Thermal Behaviour of Extracted Rubber from Hot and Warm Rubberized Asphalt Binders

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ABSTRACT: This study investigated the thermal behaviour of crumb rubber modifier (CRM) extracted from hot asphalt rubber (AR) and warm AR binders through differential scanning calorimeter (DSC) testing and thermal gravimetric analysis (TGA). Three methods were implemented to extract CRM from the modified binders, which resulted in the following findings: 1) the interaction between CRM and base binder is a component exchange process: i.e., natural rubber and styrene-butadiene rubber are released from CRM and blended with asphalt molecules; 2) different warm mix asphalt (WMA) additives have different effects on the interaction between asphalt and rubber: wax based additives penetrate into CRM while the liquid chemical additive rarely interacts with the rubber modifier; and 3) the incorporation of WMA additives, especially the wax based additives, promotes the component exchange process between rubber and asphalt.

1 INTRODUCTION

Recycling waste vehicle tires into asphalt rubber (AR) pavement is a sustainable technology which provides not only satisfying mechanical properties but also noise reduction function (Azizian et al. 2003; Shen et al. 2009; Paje et al. 2010). Specifically, AR is defined as a blend of asphalt cement, crumb rubber modifier (CRM) and other additives, with a rubber content of no less than 15% by weight of total blend (Bahia and Davies 1994). The field-blended AR is prepared by high shear mixing CRM and base asphalt at high temperature (usually above 170 ^{o}C). The performance of AR may be influenced by various factors, such as base asphalt properties, rubber size, rubber content and mixing condition (Ghavibazoo & Abdelrahman 2013; Shu and Huang 2014). In general, AR has been reported to have superior rutting, cracking and fatigue performance. However, the incorporation of CRM also leads poorer workability and faces the criticisms of higher construction temperature, extra energy cost as well as higher construction emission (Thodesen et al. 2009; Shu and Huang 2014).

Recently, various warm-mix asphalt (WMA) additives have been applied to improve the workability of high-viscosity asphalt binders like AR (Xiao et al. 2012; Oliveira et al. 2012; Zhao et al. 2012). The WMA additives can be generally classified into three categories: foaming additives, organic additives and chemical additives. Foaming additives provide better workability by causing volume expansion of asphalt binder, while organic additives and chemical additives achieve this goal by decreasing the binder viscosity and acting as a surfactant at the asphalt-aggregate interface, respectively (Rubio et al. 2102; Oliveira et al. 2012). Extensive studies have been conducted to investigate the effects of various non-foaming WMA additives on AR binder's rheological performance (Lesuer 2009; Xiao et al. 2012; Leng et al. 2013; Yu et al. 2013; Jamshidi et al. 2013), but very few of them have looked into the interaction mechanisms of different components within warm AR binder. To help fill this gap, this study aims to investigate the effects of asphalt and different WMA additives on the composition of crumb rubber through thermal analysis. To achieve this objective, three warm AR binders were prepared with Sasobit (organic additive), Evother-DAT (chemical additive), and 56# paraffin wax (organic additive), which are denoted as ARS, ARE, and ARW, respectively. Then, the crumb rubber particles in these warm AR binders were extracted using organic solvents, and characterized through two thermal analysis techniques: thermo-gravimetric analysis (TGA) and differential scanning calorimeter (DSC) analysis. The decomposition, fusion and crystallization temperatures were finally determined as the fingerprints of various components in crumb rubber, which provided qualitative and quantitative information on the interaction levels of CRM with base binder and WMA additives.

2 EXPERIMENTAL DESIGN

2.1 Materials

The AR binder was prepared by blending 18% of 40 mesh crumb rubber by the total weight of AR with the penetration grade 60/70 base asphalt using a high shear mixer. The mixing was conducted at 176 ^{o}C for one hour at a shear rate of 4000 rpm/min. Three WMA additives, including Evotherm-DAT, Sasobit, and 56$^{\#}$ paraffin were added to AR immediately afterwards, with the percentages s of 5%, 3% and 1.5%, respectively, by weight of AR, based on the manufactures' recommendations and preliminary tests. The properties of each WMA additive are shown in Table 1, and the rheological properties of prepared binders are shown in Table 2.

