https://doi.org/10.1016/j.jclepro.2016.09.043

Optimization of Preparation Procedure of Liquid Warm Mix Additive Modified Asphalt Rubber

Huayang Yu[a], Zhen Leng[b]*, Zhengyuan Zhou[c], Kaimin Shih[d], Feipeng Xiao[e], Zheming Gao[f]

Abstract

Warm mix asphalt (WMA) is an emerging clean production technology that alleviates the energy and environmental concerns of asphalt pavement industry. It is particularly suitable for asphalt rubber (AR) pavement, which provides longer service life and lower road-tyre noise but requires higher production temperature. Evotherm-DAT, a common liquid warm-mix asphalt (WMA) additive, can effectively improve the workability of AR binder, thus reducing the construction temperature of AR pavement. However, the properties of the Evotherm-DAT modified AR binders (Evo-AR) might be affected by the procedure of incorporating the WMA additive into AR, which unfortunately has not been fully studied yet. This study aims to address this issue by characterizing the rheological properties and chemical compositions of the Evo-ARs prepared by the following three procedures: 1) preparing AR first and then blending it with Evotherm-DAT (AR-E), the conventional approach; 2) mixing Evotherm-DAT and rubber first and then incorporating them to asphalt (ER-A); and 3) adding Evotherm-DAT during the mixing process of AR (REA). It was found that AR-E and REA had similar rheological properties.

[a] PhD Candidate, Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, 13900586r@connect.polyu.hk
[b] Assistant Professor, Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, zhen.leng@polyu.edu.hk (*Corresponding Author)
[c] PhD Candidate, Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Pokfulam, Hong Kong, zzy247@hku.hk
[d] Associate Professor, Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Pokfulam, Hong Kong, kshih@hku.hk
[e] Professor, Key Laboratory of Road and Traffic Engineering of the Ministry of Education, Tongji University, No. 4800, Cao'an Road, Jiading District, Shanghai 201804, fpxiao@tongji.edu.cn
[f] Research Assistant, Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, zheming.gao@polyu.edu.hk

Besides, the workability of ER-A was slightly worse than those of AR-E and REA, but still much superior to that of AR without WMA additive. The anti-rutting performance of ER-A is better than those of AR-E and REA while no obvious difference was observed in the fatigue and low temperature cracking resistance among three types of Evo-ARs. Chemical characterization indicated that the preparation procedures affected the amount of epoxy groups in Evo-ARs, which possibly contributed to the difference in their rheological properties. Overall, it was concluded that incorporating Evotherm-DAT at an early stage has insignificant negative effect on the rheological properties of warm AR binder, but allows for more energy saving and emission reduction during the mixture production process.

Key words: preparation procedure; asphalt rubber; warm mix; rheological properties; energy saving

1. Introduction

Warm mix asphalt (WMA) is a sustainable paving technology which improves the workability of asphalt mixture [1] and [2]. As a result, the application of WMA leads to lower energy consumption, emission and odors during asphalt pavement construction. Based on their working mechanisms, WMA additives can be classified into three groups: foaming additives, organic additives and chemical additives. Evotherm-DAT (Dispersed Asphalt Technology) is a liquid chemical additive containing amine agents that improves binder workability during mixing and compacting process. Typically, 5% of Eovtherm-DAT is added to asphalt binder, allowing for a construction temperature reduction of up to 55 °C [1] [2] [3] [4] and [5]. A study in Texas indicated that asphalt binders with Evotherm-DAT had lower viscosity, lower rutting factor ($G^*/\sin\delta$), similar fatigue factor ($G^*\sin\delta$), and similar low-temperature stiffness compared to their corresponding base asphalt binders [4].

Asphalt rubber (AR) refers to a blend of asphalt cement, reclaimed tire rubber and other additives, which has a rubber content of no less than 15% by weight of the total blend [6] and [7]. Mixtures with AR binders have been proven to provide superior rutting and cracking resistance compared to those with

normal binders [7], [8], [9], [10], [11] and [12]. Besides, AR is beneficial to alleviating road noise [13], which makes it extremely attractive in urban areas. Nevertheless, due to the incorporation of crumb rubber modifier (CRM), the viscosity of AR becomes much higher than conventional binder, leading to higher mixing temperature and compromised working condition [7], [8], [9], [12], [14], [15], [16] and [17].

The feasibility and engineering performance of AR mixtures containing various WMA additives, such as Evotherm, Sasobit, Cecabase, and Rediset, in AR mixtures have been verified by various studies [9], [16], [17], [18], [19] and [20]. These WMA additives were able to effectively improve the workability of AR binders without obviously compromising their mechanical properties. Yu's study [19] indicated that the AR binder with Evotherm-DAT provided enhanced performance at both high and low-temperature, and there was no complex chemical reaction between Evotherm-DAT and AR. The researchers in North Carolina applied various amine-based WMA modifiers, including bio-binder, Evotherm-3G and Rediset, to AR binders [20] and [21], and found that AR with these amine-based modifiers had better workability and less temperature susceptibility. They also concluded that additives with higher amine contents were more effective in devulcanizing rubber [20].

However, it is worth noting that different procedures can be applied to prepare AR binders with liquid WMA additives (eg: AR with Evotherm-DAT), but none of the previous studies have investigated the effect of the preparation procedure on the performance of such type of warm AR binders. The most commonly used procedure is to prepare AR binder first, and then add the liquid WMA additive into AR during the mixing of AR and aggregate. However, there are also two other options, i.e., adding the WMA additive during the mixing of base asphalt and CRM, and soaking CRM in the liquid WMA additive first and then incorporating them to base asphalt. Compared to the traditional method, the other two procedures may lead to further energy saving, since the earlier incorporation of WMA additive may

reduce the mixing temperatures of not only the asphalt mixture but also the AR binder. However, the different preparation procedures may also result in different interactions among rubber, asphalt and Evotherm-DAT, thus affecting the rheological properties of the final Evotherm-DAT modified AR binder (Evo-AR). To this end, this study aims to investigate the rheological properties of warm AR binders prepared by different mixing procedures. To achieve this objective, the rheological properties, including penetration, rotational viscosity, failure temperature, rutting factor, fatigue factor, and low temperature stiffness of the Evo-AR binders prepared with different procedures, were measured. In addition, Fourier Transform Infrared Spectroscopy (FTIR) analysis was conducted to characterize the interaction among CRM, Evotherm-DAT and base asphalt, when different preparation procedures were applied.

2. Materials and Methods

2.1 Materials

In this study, a penetration grade 60/70 (Pen 60/70) asphalt commonly used in in Hong Kong, was used as the base asphalt. AR binder was prepared by blending 18% of 40 mesh crumb rubber by the total weight of base asphalt and crumb rubber with base asphalt at 176 °C at 4000 r/min for one hour using a high shear mixer. Three Evo-AR binders, namely AR-E, ER-A and REA, were prepared following different procedures. AR-E refers to the binder prepared by mixing the prepared AR binder with Evotherm-DAT by high shear mixing at 160 °C for 10 minutes. REA refers to the binder prepared by directly mixing Pen 60/70, Evotherm-DAT and CRM at 160 °C for 1 hour. The preparation of ER-A is slightly more complicated. First, CRM was soaked in Eovtherm-DAT in a sealed beaker for 24 hours at room temperature and humidity, allowing the liquid WMA additive to be completely absorbed by crumb rubber. Then, the CRM containing Evotherm-DAT (E-CRM) was mixed with Pen 60/70 by high shear

mixing at 160 °C for 1 hour. For all Evo-AR binders, the mass ratios of Pen 60/70, CRM, and Evotherm-DAT were controlled at 1000: 220: 61.

2.2 Experimental program

Fig. 1 illustrates the experimental program of this study. The penetration (25 ℃) and softening point tests were conducted in accordance with ASTM D5 and ASTM D36, respectively [22] and [23]. A Brookfield Rotational Viscometer (RV) was used to measure the viscosities of the binders according to AASHTO T316 [24]. The viscosity tests were conducted at 135 ℃ for all binders, 160 °C for all binders except for Pen 60/70, and 176 °C for AR and AR-E. The testing temperatures were selected according to the expected production temperatures of binder samples. Three replicates were prepared for each type of binder for each of these tests.

