaviors before and after the blending
46 process. To achieve this objective, three types of WMA additives, namely Sasobit
47 (commercial organic additive), Evotherm-DAT (commercial chemical additive), and 56#
48 paraffin wax (organic additive), were used to prepare warm AR binders, and these binders
49 were denoted as ARS, ARE, and ARW, respectively, for easy reference. Then, these warm
50 AR binders were separated into two parts: the extracted CRM by removing asphalt
51 components and the rheological asphalt system by removing insoluble CRM particles.
52 Finally, the thermal behaviors of both parts were analyzed through thermo-gravimetric
53 analysis (TGA) and differential scanning calorimeter (DSC) testing, and the decomposition,
54 fusion and crystallization temperatures were determined as the fingerprints of various
55 components in crumb rubber and asphalt binders, providing both qualitative and
56 quantitative information on the interaction of CRM with base asphalt and WMA additives.

57 2 EXPERIMENTAL PROGRAM

58 2.1 Materials

59 The AR binder used in this study was prepared by blending 18% of 40 mesh (0.425 mm)
60 crumb rubber by the total weight of AR with the penetration grade 60/70 base asphalt using
61 a high shear mixer. The mixing was conducted at 176 °C for one hour at a shear rate of

62 4000 rpm. The WMA additive (Evotherm-DAT, Sasobit, or 56[#] paraffin) was added to AR
63 immediately afterwards by 10 minutes of high shear mixing. The percentages of Evotherm-
64 DAT, Sasobit, and 56[#] paraffin were 5%, 3% and 1.5%, respectively, by weight of AR,
65 based on the manufactures' recommendations and preliminary test results. The properties of
66 each WMA additive are shown in Table 1, and the rheological test results of the prepared
67 AR binders are shown in Table 2.

68 From Table 2, it can be observed that compared to base asphalt, AR provides better rutting,
69 fatigue and low-temperature cracking resistance, which is consistent with the results of
70 previous studies (2, 4, 7). All WMA additives were effective in enhancing the workability
71 of AR, but their effects on its rheological properties varied. All WMA additives negatively
72 affected the low-temperature cracking resistance and fatigue performance of AR, while
73 Sasobit was the only WMA additive improving the rutting resistance of AR. It is also
74 interesting to notice that paraffin wax had only minor negative effect on low-temperature
75 performance of AR, although the crystallizing wax has been reported to increase the
76 potential of plastic deformation or cracking (13, 14, 15).

77 *2.2 Separation of rheological asphalt system*

78 All WMA additives can be completely dissolved in asphalt while CRM remains in small
79 particulate form after interaction. As a result, AR and warm AR binders can be separated
80 into two parts: the rheological asphalt system and the insoluble CRM particles, through
81 physical and chemical separation (Figure 1). To obtain the asphalt systems, the AR and
82 warm AR binders were filtered through a 400 mesh (0.0374mm) sieve at 176 °C and 160 °C,
83 respectively, for three times to remove the residual granules. The filterable components
84 were kept and labeled as separated asphalt binders for DSC and TGA tests.

85 2.3 CRM extraction

86 To compare the components and properties of CRM before and after interaction, CRM
87 particles inside modified binders were extracted by removing asphalt components using a
88 chemical method, which is similar to that applied by Ghavibazoo and Abdelrahman (16).
89 Each warm AR binder was first mixed with an organic solvent (weight ratio of 1:10 for
90 asphalt and solvent) for one hour and then the black solution was filtered through a 200
91 mesh (0.075mm) sieve. The CRM particles remaining on the sieve were further washed
92 with extra organic solvent several times until the filtrate became colorless. Finally, the
93 washed CRM particles were kept in an oven at 150 °C for 12 hours before thermal tests.
94 Three different solvents were applied for rubber extraction, including trichloroethylene
95 (TCE), tetrahydrofuran (THF) and n-Heptane. TCE and THF have been commonly used to
96 dissolve asphalt, and they both can completely remove all asphalt components from rubber
97 particles. In comparison, n-Heptane is able to dissolve saturates, aromatics and resins, but
98 not asphaltene, which contains the heaviest and most complicated molecules of asphalt (17).
99 Different solvents were used for two purposes: 1) verifying test results; and 2) assessing
100 whether there is any interaction between rubber and asphaltene during the mixing process.

101 2.4 TGA and DSC analysis

102 The thermal analysis was conducted using the Netzch TGA/DSC, which has a working
103 temperature range of 25 °C to 1500 °C. The heating rate was controlled at 20 °C/min with a
104 maximum temperature of 600 °C. High-purity nitrogen ambient gas was applied at a flow
105 rate of 500 ml/min. During the pyrolysis process (heating without oxygen), the organic
106 volatile substances of polymers were decomposed to low molecular weight products,

107 liquids or gases. 10-20mg of separated asphalt binder or extracted CRM was used for each
108 test, and three replicates were prepared and tested for each type of binder. The original
109 CRM was washed by clean water to remove impurities.