Table 1. Properties of WMA additives (Yu et al. 2016)

	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^{o}C	N/A	N/A
Melting point	N/A	105-110^{o}C	54- 58 ^{o}C
Solubility in water	Partially soluble	Insoluble	Insoluble
Appearance			
Commercial product?	Yes	Yes	No

Table 2. Rheological properties of prepared asphalt binders

	Base asphalt	AR	ARE	ARS	ARW
Penetration at 25 ^{o}C (0.1mm)	66.5	40.2	77.4	33.1	48.3
Softening point (^{o}C)	48.5	64.5	46.5	87.4	62.3
Rotational viscosity at 135^{o}C/160^{o}C (cp)	481/-	10512/3388	6350/1813	5637/2025	5988/2487
G*/sinδ at 64^{o}C (KPa)	4.012	24.187	6.794	38.021	10.758
G* sinδ at 25^{o}C (Mpa)	3.555	1.344	2.072	1.437	2.116
J_{nr}3200 at 64^{o}C (K/Pa)	3.473	0.288	1.36	0.200	0.528
BBR stiffness at -12^{o}C	201	109	117	133	154

From Table 2, it can be observed that compared to base asphalt, AR provides better performance on rutting, fatigue and low-temperature cracking resistance. All WMA additives were effective in reducing the high-temperature viscosity of AR, but their effects on other rheological properties varied. All WMA additives negatively affected the low-temperature crack resistance of AR, while Sasobit showed positive effects on the rutting and fatigue performance of AR, and Evotherm-DAT showed obvious negative effect on the high-temperature performance of AR.

2.2 CRM extraction methods

CRM particles cannot completely dissolve in asphalt and remain in small particulate forms after the interaction with base asphalt. A method similar to that applied by researchers from North Dakota was implanted in this study to extract CRM from AR (Ghavibazoo & Abdelrahman 2013). In this method, each warm AR binder was first mixed with an organic solvent (weight ratio of 1:10 for asphalt and solvent) for one hour and then the black solution was filtered through a 200mesh (0.075mm) sieve. The CRM particles remaining on the sieve were further washed by extra organic solvent for serval times until the filtrate became colorless. Finally, the washed CRM particles were kept in oven at 150 ^{o}C for 12 h to completely evaporate the solvent.

Three different solvents were applied in this study, including trichloroethylene (TCE), tetrahydrofuran (THF) and n-Heptane. Neither the crumb rubber nor the WMA additives can dissolve in any of these solvents. TCE and THF are two organic solvents commonly used to dissolve bitumen materials, and they both can completely remove asphalt components from rubber particles. In comparison, n-Heptane is able to dissolve saturates, aromatics and resins, but not asphaltene, which contains the heaviest and most complicated molecules of asphalt (Loeber et al. 1998). Using different solvents may help reduce the test errors caused by extraction. Moreover, comparing the test results using TCE/THF and n-Heptane may help check whether there is any interaction between rubber and asphaltene during the mixing process.

2.3 TGA and DSC analysis

The thermal analysis was conducted using the Netzch TGA/DSC with a working temperature ranging from 25 ^{o}C to 1500 ^{o}C. The heating rate was controlled at 20 ℃/min with a maximum temperature of 600 ℃. High-purity nitrogen ambient gas was applied at a flow-rate of 500 ml/min. During the pyrolysis process (heating without oxygen), the organic volatile substances of CRM were decomposed to low molecular weight products, liquids or gases, resulting in mass loss as well as the endothermic or exothermic behavior. 10- 20mg of crumb rubber was tested each time, and three replicates were prepared and tested for each type of binder. The original CRM was washed by clean water to remove impurities.

The TGA was conducted to investigate the thermal decomposition pattern of crumb rubber and difference between each of its main components. Previous studies have indicated below 300 ^{o}C the oily and volatile components are decomposed while the residual materials at temperatures higher than 500 ^{o}C include the inorganic fillers, carbon black and ash residue (Seidelt et al. 2006; Fernández-Berridi et al. 2006).

DSC testing has been widely applied to determine the thermal transitions of polymeric materials (Tan & Guo 2014). The melting points and glass transition temperatures of the tested polymers can be obtained through DSC analysis. The endothermic or exothermic peaks from DSC testing indicate that the fusion or crystallization has happened at specific temperatures, at which the heat capacity of a certain component changes. Based on the available studies (Chen & Qian 2003; Martínez et al. 2013), crumb rubber may show two distinguishable endothermic peaks from 300 ^{o}C to 500 ^{o}C, which are related to the following two polymeric compounds in CRM: natural rubber (NR) and synthetic rubber (SR).