The high-temperature performance of the binders was characterized by two parameters: the rutting factor (for both unaged and rolling thin film oven (RTFO) aged samples) and non-recoverable creep compliance (for only RTFO aged samples). A Bohlin Dynamic Shear Rheometer (DSR) was used. For all samples, the diameter of the plates was 25 mm and the gap between two plates was 2 mm [25]. The rutting factor test started at 64 °C, and the test temperature was automatically raised to the next PG grade temperature if the rutting factor value was larger than the value specified in AASHTO M320, i.e., 1 kPa for unaged binder and 2.2 kPa for RTFO binder [26]. The non-recoverable creep compliance (J_{nr}) was determined through the multiple stress creep recover (MSCR) test according to AASHTO MP19 [27]. Each cycle was composed of 1s creep loading followed 9s recovery at 64 °C. Each testing specimen was subjected to ten creep and recovery cycles at a creep stress level of 0.1 kPa followed by ten cycles at 3.2 kPa. Two replicates were prepared and tested for each type of binder.

The fatigue factors of the Pressure Aging Vessel (PAV) aged binder samples were measured to evaluate their intermediate-temperature performance. This test was conducted at 3 ℃ decrement, starting at

25 °C and ending when the measured factor was larger than 5000 kPa [28]. The 2 cm gap and 8 mm diameter plates were used [25], and two replicates were prepared and tested for each binder.

The low-temperature performance of test samples were measured by creep stiffness and m-value (for PAV aged samples) [29]. A Cannon Bending Beam Rheometer (BBR) was used and two replicates were prepared and tested for each type of binder.

The FTIR tests were conducted to evaluate the difference in chemical bonds of the binders at various band regions [9] and [30]. In this test, the test binder was first pressed to pellets with a thickness of approximately 1 mm, and then placed in a transmission holder and scanned. Three replicates were prepared and tested for each type of binder.

3. Results and discussion

3.1 Penetration and softening point

The results of the penetration and softening point tests are presented in Fig. 2. The penetration test evaluates the consistency of asphalt binder while the softening point test assesses the maximum service temperature. It was found that all Evo-ARs had much higher penetration values compared to AR regardless of the preparation procedure. This is mainly attributed to the liquid nature of Evotherm-DAT. Besides, smaller softening points were observed for all Evo-ARs compared to the regular AR binder. Finally, no significant difference was found in the penetrations and softening points of the Evo-AR binders prepared by different procedures.

3.2 Workability

Rotational viscosity is an important, although not the unique, parameter to characterize the workability of an asphalt binder [31]. As Fig. 3 shows, all Evo-ARs had lower viscosities than AR within the temperature range of 135 °C to 176 °C, but their viscosities at 135 °C are much higher than that of Pen

60/70. It was also observed that the viscosity of AR-E at 176 °C is slightly higher than that at 160 °C, which contradicts to the expectation. A careful review of the testing process revealed that this is mainly due to the evaporation of some fluxible components in Evotherm-DAT when the temperature was above 160 °C. Among various Evo-AR binders, AR-E and REA had similar viscosities at both 135 °C and 160 °C, while ER-A had a higher viscosity at 135 °C but a similar one at 160 °C.

3.3 Permanent deformation

Failure temperature and rutting factor

Fig. 4a presents the failure temperature test results, while Fig. 4b and Fig. 4c show the rutting factors of unaged binders and RTFO aged binders, respectively, at different temperatures. As expected, short-term aging led to increased $G^*/\sin\delta$. No significant difference in failure temperature can be noticed between the binders before and after RTFO, and adding Evotherm-DAT generally led to lower failure temperature. Among various preparation procedures, AR-E and REA showed similar high-temperature performance, as indicated by their similar failure temperatures, while the failure temperature of ER-A is approximately 10 °C higher. The comparison between AR and AR-E shows that Evotherm-DAT negatively affected the binder stiffness at high temperature. However, the reduced stiffness can be compensated by first soaking rubber in Evotherm-DAT (the ER-A method). This indicates that different preparation procedures may lead to different distributions of surfactants and crumb rubber in binder, thus different binder properties. Fig. 4d and Fig. 4e illustrate the relationships between the phase angle (δ) and temperature. It can be seen that the RTFO binders had smaller phase angles than the unaged binders. In other words, short-term aging made the asphalt binders less viscous. Under both unaged and short-term aged conditions, ER-A was more viscous than other Evo-AR binders.

Multiple stress creep and recovery (MSCR) test

153 Table 1 presents the results of J_{nr}, % recovery, and traffic levels determined according to AASHTO
154 MP19-10. It can be seen that the J_{nr} differences of all binders containing CRM exceed the maximum
155 allowable value of 75%, which is consistent with the findings by Wills et al. [32]. This phenomenon was
156 mainly due to the binders' extremely low J_{nr} values at 0.1 kPa. Even though the maximum J_{nr} difference
157 requirement cannot be met, the low J_{nr} 0.1 and J_{nr} 3.2 values still prove that AR binders have adequate
158 resistance to permanent deformation at high service temperature. The MSCR results also show that all
159 binders with CRM had much lower J_{nr} values compared to Pen 60/70, especially at the stress of 0.1 kPa.
160 The J_{nr} value of AR-E is significantly higher than that of AR, indicating the possibility of strong
161 interaction among the Evotherm-DAT and the components in AR binder. Consistent with the failure
162 temperature and rutting factor test results, AR-E and REA performed similarly according to the
163 parameters, such as J_{nr} and % Recovery. They both meet the traffic level "H" requirement according to
164 the AASHTO specification. Although ER-A has larger J_{nr} values than AR, it still can meet the
165 requirement of the highest traffic level, "E".

166 *Frequency sweep and viscous flow*

167 Frequency sweep and viscous flow tests were conducted to investigate the binder performance at the
168 maximum pavement service temperature (64 °C) at different loading frequencies (0.1 Hz-10 Hz) and
169 shear stress levels (0-2000 Pa) [9] and [33]. The results of frequency sweep results in Fig. 5a indicate
170 that an increase in frequency leads to larger complex modulus. The phase angles are relatively constant
171 at low frequencies (less than 0.1 Hz) but drop quickly as the frequency is increased to 10 Hz. It can also
172 be observed that Evotherm-DAT made the AR binder softer. Among three Evo-ARs, ER-A had the
173 lowest phase angle and the highest complex modulus at almost all test frequencies, indicating better
174 rutting resistance.

175 The absolute viscosities of the test samples at varying shear stresses (0-2000 Pa) are shown in Fig. 5b.
176 All binders exhibited increasing shear rate and decreasing absolute viscosity with the increase of shear
177 stress. Similar to the results of rutting factor and MSCR, viscous flow data indicate that the addition of
178 Eovtherm-DAT, regardless of the preparation procedure, made the AR binder softer at the maximum
179 pavement service temperature, leading to lower rutting resistance. However, compared to the base
180 binder, the Evo-AR binders were much stiffer and less sensitive to the shear stress.

181 3.4 Fatigue

182 The intermediate-temperature performance of the PAV-aged binders was characterized by the
183 Superpave fatigue factor ($G^*\sin\delta$). Fig. 6a illustrates the relationship between the logarithm of $G^*\sin\delta$
184 and temperature while Fig. 6b shows the threshold temperature corresponding to a fatigue factor of 5.0
185 MPa. It can be seen that the fatigue factor of all binders decrease proportionally with temperature. The
186 threshold temperatures of all binders are less than 25 °C. Evotherm-DAT negatively affected the fatigue
187 resistance of AR. The fatigue failure temperatures of the Evo-AR binders were approximately 8 °C
188 higher than that of AR, but nearly 4 °C lower than that of Pen 60/70. Besides, no specific difference was
189 observed in the fatigue resistances of AR-E, ER-A and REA.

190 3.5 Low-temperature cracking

191 The low-temperature performance of the binders was characterized by stiffness and m-value measured
192 through BBR tests. Table 2 presents the stiffness' and m-values of all binders. It can be seen that the
193 binders with CRM showed better low-temperature cracking resistance than Pen 60/70. All binders had
194 satisfying cracking resistance at -12 °C (stiffness≤300 and m-value>0.3). Similar to the rutting factor
195 and fatigue factor test results, AR-E and ERA had similar stiffness' and m-values. Compared to AR,
196 AR-E and ERA had worse cracking resistance at -12 °C, but superior performance at -18 °C. The
197 stiffness of ER-A is slightly higher than those of the other two Evo-AR binders.

