

1 **Effect of different viscous rejuvenators on chemical and mechanical behavior of aged and**  
2 **recovered bitumen from RAP**

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17 **Abstract:** Due to scarcity of virgin natural materials, the use of reclaimed asphalt pavement (RAP)  
18 has been promoted and encouraged in the pavement engineering. However, note that the  
19 bituminous binder in RAP has been seriously aged due to long-term service exposure to the  
20 atmosphere. It is thus paramount to effectively restore the properties of RAP by adding a proper  
21 rejuvenator. In this study, five rejuvenators were designed with different viscosities and applied to  
22 rejuvenate the aged binder. The changes in chemical compositions of bitumen caused by ageing  
23 and rejuvenating were evaluated by a SARA (Saturate, Aromatic, Resin and Asphaltene) analysis  
24 method. Brookfield viscosity, Dynamic Shear Rheometer (DSR) and Direct Tension (DT) were  
25 further conducted to evaluate the physical and mechanical properties of bituminous binders.  
26 Surface Free Energy test was applied to characterize the adhesion and moisture damage behavior  
27 of aged and rejuvenated binders. The experimental results showed that the ageing process  
28 increased resins and asphaltenes, which in turn improved the colloidal stability of the aged binder.  
29 The five rejuvenators designed in this research had a similar effect in restoring the rheological  
30 properties and stiffness of the aged bitumen to a similar level as that of the virgin binder. However,  
31 the rejuvenator viscosity had different impacts on tensile elongation at break, brittle fracture stress,  
32 adhesion property and moisture resistance of the rejuvenated binders, in which the rejuvenator  
33 with an optimal viscosity may obtain the best rejuvenating performance.

34 **Keywords:** Reclaimed asphalt pavement; Ageing; Rejuvenator; Chemical composition; Rheology

35 **1. Introduction**

36 In flexible pavements, the most widely used road material, hot mix asphalt (HMA), has to sustain

37 repeated traffic loading and environmental attacks during its service life, which always results in  
38 distresses, such as cracking and rutting [1][2]. When its performance is deteriorated to a certain  
39 level, the HMA pavement surface has to be removed and reconstructed, and reclaimed asphalt  
40 pavement (RAP) is then generated [3][4]. Statistically, the total RAP generation is reached up to  
41 220 million tons in China and this data is still increasing year by year [5]. At the same time, a huge  
42 demand of HMA is needed for rapid road construction, which is to be produced and consumed  
43 more non-renewable natural resources, such as aggregate and bitumen. With the increasing  
44 awareness of environmental protection and sustainable development, the use of recycled  
45 materials in pavements (i.e. RAP) has been promoted and encouraged by many countries [6][7],[8].

46 Different from new HMA, the binder in RAP is highly aged due to its long-term exposure to the  
47 atmosphere [9][10]. The main mechanism of bitumen ageing are the combined effect of oxidative  
48 condensation and light components evaporation, which results in noticeable changes in bitumen  
49 compositions (i.e. resins and asphaltenes) and mechanical properties (increased viscosity and  
50 stiffness) [11][12]. For the hot-mix recycling, in practice adding a low rate (less than 20%) of RAP  
51 has a minimum effect on the mechanical performance of the final asphalt mixture [13]. However,  
52 when incorporating a significant amount of RAP (more than 30%), the produced HMA has  
53 potentially higher susceptibility to raveling and cracking [14][15]. Therefore, it seems important to  
54 compensate the deteriorated mechanical properties of the RAP binder by selecting a proper  
55 rejuvenator in order to avoid premature distresses of the recycled HMA.

56 In chemical terms, the bitumen components can be classified into four fractions based on their  
57 molecular size and solubility, which are SARA (Saturates, Aromatics, Resins, and Asphaltenes) [16].  
58 The internal structure of bitumen is a stable colloidal suspension system where asphaltenes  
59 dispersed in maltenes (saturates and aromatics) with resins act as a peptizing agent [17]. Because  
60 of the ageing effect, some aromatics evolve into resins, which in turn generate asphaltenes. Finally,  
61 the aged binder results in reduction in the aromatics content and an increase in the resin and  
62 asphaltenes content, in which the saturates content approximately remains unchanged [18]. With  
63 respect to the mechanical point of view, the ageing effect increases the binder viscosity as a result  
64 of the increases of polar components, especially asphaltenes [19][20]. In addition, variations in  
65 polar fractions of bitumen are also responsible for the increment of complex shear modulus at low  
66 frequency/high temperatures [21]. It is acknowledged that ageing process results in changes in  
67 chemical composition of bitumen, which in turn leads to variations in rheological and mechanical  
68 performance.