3 RESULTS AND DISSUSSION

3.1 Thermal behavior of original crumb rubber

Figure 1 shows the TG and DSC curves of the original crumb rubber. The TG curve describes the weight change versus temperature while the DSC curve represents the heat flux versus temperature. The TG curve exhibits two main regions of weight loss, i.e., 100-130 ^{o}C and 300- 500 ^{o}C. The DSC curve shows three main endotherms and one exotherm. These thermal features are caused by various components in the tested CRM, including NR, SR and minor constituents of oil, plasticizer and water. The first mass loss and endothermic peak are attributed to the evaporation of water, followed by the decomposition of oil, plasticizer and other additives at lower temperature range (<300 ^{o}C). As the temperature was further raised to above 300 ^{o}C, two peaks can be noticed at 329 ^{o}C and 410 ^{o}C in the DSC curve, which are ascribed to the degradation of NR and SR, respectively.

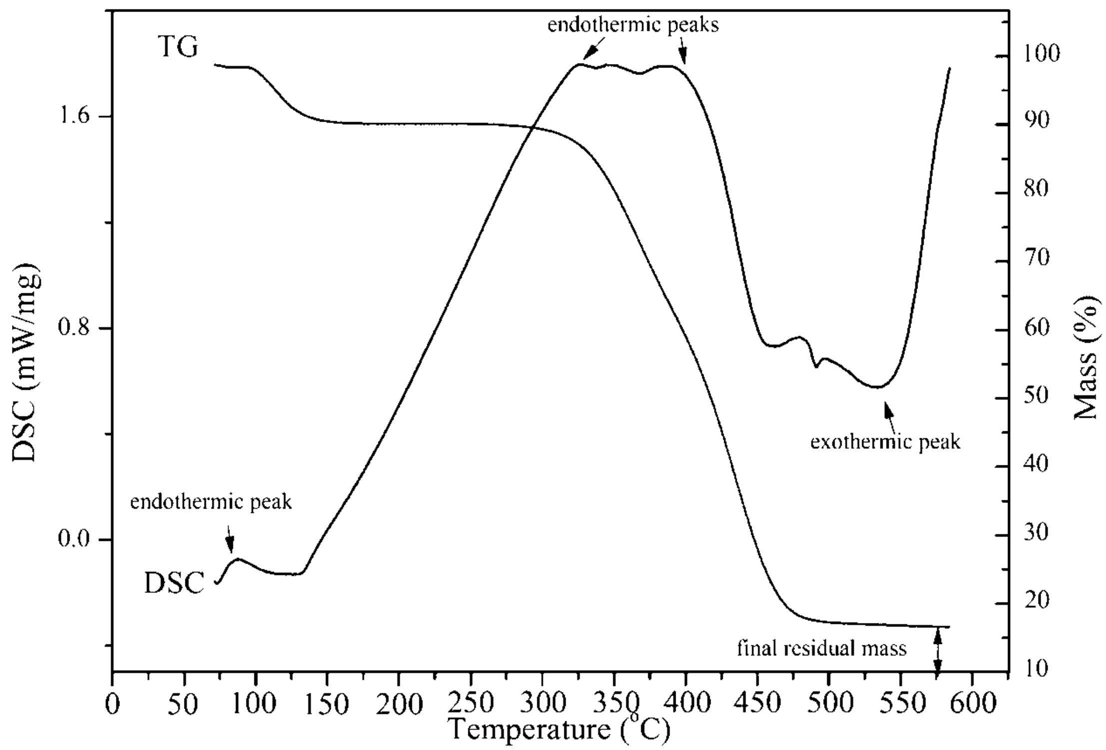

Figure 1 DSC and TG curves of original CRM

3.2 Interaction between asphalt and CRM

Figure 2 shows the test results of the extracted CRM samples using TCE as the solvent. Compared to the original CRM, the extracted CRM shows a similar pattern in the TG curve. As expected, the main weight loss of both samples occurred within the temperature from 300 ^{o}C to 500 ^{o}C. However, the final residual mass percentage of the extracted CRM (26wt%) is higher than that of the original CRM (17wt%), indicating that the interaction of rubber with base asphalt may have consumed part of the decomposable polymers.

Similar findings can be obtained from the DSC testing result. The DSC curve of the original CRM has two endothermic peaks from 300 ^{o}C to 500 ^{o}C, while the extracted CRM only has one, According to the previous studies (Chen and Qian 2003; Ghavibazoo and Abdelrahman 2013), the peak within the range of 300 ^{o}C to 400 ^{o}C is due to the NR portion of CRM while the one within the range of 400 ^{o}C to 500 ^{o}C is related to the SR. Thus, the interaction of CRM with asphalt has caused the dissolution of NR in asphalt during the mixing process, which positively affects the rheological properties of base asphalt.