198 3.6 Mechanism investigation

199 Fig. 7a and Fig. 7b show the FTIR spectra of Evotherm-DAT and Pen 60/70, respectively. Evotherm-
200 DAT mainly contains carbon, oxygen, hydrogen, nitrogen, and sulfur elements, which are very close to
201 the components of asphalt, but significant difference exists in their functional groups in FTIR spectra.
202 According to Fig. 7, Evotherm-DAT shows more complex chemical composition compared to base
203 asphalt. Its peaks at approximately 3400 cm^{-1}, 2682 cm^{-1} and 1358 cm^{-1} are most likely due to the
204 presence of amines, amino ions and sulfur-containing organics, respectively [34].

205 Fig. 8a and Fig. 8b show the FTIR spectra of CRM and CRM with Evotherm-DAT (E-CRM) while Fig.
206 9a and Fig. 9b show their morphologies, respectively. As expected, E-CRM is relatively more saturated
207 with smoother surface. Most peaks occurring in the spectra of Evotherm-DAT and CRM can also be
208 noticed in the spectra of E-CRM. However, the strong and broad peak at 3400 cm^{-1} indicating O-H and
209 N-H stretching shows up in the spectra of E-CRM samples, but it is not so remarkable in the spectra of
210 either rubber or Evotherm-DAT samples. This suggests that the generation of hydrogen bond between
211 O-H/N-H group of rubber and $-COO^-$ group of Evotherm-DAT samples during the soaking process. The
212 chemical reaction between Evotherm-DAT and crumb rubber leads to a tighter bonding on interacting
213 surface, which may affect the final performance of Evo-AR binder.

214 Fig. 9a shows the FTIR spectra of AR binder. Its major absorption bands occur at locations similar to
215 those of Pen 60/70. However, peaks at 1703 cm^{-1} and 3400 cm^{-1} (carbonyl group and hydrogen-bonded
216 hydroxyl group) are observed in AR, which do not show in either Pen 60/70 or CRM. These peaks
217 indicate the oxidization of unsaturated functional groups and the formation of hydrogen bond during the
218 heating and mixing processes of asphalt and rubber. This result proves that direct chemical bonds exist
219 among CRM and base asphalt, which leads to a more stable interior structure and superior rheological

performance [35]. This result also suggests that the CRM modification is not only physical, but also chemical with slight effects on the chemical bonding and functional groups.

Comparing the Evo-ARs prepared by different mixing procedures, it was found that the spectra of AR-E and REA are very close to each other, indicating that their chemical components are similar [20]. This observation corresponds well with the rheological test results. ER-A also shows similar spectra, but the intensity of the peak at about 1200 cm^{-1} for C-O stretching of epoxy group is larger, which indicates that epoxy groups was activated by other functional groups in ER-A showing a higher stretching intensity in FTIR spectra. By using the spectra of AR as a reference, it is believed that epoxy group was fixed by rubber or Evotherm-DAT molecules through hydrogen bond. As a result, it seems that rubber and base asphalt reacts better in ER-A than in other two Evo-ARs.

Possible micro models can be proposed to illustrate the interaction among asphalt, rubber and Evotherm-DAT (Fig. 10), according to FTIR results. In base asphalt, the hydrocarbon group (hydrophobic structure) is considered uniformly but loosely distributed (Fig. 10a). The incorporation of CRM may redistribute the hydrocarbon chains by physical absorbing and chemical bonding [36] and [37], leading to steadier and more compacted micro structures (Fig. 10b). Fig. 10c describes the molecular distribution in AR-E and REA. In AR-E, the active hydrophilic molecules from Evotherm-DAT (containing hydroxyl groups) destroyed the formed structure of AR and asphalt; while in REA the hydrophilic and hydrophilic molecules had disorderly and unsystematic distribution. Lastly, in ER-A, as Evotherm-DAT and rubber was pre-bonded before mixing with asphalt, most hydroxyl groups were fixed to rubber surface through hydrogen or covalent bonds (Fig. 9a). In this case, hydrophilic molecules had limited influence on the interaction between asphalt and rubber (Fig. 10d). Besides, as rubber particles in ER-A were surrounded by Evotherm-DAT, which contains more aromatics than base asphalt, better devulcanization and depolymerization of crumb rubber may be achieved [20], resulting in superior rheological properties.

4. Conclusions

Evotherm-DAT, a common chemical warm mix additive, can be incroporated to AR following different procedures, resulting in different workabilities and performances of warm AR binders. A series of rheological property and chemical analysis tests were conducted in this study to characterize the physical and chemical properties of Evo-AR binders prepared by three different procedures, which resulted in the following conclusions:

1. In general, AR binders with Evotherm-DAT additive provided poorer high-temperature performance but similar intermedia- and low-temperature performance compared to the AR binder without warm mix additives, regardless of the preparation procedure.
2. Adding Evotherm-DAT during the mixing process of AR binder (i.e., REA) can help lower the preparation temperature of AR without compromising the performance of the warm AR binder.
3. Evo-AR binders prepared by first soaking rubber in Evotherm-DAT and then incorporating them to base asphalt (i.e., ER-A) showed better high-temperature performance than those prepared by the conventional procedure (i.e., AR-E).
4. Incorporating Evotherm-DAT at an earlier stage during the warm AR preparation process (i.e., the two non-traditional processes: REA and ER-A) had very marginal negative effect on the rheological properties of AR binder. However, it led to more energy saving, because it not only reduces the temperature of mixing AR binder with aggregate, but also that of mixing rubber with base asphalt.

It is worth noting that this study focuses on the effects of different procedures on the rheological properties of warm AR binder. Effects of these procedures on the performance of warm AR mixtures will be investigated in the future study.

Acknowledgement

The authors sincerely acknowledge the funding support from the Hong Kong Research Grants Council (Project Number: 539113). Besides, the sponsorship from the "Ten Thousand People's Scheme" from PRC Ministry of Education on the collaborative study between The Hong Kong Polytechnic University and Tongji University is also greatly appreciated. Trademark or manufacturers' names appear in this paper only because they are considered essential to the object of this paper.

References

[1] Rubio, M. C., Martínez, G., Baena, L., & Moreno, F. Warm mix asphalt: an overview. *Journal of Cleaner Production*, Vol. 24, 2012, pp. 76-84.

[2] Oliveira, J. R., Silva, H. M., Abreu, L. P., & Fernandes, S. R. Use of a warm mix asphalt additive to reduce the production temperatures and to improve the performance of asphalt rubber mixtures. *Journal of Cleaner Production*, Vol. 41, 2013, pp.15-22.

[3] Hamzah, M. O., Jamshidi, A., & Shahadan, Z. Evaluation of the potential of Sasobit® to reduce required heat energy and CO 2 emission in the asphalt industry. *Journal of Cleaner Production*, Vol. 18, 2010, pp. 1859-1865.

[4] Arega, Z., Bhasin, A., Motamed, A., & Turner, F. Influence of warm-mix additives and reduced aging on the rheology of asphalt binders with different natural wax contents. *Journal of Materials in Civil Engineering*, Vol. 23, No. 10, 2011, 1453-1459.

[5] Pérez-Martínez, M., Moreno-Navarro, F., Martín-Marín, J., Ríos-Losada, C., & Rubio-Gámez, M. C. Analysis of cleaner technologies based on waxes and surfactant additives in road construction. *Journal of Cleaner Production*, Vol. 65, 2014, pp. 374-379.

[6] ASTM Standard D6114. Standard Specification for Asphalt-Rubber Binder. *American Society for Testing and Materials*, 2009.

[7] Bahia, H. U., & Davies, R. Effect of crumb rubber modifiers (CRM) on performance related properties of asphalt binders. *Asphalt paving technology*, 1994, Vol. 63, pp. 410-414.

[8] Garcia-Morales, M., Partal. P., Navarro, F. J., & Gallegos, C. Effect of waste polymer addition on the rheology of modified bitumen. *Fuel*, Vol. 85, No.7, 2006, pp. 936-943.

[9] Xiao, F, Punith, V, and Amirkhanian, S. N. Effects of non-foaming WMA additives on asphalt binders at high performance temperatures. *Fuel*, Vol. 94, 2012, pp. 144-155.