110 The TGA tests were conducted to investigate the thermal decomposition pattern of the test
111 samples and difference between each of its main components. In these tests, the
112 decomposition temperature of each component was its fingerprint (18, 19, 20). TG curves
113 describing the relationship between the mass of test sample and temperature can be
114 obtained from the TGA tests. In this study, the initial decomposition temperature, i.e., the
115 temperature corresponding to 1% mass loss, the temperature range for main decomposition,
116 and the final residual mass were recorded for analysis (21).

117 The DSC tests were conducted to determine the thermal transition temperatures of asphalt
118 and crumb rubber (22, 23, 24, 25). In these tests, the heat flows of the testing materials
119 were monitored and compared to those of the reference sample (an empty aluminum pan in
120 this study). As the pressure in the DSC chamber was kept constant, the change in heat flow
121 is equivalent to the enthalpy change. The heat flow difference between the testing material
122 and the reference sample can be either positive or negative. An endothermic process
123 implies that the heat flow to the sample is higher than that to the reference, which is
124 attributable to polymer melting or decomposition reactions; while an exothermic process
125 indicates the opposite, which is caused by fusion or crystallization, cross-linking and
126 oxidation reaction.

127

128 3 RESULTS AND DISSUSSION

129 *3.1 Thermal behavior of raw materials*

130 Figure 2(a) shows the TG and DSC curves of the original crumb rubber. The TG curve
131 exhibits two main regions of weight loss: 100-130 °C and 300-500 °C, while the DSC curve
132 shows three main endotherms and one exotherm. These thermal features are caused by the
133 components in the CRM sample, including natural rubber (NR), synthetic rubber (SR) and
134 minor constituents of oil, plasticizer and water. The first mass loss and endothermic peak
135 are due to the evaporation of water, followed by the decomposition of oil, plasticizer and
136 other additives at lower temperature range (<300 °C). As the temperature was further raised
137 to above 300 °C, two peaks can be noticed at 329 °C and 410 °C in the DSC curve, which is
138 attributable to the degradation of NR and SR, respectively (26, 27, 28).

139 Figure 2(b) illustrates the thermal behavior of base asphalt. It can be noticed that the base
140 asphalt and CRM have similar temperature range for main decomposition (approximately
141 300 °C to 500 °C), indicating limited effect of incorporating CRM on the thermal stability
142 of base asphalt. The DSC curve of base asphalt shows a large exothermic peak from 97 °C
143 to 361 °C, which cannot be observed in that of CRM. However, since the DSC curve of
144 asphalt is quite complicated due to the overlapping (14), additional thermal tests were
145 conducted on the four fractions of base asphalt, i.e., saturate, aromatic, resin and asphaltene
146 (SARA).

147 Figure 3 shows the test results and typical molecular structures of each fraction. It can be
148 seen that the initial decomposition temperatures and residue mass percentages of the four
149 fractions successively increase from saturate to asphaltene. In other words, the heavier the
150 fraction, the more final residual mass and hence more stable thermal behavior (20). Similar

151 to the DSC curve of base asphalt, broad exothermal peaks also occur in those of aromatic,
152 saturate and resin, indicating that this exothermal behavior of asphalt is mainly caused by
153 its lighter components. One possible explanation of the exothermal process is the cross-
154 linking or chemical degradation of polymeric components. From the molecular perspective,
155 saturate and aromatic fractions contain naphthenic cycles with low molecular weight and low
156 polarity while resin contains more cyclic structures connected by aliphatic bridges (29).
157 Those side chains of ring structures are easily broken at high temperature and then
158 reconstructed to more stable heteroatoms with larger molecular mass. In comparison,
159 asphaltene is much more thermally stable, because its molecular structure mainly consists
160 of polyaromatic long carbon rings with various heteroatoms and trace amounts of heavy
161 metals like vanadium and nickel (30, 31). As a result, the decomposition of base asphalt
162 should happen within two main temperature ranges, lower than 400 °C and 400-550 °C, due
163 to the volatilization of the maltenes, such as saturates, aromatics and apolar agents from
164 resins, and the thermal decomposition of asphaltenes, and residual saturates, aromatics and
165 resins, respectively.

166 *3.2 Interaction between asphalt and CRM*

167 Figure 4 shows the TG and DSC curves of the extracted CRM when different solvents, i.e.,
168 TCE, THF and n-heptane, were used. It can be seen that the three TG curves are very close
169 to each other and the peaks in the three DSC curves occur at almost the same positions.
170 This indicates that the effect of solvent on the test results is insignificant. As
171 aforementioned, TCE and THF can completely dissolve base asphalt while n-heptane
172 cannot dissolve asphaltene. Thus, the testing results show no evidence on the penetration of

173 asphaltene into CRM or bonding of asphaltene to CRM surface during the CRM-asphalt
174 interaction.