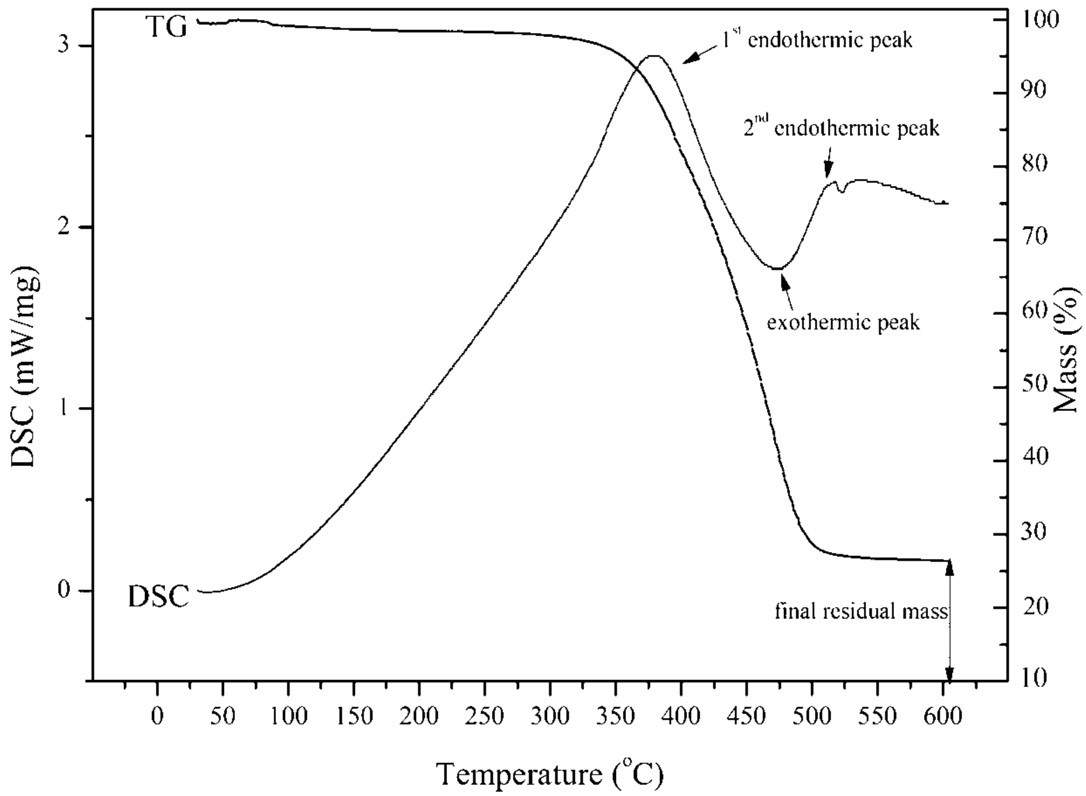

Figure 2. DSC and TG curves of extracted CRM by TCE solvent

Figure 3 shows the TG and DSC curves of the extracted CRM when different solvents were used. It can be seen that the three TG curves are very close to each other and the peaks in the three DSC curves occurred at almost the same positions. As described earlier, TCE and THF can completely dissolve base asphalt while n-heptane cannot dissolve the asphaltene. Thus, the testing results show no evidence that asphaltene has penetrated into CRM or bonded to CRM surface during the rubber-asphalt interaction.