[10] Huang, Y., Bird, R. N., & Heidrich, O. A review of the use of recycled solid waste materials in asphalt pavements. *Resources, Conservation and Recycling*, Vol. 52, No.1, 2007, pp. 58-73.

[11] Shu, X., & Huang, B. Recycling of waste tire rubber in asphalt and portland cement concrete: An overview. *Construction and Building Materials*, Vol. 67, 2014, pp. 217-224.

[12] Pasquini, E., Canestrari, F., Cardone, F., & Santagata, F. A. Performance evaluation of gap graded asphalt rubber mixtures. *Construction and Building Materials*, Vol. 25, No.4, 2011, pp. 2014-2022.

[13] Paje, S. E., Bueno, M., Terán, F., Miró, R., Pérez-Jiménez, F., & Martínez, A. H. (2010). Acoustic field evaluation of asphalt mixtures with crumb rubber. *Applied Acoustics*, Vol.71, No.6, 2011, pp. 578-582.

[14] Huang, B., Mohammad, L., Graves, P., & Abadie, C. Louisiana experience with crumb rubber-modified hot-mix asphalt pavement. *Journal of the Transportation Research Board*, No.1780, 2002, pp. 1-13.

[15] Navarro, F. J., Partal, P., Martınez-Boza, F., & Gallegos, C. (2004). Thermo-rheological behaviour and storage stability of ground tire rubber-modified bitumens. *Fuel*, Vol. 83, No. 14, pp. 2041-2049.

[16] Rodríguez-Alloza, A. M., Gallego, J., Pérez, I., Bonati, A., & Giuliani, F. High and low

311 temperature properties of crumb rubber modified binders containing warm mix asphalt
312 additives. *Construction and Building Materials,* Vol. *53,* 2014, 460-466.
313 [17] Yu, X., Wang, Y., & Luo, Y. Effects of types and content of warm-mix additives on
314 CRMA. *Journal of Materials in Civil Engineering*, Vol. 25, No.7, 2012, pp. 939-945.
315 [18] Banerjee, A., de Fortier Smit, A., & Prozzi, J. A. The effect of long-term aging on the rheology
316 of warm mix asphalt binders. *Fuel*, Vol. 97, 2012, pp. 603-611.
317 [19] Yu, X., Leng, Z., & Wei, T. Investigation of the rheological modification mechanism of warm-
318 mix additives on crumb-rubber-modified asphalt. *Journal of Materials in Civil Engineering*, Vol.
319 26, No.2, 2013, pp. 312-319.
320 [20] Fini, E. H., Oldham, D. J., & Abu-Lebdeh, T. Synthesis and Characterization of Biomodified
321 Rubber Asphalt: Sustainable Waste Management Solution for Scrap Tire and Swine
322 Manure. *Journal of Environmental Engineering*, Vol. *139, No.* 12, 2013, pp. 1454-1461.
323 [21] Bocoum, A., Hosseinnezhad, S., & Fini, E.H. Investigating effect of amine based additives on
324 asphalt rubber rheological properties. *Proceedings of 12th ISAP International Conference on*
325 *Asphalt Pavements*, Vol. 1, 2014, pp. 921-931.
326 [22] ASTM Standard D5. Standard Test Method for Penetration of Bituminous Materials. *American*
327 *Society for Testing and Materials,* 2013.
328 [23] ASTM Standard D36. Standard Test Method for Softening Point of Bitumen (Ring-and-Ball
329 Apparatus). *American Society for Testing and Materials,* 2006.
330 [24] AASHTO Standard T316. Standard Method of Test for Viscosity Determination of Asphalt
331 Binder Using Rotational Viscometer. *American Association of State and Highway*
332 *Transportation Officials,* 2010.
333 [25] Tayebali, A. A., Vyas, B. B., & Malpass, G. A. Effect of crumb rubber particle size and

concentration on performance grading of rubber modified asphalt binders. *ASTM Special Technical Publication 1322,* 1997, pp. 30-47.

[26] AASHTO Standard M320. Standard Specification for Performance-Graded Asphalt Binder. *American Association of State and Highway Transportation Officials,* 2010.

[27] AASHTO Standard MP19. Standard Specification for Performance-Graded Asphalt Binder Using Multiple Stress Creep Recovery (MSCR) Test, *American Association of State and Highway Transportation Officials*, 2010.

[28] AASHTO Standard T315. Standard Method of Test for Determining the Rheological Properties of Asphalt Binder Using a Dynamic Shear Rheometer (DSR). *American Association of State and Highway Transportation Officials,* 2009.

[29] AASHTO Standard T313. Standard Method of Test for Determining the Flexural Creep Stiffness of Asphalt Binder Using the Bending Beam Rheometer (BBR). *American Association of State and Highway Transportation Officials*, 2012.

[30] Hossain, Z., Lewis, S., Zaman, M., Buddhala, A., & O'Rear, E. Evaluation for warm-mix additive-modified asphalt binders using spectroscopy techniques. *Journal of Materials in Civil Engineering,* Vol. 25, No.2, 2012, pp. 149-159.

[31] Hanz, A., Faheem, A., Mahmoud, E., & Bahia, H. Measuring effects of warm-mix additives: Use of newly developed asphalt binder lubricity test for the dynamic shear rheometer. *Journal of the Transportation Research Board,* No. 2180, 2010, pp. 85-92.

[32] Willis, J. R., Turner, P., Plemmons, C., Rodezno, C., Rosenmayer, T., Daranga, C., & Caelson, D. Effect of rubber characteristics on asphalt binder properties. *Road Materials and Pavement Design,* Vol. 14, No. 2, 2013, pp. 214-230.

[33] Xiao, F., Amirkhanian, A. N., & Amirkhanian, S. N. Influence of carbon nanoparticles on the

rheological characteristics of short-term aged asphalt binders. *Journal of Materials in Civil Engineering*, Vol. 23, No. 4, pp. 423-431.

[34] Fini, E. H., Kalberer, E. W., Shahbazi, A., Basti, M., You, Z., Ozer, H., & Aurangzeb, Q. Chemical characterization of biobinder from swine manure: Sustainable modifier for asphalt binder. *Journal of Materials in Civil Engineering*, Vol. 23, No.11, 2011, pp. 1506-1513.

[35] Gawel, I., Stepkowski, R., & Czechowski, F. Molecular interactions between rubber and asphalt. *Industrial & engineering chemistry research*, Vol. 45, No. 9, 2006, pp. 3044-3049.

[36] Leite, L. F. M., Constantino, R. S., & Vivoni, A. Rheological studies of asphalt with ground tire rubber. *Road Materials and Pavement Design*, Vol. 2, No.2, 2001, pp. 125-139.

[37] Ghavibazoo, A., & Abdelrahman, M. Composition analysis of crumb rubber during interaction with asphalt and effect on properties of binder. *International Journal of Pavement Engineering*, Vol. 14, No. 5, 2013, pp. 517-530.

List of figures and tables

Figures:

Tables:

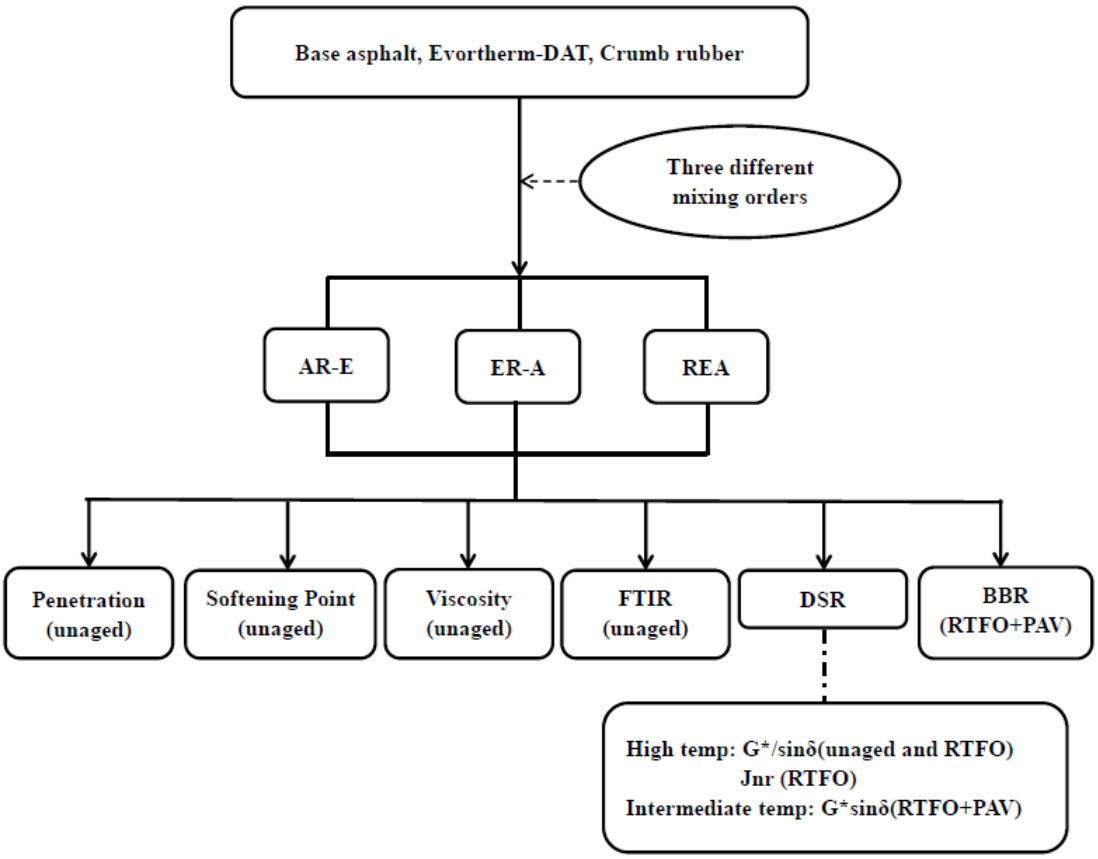
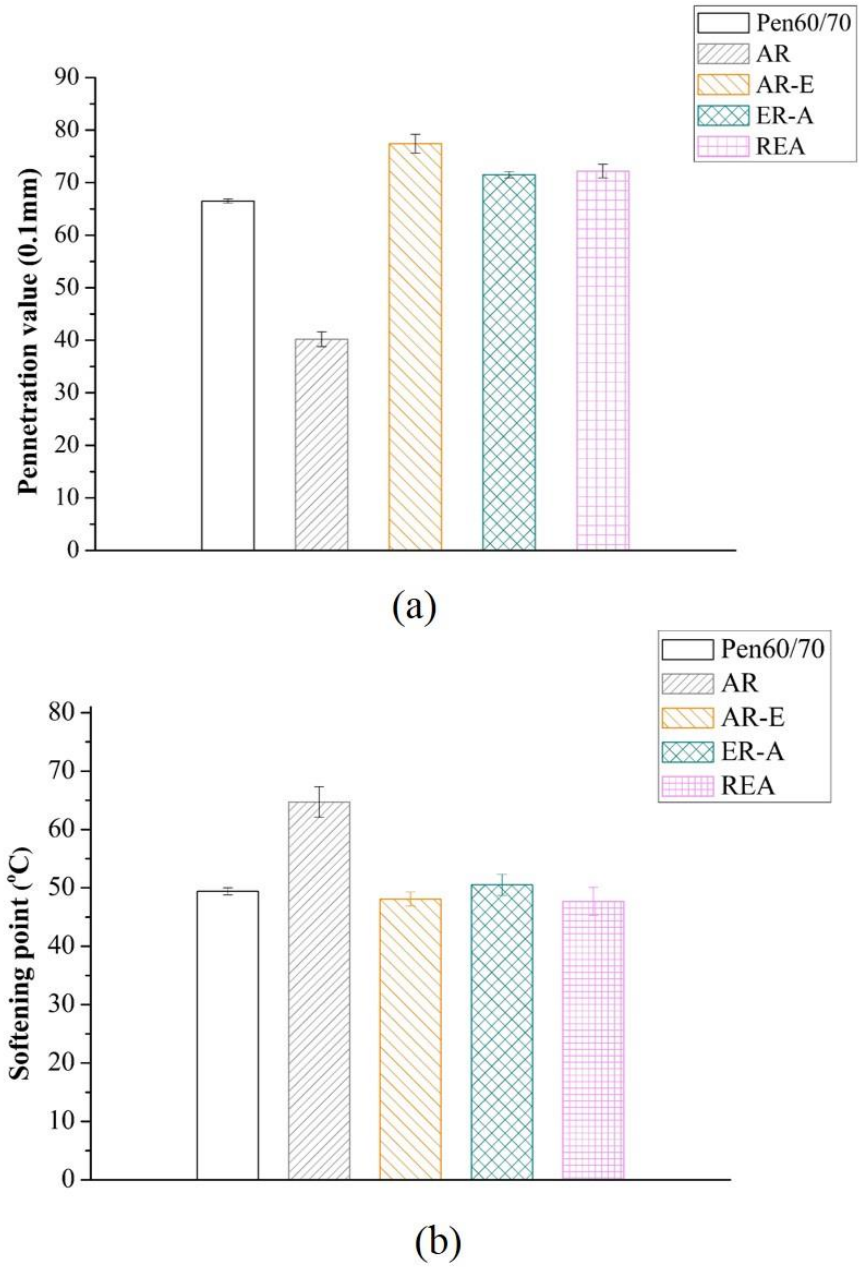