175 Compared to the original CRM, the extracted CRM shows a similar pattern in the TG curve
176 but a different shape in the DSC curve. The main weight loss of the extracted CRM still
177 occurs from 300 °C to 500 °C. However, the final residual mass percentage of the extracted
178 CRM (about 26 wt%) is higher than that of the original CRM (17 wt%), indicating that the
179 interaction of rubber with base asphalt may have consumed part of the decomposable
180 polymers. Similar findings can also be observed from the DSC testing results. The DSC
181 curve of the original CRM has two clear endothermic peaks from 300 °C to 500 °C, while
182 the extracted CRM only has one, indicating that the components in the original CRM is
183 more complicated. It has been reported that the peak within the range of 300 °C to 400 °C is
184 due to the NR component of CRM while the one within the range of 400 °C to 500 °C is
185 related to the SR (16, 26). Thus, the interaction between CRM and asphalt has caused the
186 dissolution of NR in asphalt during the mixing process, which positively affects the
187 rheological properties of asphalt.

188 The thermal behaviors of the separated rheological asphalt system also demonstrate that
189 there is interaction between base asphalt and CRM (Figure 5). No exothermic peak was
190 noticed between 97.1 °C and 361 °C in the DSC curve of the separated asphalt, indicating
191 fewer unstable fractions, such as saturate and aromatic, exist in the modified asphalt.
192 Besides, the final residual mass of the separated asphalt system from AR is nearly 9%
193 larger than that of base asphalt, implying more heavy fractions in the binder system.

194 The thermal analysis results are consistent with the findings on the interaction between
195 asphalt and CRM using other analysis techniques (32, 33). Polymer with high molecular

196 weight from CRM, such NR and SR, are released and mixed with the components of base
197 asphalt. The released large molecules enhance the rigidity of the network structure formed
198 by asphalt molecules, leading to larger complex modulus (G^*) and higher stiffness of
199 modified asphalt. Meanwhile, the more flowable components of base asphalt (saturates and
200 aromatics) penetrate into CRM, filling up the micro pores or voids left by NR and SR. In
201 this case, the percentage of heavy portions in asphalt system (mainly asphaltene) increases,
202 and the strong attractive interactions among the asphaltene particles lead to dramatically
203 increased viscosity of asphalt (34).

204 *3.3 Effects of warm mix additives on CRM*

205 Figure 6 shows the thermal analysis results of the CRM samples extracted from warm AR
206 binders. For brevity, only the results of the CRM extracted by TCE are presented in this
207 paper, as similar curves were obtained when different solvents were used. It can be seen
208 that when the temperature is lower than 150 °C (the temperature at which the extracted
209 CRM had been preserved for 12 hours), there are exothermic peaks for the CRM extracted
210 from ARS and ARW, but no obvious mass loss can be observed. According to the thermal
211 test results in Sections 3.1 and 3.2, neither asphalt nor rubber components exhibit
212 exothermal behavior at this location. Thus, the exothermic peaks at this location should be
213 the indicators of the crystallization of n-alkanes from wax-based WMA additives (14). In
214 other words, n-alkanes from the wax-based additives, i.e., Sasobit and 56[#] paraffin wax, not
215 only interact with asphalt components but also penetrate into CRM particles. In addition,
216 the heat capacity variation of 56[#] paraffin wax was found to be more significant than that of
217 the Sasobit according to the DSC results. The relatively poor heat capacity of wax leads to

218 poor temperature stability of asphalt with high wax content. As a result, the low-
219 temperature cracking resistance of the ARW is the worst among the three warm ARs.

220 The TG curves illustrate that the CRM from ARW has more oily components than the
221 others (nearly 5.4% of mass loss before 300 °C), which may be attributed to the penetration
222 of some oily components of paraffin wax into the CRM during the mixing process. In
223 comparison, Sasobit had little effect on the oily component ratio of CRM. This difference
224 may be caused by the different preparation techniques of these two additives. It has been
225 reported that the carbon chain in Sasobit is much longer than that in regular wax, which
226 leads to a higher melting point and better temperature stability (35). The chemical additive,
227 Evotherm-DAT, showed insignificant effect on the exothermic and endothermic behaviors
228 of the extracted CRM. One possible reason is that some light components had already
229 evaporated during the mixing process, and the residual surfactant was evenly dispersed
230 among the carbon chains of base asphalt without penetrating into CRM. However, it may
231 also be ascribed to the dissolving effect of the organic solvents, which desires further
232 investigation.