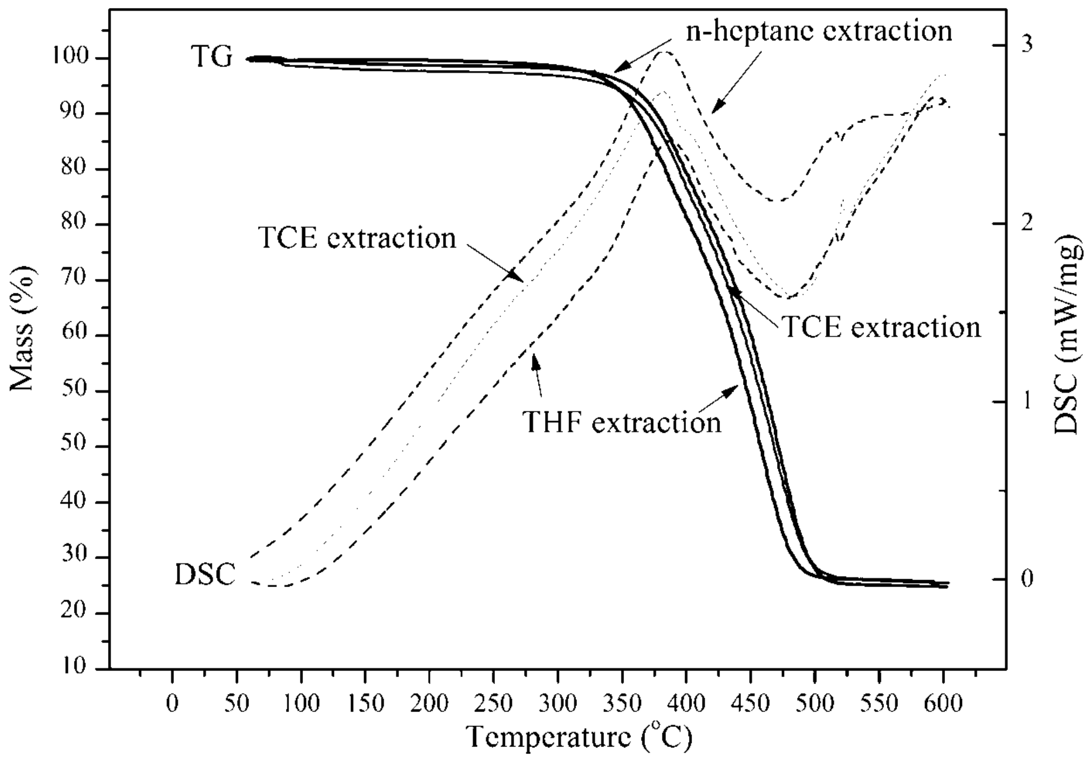

Figure 3. DSC and TG curves of extracted CRM extracted by different solvents

3.3 Effects of warm mix additives

Figure 4 shows the thermal analysis results of the CRM samples extracted from warm AR binders. For brevity, only the results of the CRM extracted by TCE are presented, as similar curves were obtained when different solvents were used. When the temperature is lower than 150 ^{o}C (the temperature at which extracted rubber has been preserved for 12 hours), exothermic peak can be noticed for the rubber extracted from ARS and ARW, even though no obvious mass loss can be observed. The exothermic peaks at this location are indicators of material crystallization. It is know that the asphalt components such as aromatic and saturated hydrocarbons do not crystallize at this temperature (Benbouzid & Hafsi 2007). Thus, the crystallization phenomenon should be caused by n-alkanes (paraffin) in CRM mainly from the wax-based WMA additives. In other words, n-alkanes from the wax based additives, i.e., Sasobit and 56$^{\#}$ paraffin wax, not only mix with asphalt components but also penetrate in to particles. In addition, the heat capacity variation of 56$^{\#}$paraffin wax was found more significant than that of the Sasobit according to the DSC results. The relatively poor heat capacity of wax leads to poor temperature susceptibility of asphalt with high wax content. As a result, the low-temperature cracking resistance of the ARW is the worst among the three warm ARs.