Fig. 1 Experimental program



412

413 Fig. 2 Rheological test results: (a) Penetration at 25°C; (b) Softening point

414

415

416

417

418

419

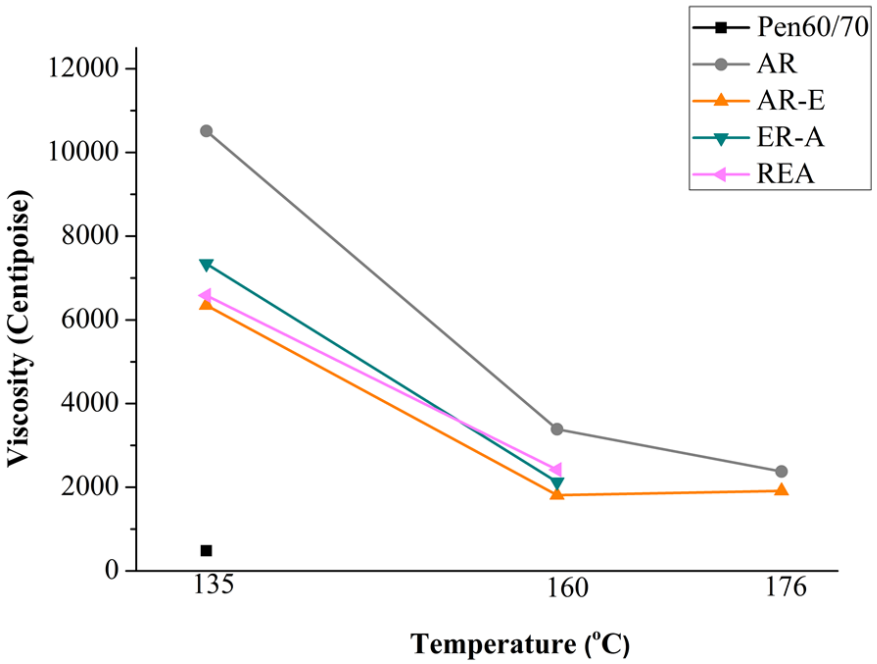


Fig. 3 Rotational viscosity test results

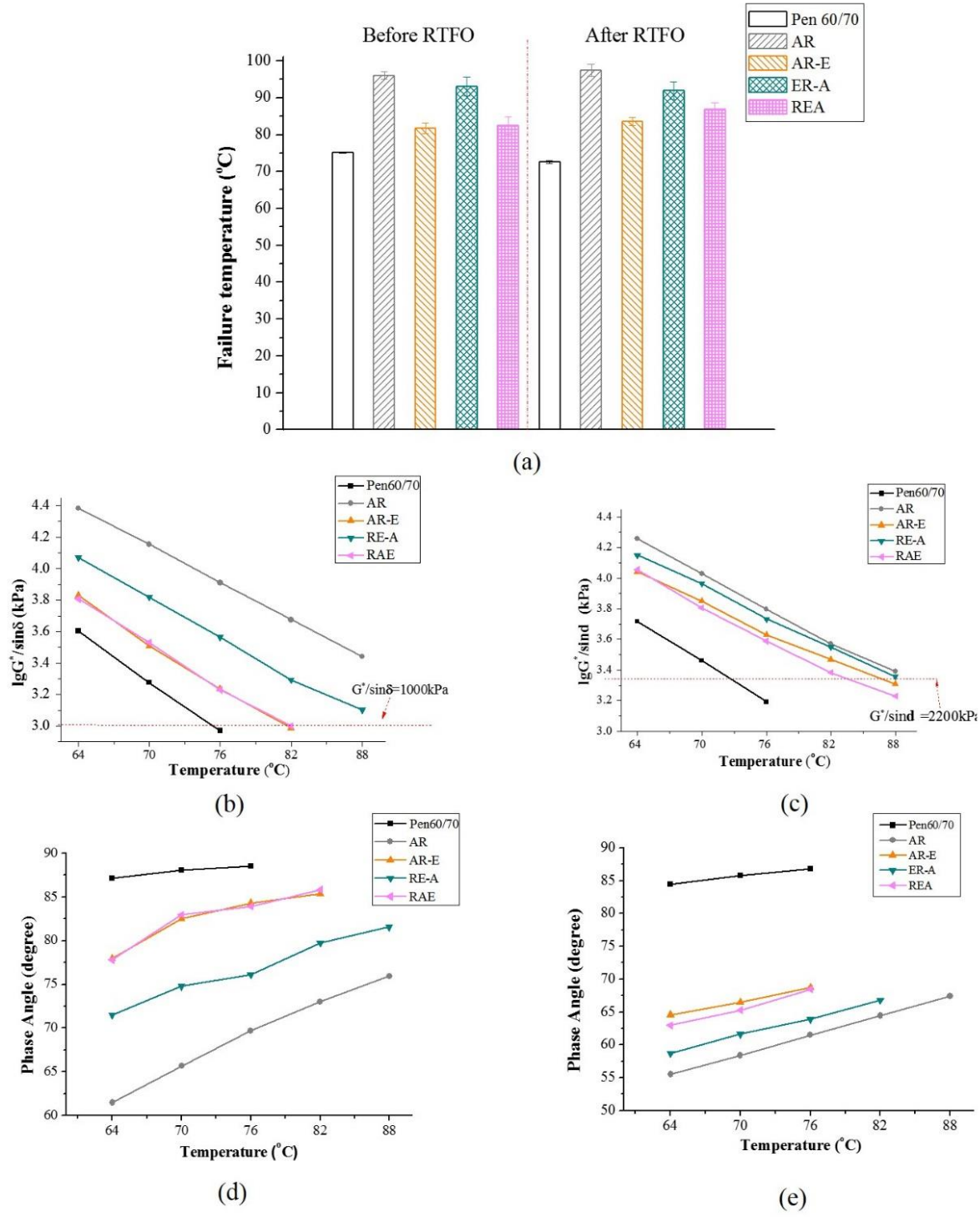
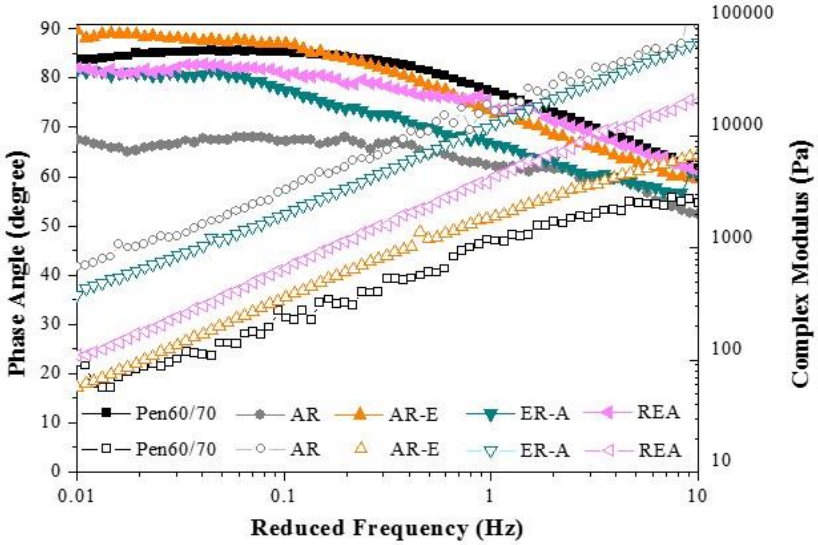
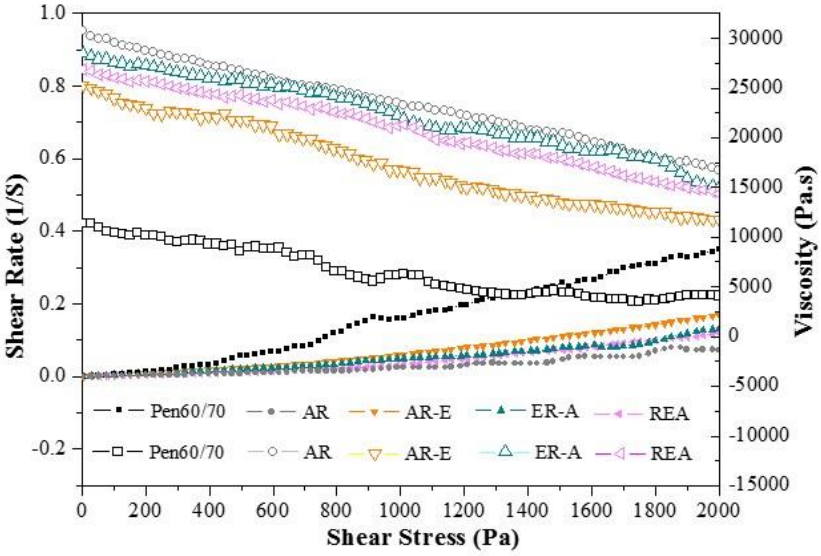


Fig. 4 High-temperature test results: (a) failed temperature; (b) rutting factor (unaged samples) (c) rutting factor (RTFO samples); (d) phase angle (unaged samples); (e) phase angle (RTFO samples)

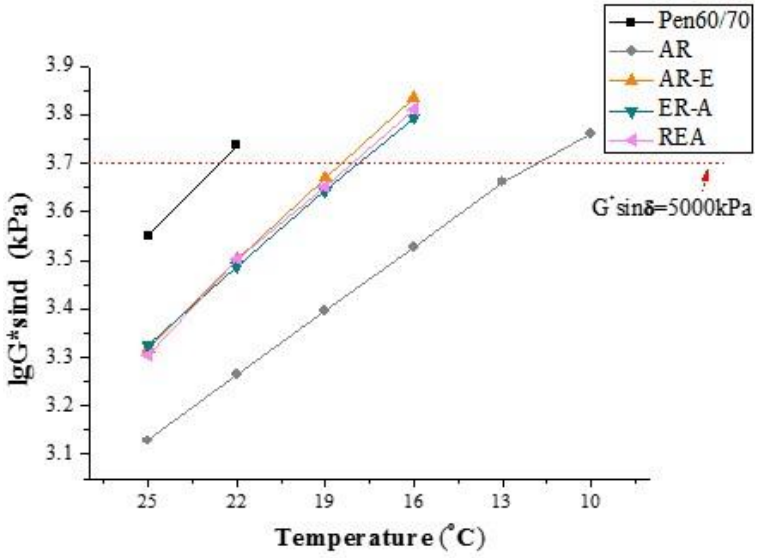


(a)