233 Table 3 summarizes the percentages of different components in the extracted CRMs from
234 AR, ARE, ARS, ARW and AR2 (same as AR, but with longer (70 minutes) mixing time).
235 It can be seen that the component concentrations in AR and AR2 are very close to each
236 other, indicating that the rubber has almost reached the maximum dissolution level under
237 the mixing condition adopted in this study. In comparison, the NR and SR contents of the
238 CRM from warm ARs are lower than those of the CRM extracted from AR, possibly due to
239 the mixing condition. The dissolution level of CRM also varied obviously among different
240 warm ARs. It seems that SR is easier to be released from CRM in less viscous asphalt,

241 especially when wax-based additives are used. As a result, incorporation of WMA additives
242 at an earlier stage may result in better reaction between crumb rubber and base asphalt.

243 *3.4 Effects of warm mix additives on rheological asphalt systems*

244 Figure 7 illustrates the DSC and TG results of the separated asphalt systems from warm AR
245 binders. The main characteristics of the TG and DSC curves of the separated asphalt
246 systems, including the initial decomposing temperature (T_i), the temperature corresponding
247 to the maximum mass loss rate (T_m), the final residue mass ratio (M_f) and the temperatures
248 corresponding to endothermic (T_{en}) and exothermic (T_{ex}) peaks, are listed in Table 4.
249 Similar to the base asphalt and the separated asphalt system from AR, the separated asphalt
250 systems from warm AR binders in general show endothermic trends in the their DSC heat
251 flow curves due to the melting and vitalization of asphalt fractions and additive components.
252 The TG curves indicate that the final residual mass ratios of the three separated asphalt
253 systems from WARs are also much the same, and slightly smaller than that from AR.
254 Among the three samples, those from ARS and ARW show similar patterns in DSC and TG
255 curves, while distinct difference can be observed on that from ARE. The sample from ARE
256 exhibits lower initial decomposing temperature and two obvious exothermic peaks before
257 400 °C. In addition, the peak at 340.2 °C does not occur in any other asphalt samples. These
258 two exothermic peaks are believed to be caused by Evotherm-DAT. Although part of
259 Evotherm-DAT evaporated during the mixing process, the remaining chemical agents still
260 affect the thermal behavior of the asphalt system.

261 4. CONCLUSIONS

262 In this study, thermal analyses were conducted to investigate the interaction mechanism of
263 different components in warm AR binders. Specifically, TGA and DSC tests were
264 performed to characterize the pyrolysis and reaction mechanisms of the extracted CRMs
265 and separated asphalt systems from hot and warm AR binders. The following points
266 summarize the main findings of this study:

- 267 · The four asphalt components, SARA, have significantly different thermal behaviors.
- 268 · The interaction between CRM and asphalt affects the composition of the extracted
269 CRM from AR. NR in CRM is easier to be released and mixed with asphalt
270 molecules than SR.
- 271 · Asphaltene does not penetrate into CRM during the AR mixing process.
- 272 · Wax-based WMA additives penetrate into CRM during the mixing process of warm
273 AR, but the conventional wax with shorter carbon chain interacts more easily with
274 CRM than the commercial wax-type additive, Sasobit.
- 275 · The incorporation of WMA additives, especially wax-based additives, promotes the
276 interaction between CRM and base asphalt.

277 This study has proven that thermal analysis has high potential to be used as an effective tool
278 to investigate the interaction mechanism between asphalt and various modifiers. Further
279 study is recommended on developing quantitative relationship models between the thermal
280 test results and the rheological properties of modified asphalt.

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378 LIST OF FIGURES AND TABLES

379 *Figures*

380 Figure 1 Sample preparation process

381 Figure 2 DSC and TG curves of original CRM and base asphalt: (a) CRM (b) base binder

382 Figure 3 Thermal behavior of different fractions from base asphalt

383 Figure 4 DSC and TG curves of extracted CRM by different solvents

384 Figure 5 DSC and TG curves of separated asphalt from AR

385 Figure 6 Thermal test results of extracted CRM from warm AR binders

386 Figure 7 Thermal test results of separated asphalt systems from warm AR binders

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388 *Tables*

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391 Table 3. Component concentrations of extracted CRM samples from AR and warm ARs