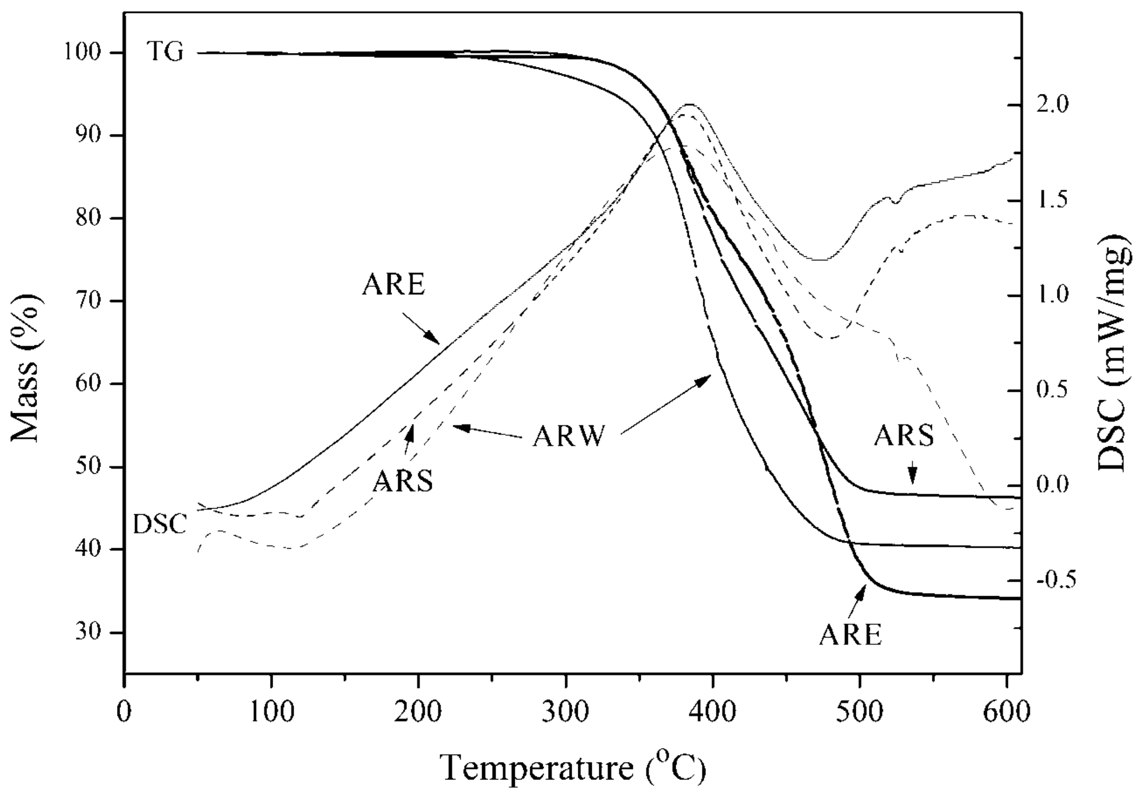

Figure 4. DSC and TG curves of extracted CRM extracted from different warm AR binders

The TG curves illustrate that crumb rubber from ARW has more oily components than the others (nearly 5.4% of mass loss before 300 °C), which may be attributed to the penetration of some oily components from paraffin wax into the crumb rubber during the mixing process. In comparison, the commercial wax based additive, Sasobit, had little effect on the oily component ratio of CRM. This difference may be caused by the different preparation techniques of these two additives. It has been reported that the carbon chain length of Sasobit is much longer than that of regular wax, which leads to a higher melting point and better temperature stability (Tasdemir 2009; Jamshidi et al. 2013). The incorporation of the chemical additive, Evotherm-DAT, seems to have limit influence on the exotherm and endotherm behavior of CRM. One possible reason is that some components had already evaporated during the mixing process, and the residual surfactants were evenly dispersed among the carbon chains of base asphalt without penetrating into crumb rubber. Since Evotherm-DAT had little interaction with CRM, its effect on the rheological properties of AR should be mainly attributed to its liquid nature and the interaction with asphalt molecules.

Table 3 summarizes the percentages of different components in the extracted CRMs from AR, ARE, ARS, ARW and AR2 (with 70 minutes mixing time, same as warm ARs). The component concentrations in AR and AR2 are very close to each other, indicating that the rubber has almost reached the maximum dissolution level under the mixing condition adopted in this study. In comparison, the NR and SR contents of CRM from warm ARs are lower than those of CRM extracted from AR, possibly due to the mixing condition. The dissolution level of CRM also varied obviously within different warm ARs. It seems that SR is easier to be released from CRM in less viscous asphalt, especially when wax based additives are used.

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 (with 70 minutes mixing time)	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

4. CONCLUSIONS

In this study, the TGA and DSC tests were performed to characterize the pyrolysis and reaction mechanisms of crumb rubber extracted from hot AR binder and warm AR binders with various WMA additives. The following points summarize the main findings of this study:

- The interaction between CRM and asphalt affects the composition of the extracted crumb rubber from AR. NR in CRM is easier to be released and mixed with asphalt molecules than SR.
- Asphaltene does not penetrate into CRM during the mixing process of AR.
- Wax based additives penetrate into CRM during the mixing process of warm AR, and the conventional wax with shorter carbon chain length is easier to interact with rubber than the commercial wax-type additive, Sasobit.
- Evotherm-DAT was found to have limited interaction with crumb rubber.
- The incorporation of WMA additives, especially wax based additives, promotes the interaction between CRM and base asphalt.

In summary, this study has shown the high potential of applying thermal analysis methods to investigate the interaction mechanism between asphalt and various modifiers. Future study is recommended on developing the quantitative relationship models between the thermal test results and the rheological properties of modified asphalt.

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