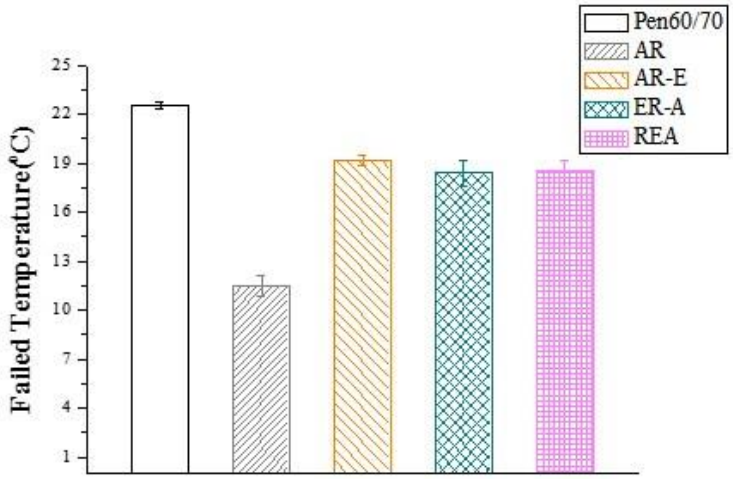


(b)

Fig. 5 Rheological performance at high temperature: (a) frequency sweep test results; (b) viscus flow test results

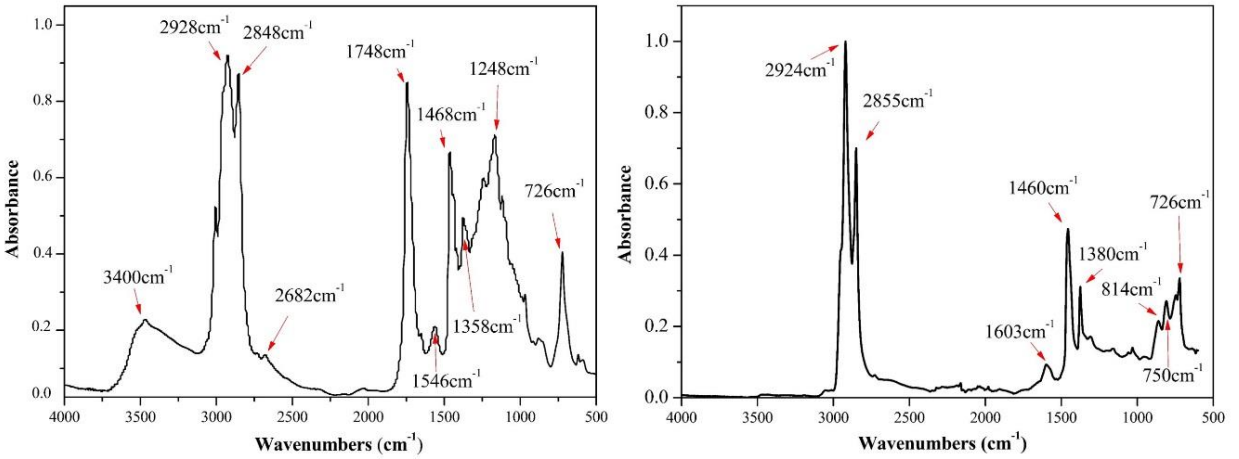


(a)



(b)

Fig. 6 Rheological performances at intermediate-temperature: (a) fatigue factor versus temperature; (b) failure temperature



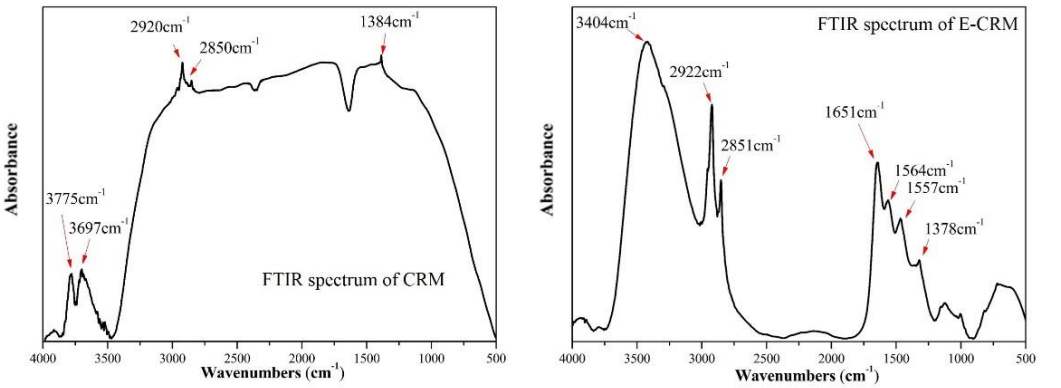
Main functional groups in Eovtherm-DAT:

3400 cm^{-1} (O-H or N-H stretching vibration of hydrogen-bonded hydroxyl and amino groups), 2928 cm^{-1} (asymmetric C-H stretching vibration of methylene group), 2848 cm^{-1} (symmetric C-H stretching vibration of methylene group), 2682 cm^{-1} ($N\text{-}H^{+}$ stretching vibration of amine ions), 1748 cm^{-1} (C=O stretching and C-O of carboxylic groups), 1546 cm^{-1} (asymmetric N-O stretching of nitro group), 1468 cm^{-1}($\text{-}CH_2\text{-}$ scissor vibration of methylene group), 1358 cm^{-1} (symmetric SO_2 stretching of sulphone group), 1248 cm^{-1} (C-O stretching and carboxylic group), and 726 cm^{-1} (C-C rocking vibration of alkane groups);

Main functional groups in Pen 60/70 base binder:

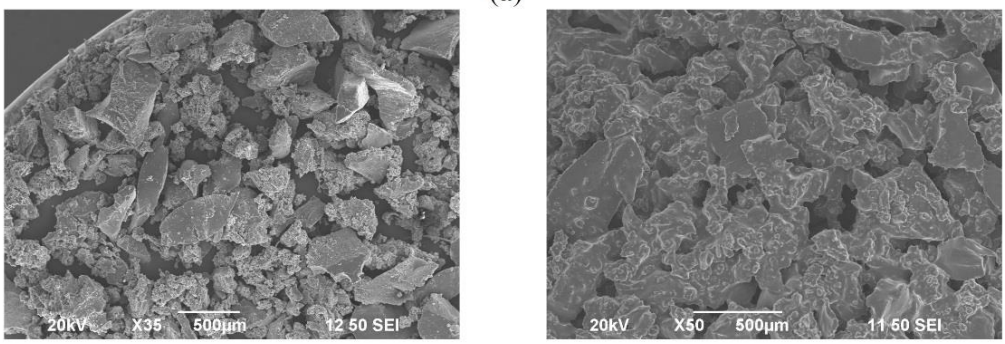
2924 cm^{-1}(asymmetric C-H stretching vibration of methylene group), 2855 cm^{-1} (symmetric C-H stretching vibration of methylene group), 1603 cm^{-1} (C=C stretching vibration of conjugated vinyl group), 1460 cm^{-1} ($\text{-}CH_2\text{-}$ scissor vibration of methylene group), 1380 cm^{-1} (C-H symmetric deformation vibration of methyl group), 1312 cm^{-1} (C-H symmetric deformation vibration of sulfide-methyl group), 814 cm^{-1}(=C-H out-of-plan deformation of vinyl group), 750 cm^{-1} (C-Cl stretching of organic choline) and 726 cm^{-1}(C-C rocking vibration of alkane groups).

Fig. 7 FTIR spectrums of Eovtherm-DAT (left) and Pen60/70 (right)