392 Table 4. Main features in separated binder thermal behavior

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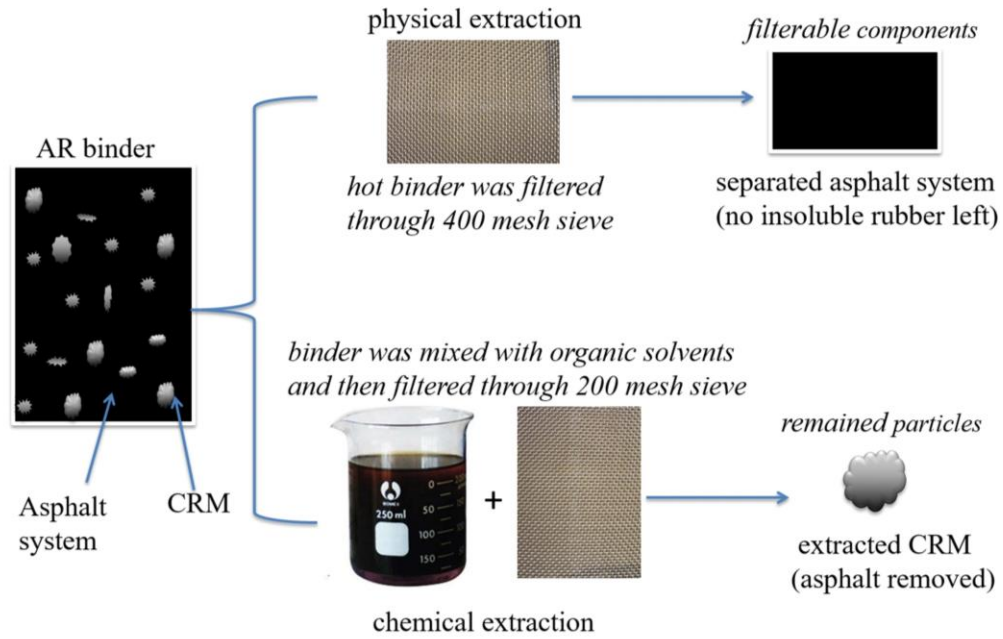
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Figure 1 Sample preparation process

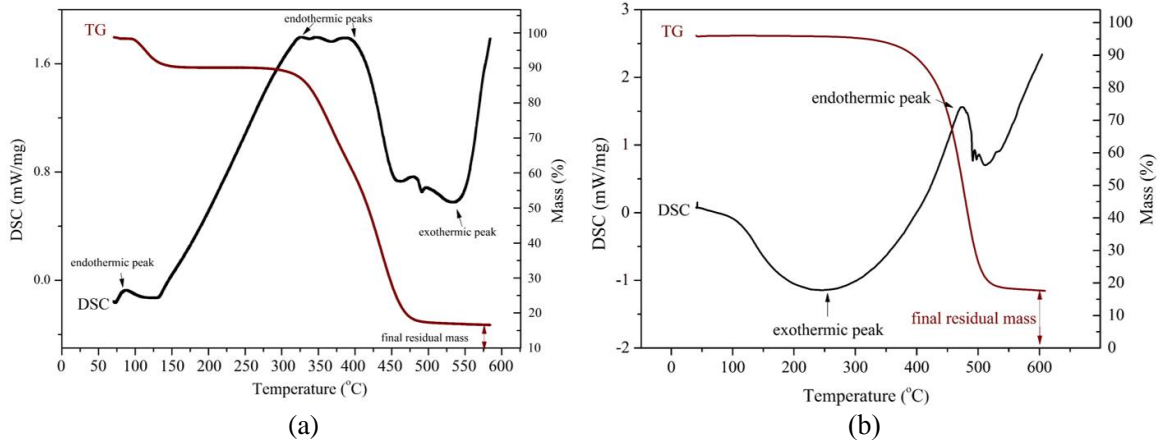
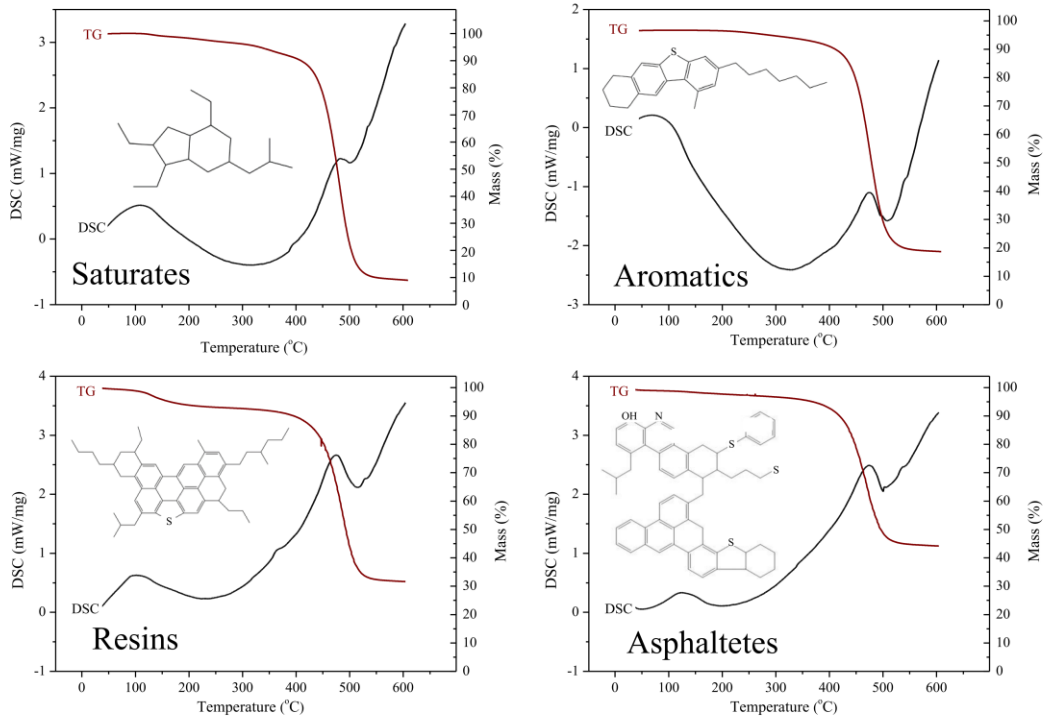


Figure 2 DSC and TG curves of original CRM and base asphalt: (a) CRM (b) base binder

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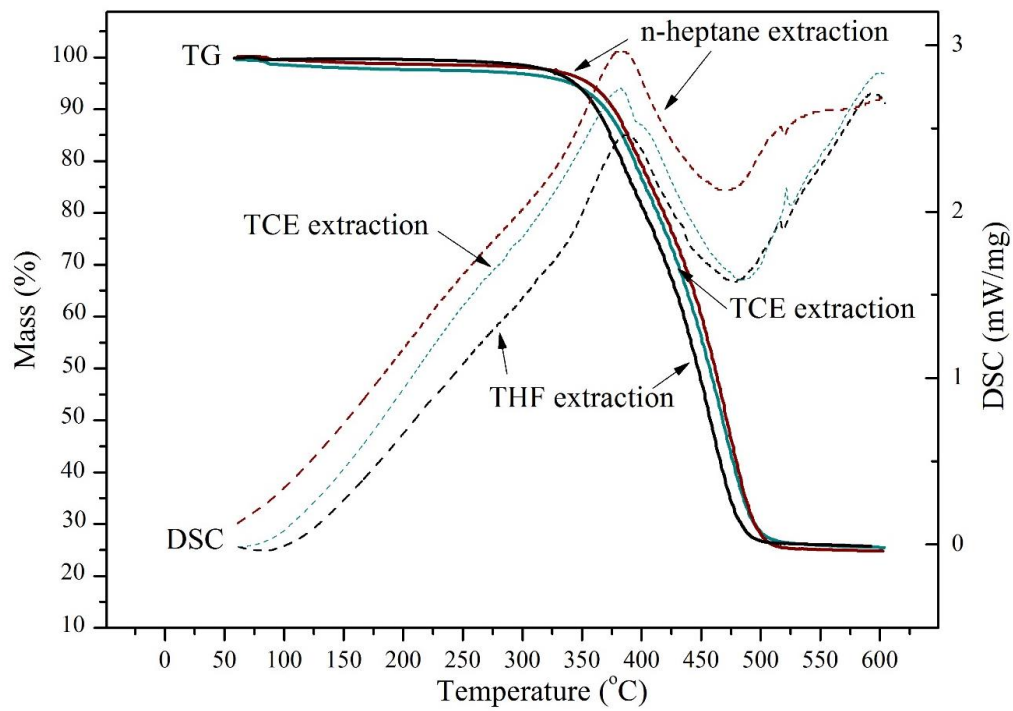
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Figure 3 Thermal behavior of different fractions from base asphalt

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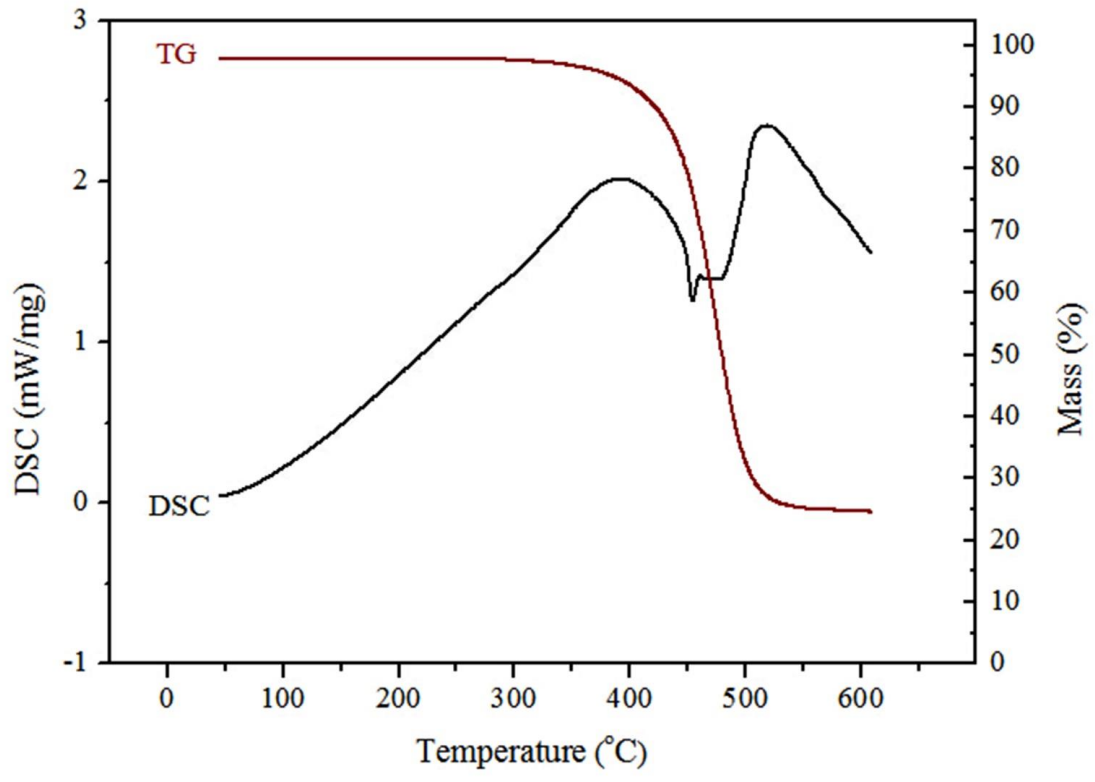
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Figure 4 DSC and TG curves of extracted CRM by different solvents