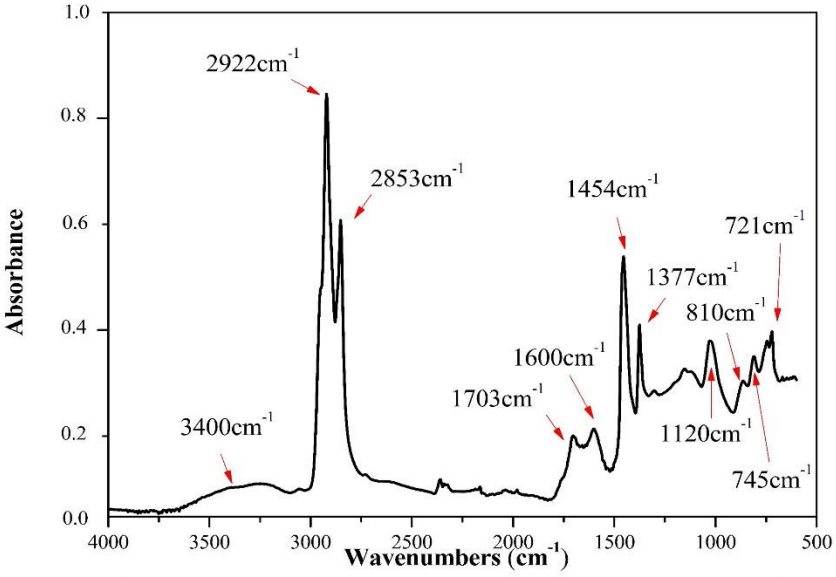
Main functional groups in CRM:
3775 cm^{-1}(O-H stretching of none hydrogen-bonding primary alcohols), 3697 cm^{-1} (N-H stretching of none hydrogen-bonding primary amines), 2920 cm^{-1} (asymmetric C-H stretching vibrations of methylene group), 2850 cm^{-1} (symmetric C-H stretching vibrations of methylene group) and 1384 cm^{-1} (C-H deformation of methyl group);
Main functional groups in E-CRM:
3404 cm^{-1}(O-H or N-H stretching vibration of hydrogen-bonded hydroxyl and amino groups), 2922cm^{-1} (asymmetric C-H stretching vibrations of methylene group), 2851 cm^{-1}(symmetric C-H stretching vibrations of methylene group), 1651 cm^{-1} (C=O stretching of secondary amides), 1564cm^{-1} (asymmetric vibration of carboxylic acid salts), 1557cm^{-1} (N-H vibration of hydrogen-bonded *trans*-form amides), 1378cm^{-1} (C-H deformation of methyl group).

(a)



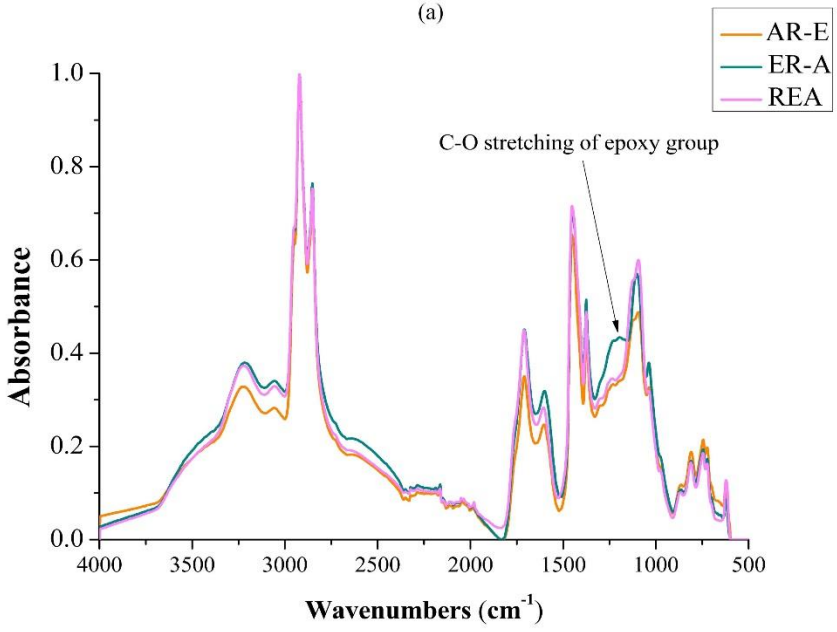
(b) (c)

Fig. 8 FTIR and SEM analysis of CRM and E-CRM: (a) FTIR spectrums of CRM (left) and E-CRM (right); (b) SEM images of CRM (left) and E-CRM (right)



Main functional groups in AR:
3400 cm^{-1} (O-H stretching vibration of hydrogen-bonded hydroxyl group),
2922 cm^{-1} (asymmetric C-H stretching vibrations of methylene group),
2853 cm^{-1} (symmetric C-H stretching vibrations of methylene group),
1703 cm^{-1} (C=O stretching of carbonyl group),
1600 cm^{-1}(C=C stretching vibration of conjugated vinyl group),
1454 cm^{-1} (-CH_2- scissor vibration of methylene group),
1377 cm^{-1} (C-H deformation of methyl group),
1120cm^{-1} (C-O-C asymmetric stretch of esters),
810 cm^{-1}(=C-H out-of-plan deformation of vinyl group),
745 cm^{-1} (C-Cl stretching of organic choline) and
721 cm^{-1} (C-C rocking vibration of alkane groups).

(a)



(b)

Fig. 9 FTIR spectrums of test binders: (a) AR; (b) three Evo-ARs

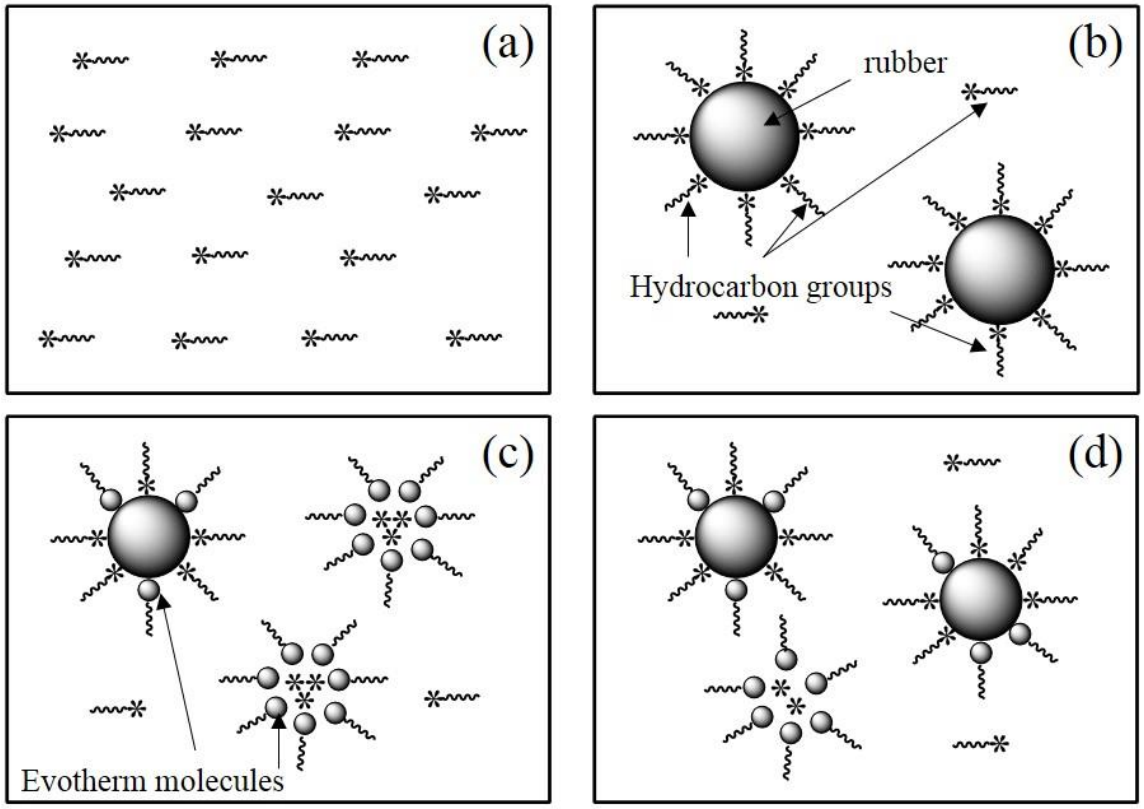


Fig. 10 Micro models for components in Evo-ARs

Tab. 1 MSCR test results

ID	J_{nr}			%Recovery		Traffic level
	0.1k/Pa	3.2k/Pa	J_{nr} %Diff	0.1k/Pa	3.2k/Pa	
Pen60/70	3.172	3.473	9.42	5.41	2.07	S
AR	0.151	0.288	91.7	71.8	54.2	E
AR-E	0.311	1.360	339	70.0	34.1	H
ER-A	0.174	0.44	153	75.0	61.3	E
REA	0.412	1.260	206	67.7	34.9	H

523 Tab. 2 BBR test results

	-12 °C		-18 °C		-24 °C	
Binder	Stiffness	m-value	Stiffness	m-value	Stiffness	m-value
Pen 60/70	201	0.318	317	0.245	522	0.152
AR	109	0.346	213	0.283	406	0.188
AR-E	127	0.323	181	0.269	439	0.201
ER-A	165	0.347	202	0.291	433	0.192
REA	115	0.305	168	0.276	383	0.248

524

525