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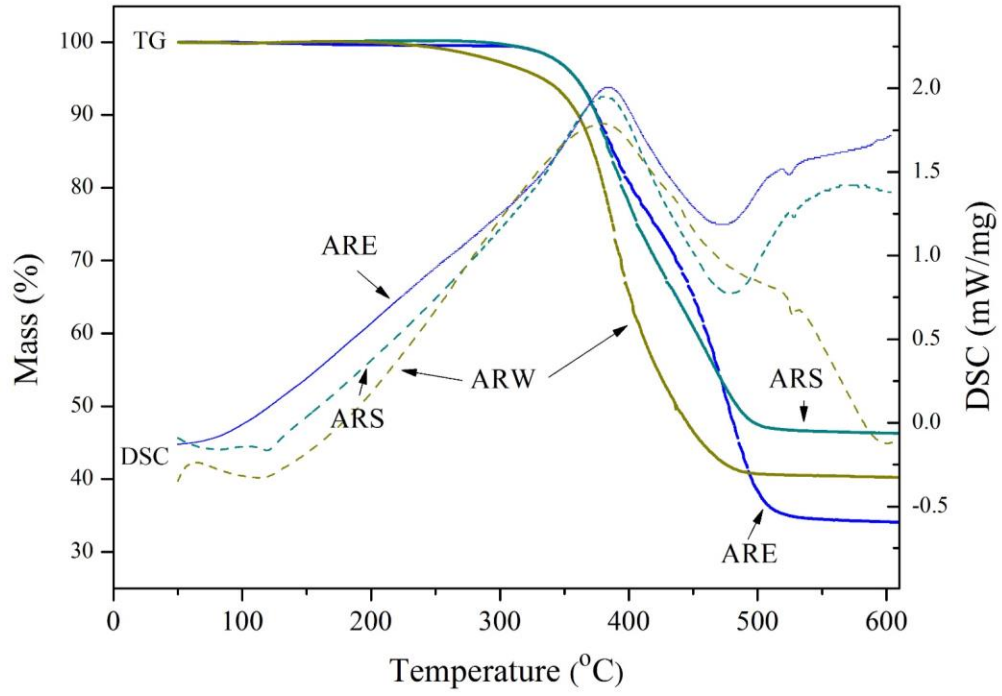
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Figure 5 DSC and TG curves of separated asphalt from

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Figure 6 Thermal test results of extracted CRM from warm AR binders

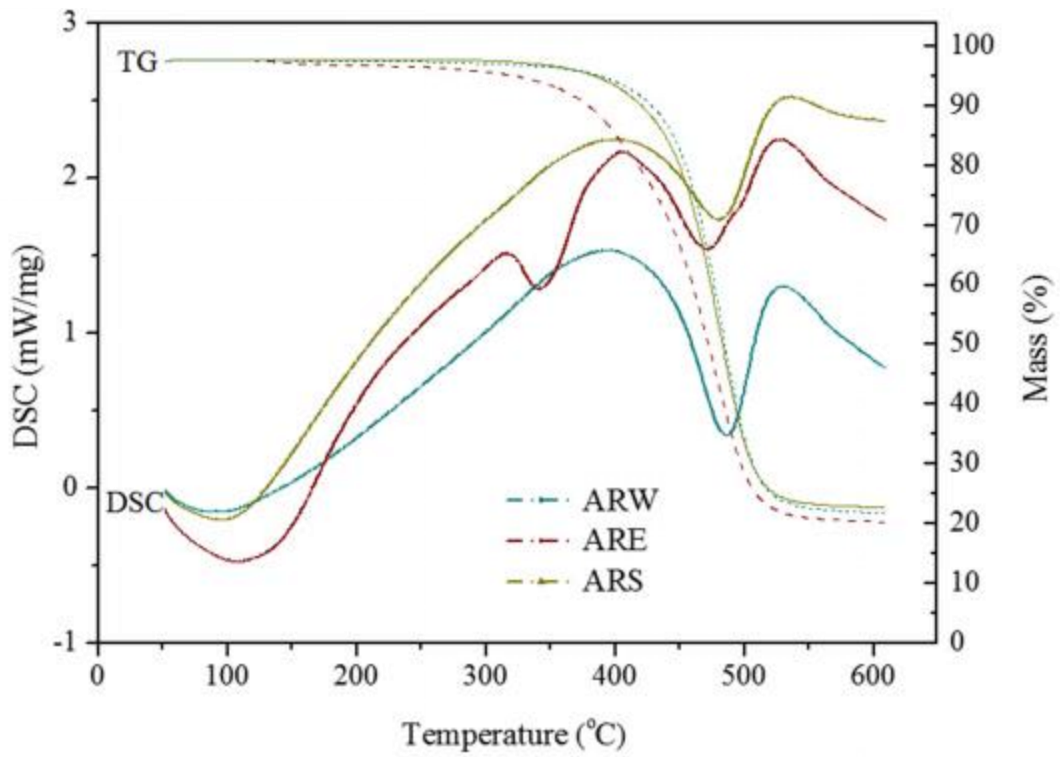
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Figure 7 Thermal test results of separated asphalt systems from warm AR binders

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Table 1. Properties of WMA additives

	Evotherm-DAT	Sasobit	56 [#] paraffin wax
Ingredients	Fatty amine derivatives, Alkylamines	Solid saturated hydrocarbons	Solid saturated hydrocarbons
Physical state	Liquid	Solid	Solid
Color	Caramel	Milky-white	Light-white
Odor	Amine-like	None	None
Bulk density	>1.0g/cm ³	0.622g/ cm ³	0.85g/ cm ³
PH value	9 -10	N/A	N/A
Boiling point	150 -170 °C	N/A	N/A
Melting point	N/A	105 – 110 °C	54 -58 °C
Solubility in water	Partially soluble	Insoluble	Insoluble
Appearance			

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Table 2. Rheological properties of prepared asphalt binders

Performance	Parameters	Method	Pen60/70	AR	ARE	ARS	ARW
General	Penetration at 25 °C (0.1mm)	ASTM D5	66.5	40.2	77.4	33.1	48.3
	Softening point (°C)	ASTM D36	48.5	64.5	46.5	87.4	62.3
	Ductility at 25 °C (cm)	ASTM D113	77.5	22.5	16.5	20.5	18
Workability	Viscosity at 135 °C (cp)	AASHTO T316	481	10512	6350	5637	5988
	Viscosity at 160 °C (cp)		N/A	3388	1813	2025	2487
Rutting	$G^*/\sin\delta$ at 64 °C (KPa)	AASHTO M320	4.012	24.187	6.794	38.021	10.758
	Failure temperature (°C)		70.2	91.0	81.7	96.3	88.5
	J_{nr3200} at 64 °C (K/Pa)	ASTM D7405	3.473	0.288	1.36	0.200	0.528
Fatigue	$G^* \sin\delta$ at 25 °C (MPa)	AASHTO M320	3.555	1.344	2.072	1.437	2.116
	Failure temperature (°C)		22.85	11.55	18.72	14.90	17.74
Low-temp cracking	Creep stiffness at -12 °C (MPa)	AASHTO T313	201	109	117	133	154
	m-value at -12 °C		0.318	0.346	0.323	0.301	0.308

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Table 3. Component concentrations of extracted CRM samples from AR and warm ARs

Extracted source	Oil components (%)	NR and SR (%)	Fillers (%)
AR	1.7	72.2	26.1
AR2	1.8	72.4	25.8
ARE	0.8	64.6	34.6
ARS	0.9	52.9	46.2
ARW	5.4	55.3	39.3

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Table 4. Main features in separated binder thermal behavior

Binder source	T _i (°C)	T _m (°C)	M _f (%)	T _{en} (°C)	T _{ex} (°C)
Pen 60/70	215.7	461.1	18.8	462.6	246.5/493.8
AR	256.7	466.8	24.0	401.5/533.2	442.3
ARE	122.5	467.7	20.4	314.3/403.5/526.7	115.0/340.2/474.6
ARS	252.4	474.3	23.2	395.3/533.2	105.1/484.6
ARW	197.2	477.0	21.6	390.7/529.9	82.8/481.4

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