69 More researches have investigated the feasibility of using rejuvenators to restore properties of the  
70 aged binder with the view of increasing the RAP usage in recycling asphalt mixtures. Normally,  
71 rejuvenators can be defined as softening additives or recycling agents, which help to restore  
72 mechanical properties of the aged binder [22][23]. The addition of rejuvenators softens the aged  
73 binder by increasing the maltenes content, which in turn reduces its stiffness and increases its  
74 ductility. Based on previous researches, several types of materials including plant oils, waste-  
75 derived oils as well as refinery-based oils have the possibility to be used as rejuvenators [10],[24].  
76 Mangiafico et al. [25] investigated the influence of bio-based oil on properties of the recycled HMA,  
77 and their results indicated that the bio-based oil reduced the complex modulus and enhanced the  
78 fatigue performance of the recycled HMA with a high RAP content. Another study suggested that  
79 vegetable oil and maltene obtained similar effect on flowability improvement of highly aged

80 binders, while the aged binder rejuvenated by vegetable oil has the best thermal behavior [26].  
 81 However, it should be noticed that the vegetable oil might cause high moisture susceptibility of the  
 82 recycled HMA and adhesion enhancing additive might be necessary to be incorporated [27].  
 83 Recycled motor oils were also employed as rejuvenators and suggested that the recycled HMA  
 84 rejuvenated by recycled motor oil reduced the mixing temperature and postponed the permanent  
 85 deformation [28]. Asli et al. [29] investigated the novelty of using waste cooking oil to rejuvenate  
 86 aged binders. The results indicated that the waste cooking oil not only reduced the ratio of  
 87 Asphaltenes/Maltenes, but also rejuvenated physical properties of the RAP binder. Composite  
 88 castor oil and pongamia oil were selected to restore properties of aged binder and revealed that  
 89 the rejuvenated binder obtained similar rutting resistance and better fatigue resistance than that  
 90 of the virgin binder [30]. In summary, it is a consensus that incorporating rejuvenators might be an  
 91 effective method to promote the application of RAP materials in the HMA production. However,  
 92 all the studies abovementioned mainly focused on the restoring effect of different rejuvenators on  
 93 the properties of aged binders and recycled mixtures. A systematic exploration of the influence of  
 94 the rejuvenator's viscosity on chemical compositions, rheological and mechanical properties of  
 95 aged binders is still absent. Therefore, there is a need to explore the influence of rejuvenators with  
 96 different viscosities on the comprehensive performance of aged binders.

97 In this study, five rejuvenators designed with different viscosities were applied to restore the  
 98 properties of aged binder. The changes in chemical compositions caused by ageing and  
 99 rejuvenating were explored by the SARA fractionating method. Viscosities of bituminous binders,  
 100 rejuvenators as well as rejuvenated binders at different temperatures were characterized through  
 101 Brookfield viscosity test. Dynamic Shear Rheometer (DSR) and Direct Tension (DT) tests were  
 102 performed to evaluate the rheological property and fracture resistance of bituminous binders,  
 103 respectively. In order to understand the adhesion behavior and moisture sensitivity of the  
 104 rejuvenated bitumen, Surface Free Energy test was conducted to evaluate the bonding properties  
 105 of the aggregate-bitumen interface.

106 **2. Materials and experimental methods**

107 **2.1 Materials**

108 One type of virgin bitumen with a penetration grade of 70 dmm was supplied by Sinopec Qilu  
 109 Petrochemical Company. Laboratory ageing acceleration methods were applied to simulate the  
 110 ageing process of bituminous binder at different stages. The virgin bitumen was first conditioned  
 111 using the Rolling Thin Film Oven Test (RTFOT), which aimed at simulate the short-term ageing  
 112 process during mixing and paving (T0609-2011). After that, the short-term aged binder was further  
 113 subjected to the Pressure Ageing Vessel (PAV) (T0630-2011) method to simulate the long-term  
 114 ageing during service life. Finally, conventional properties of the virgin bitumen and aged bitumen  
 115 were characterized according to the Chinese standards JTG E20-2011 and the results are shown in  
 116 Table 1.

117 Table 1. Conventional physical properties of virgin bitumen and aged bitumen

Physical parameter	Virgin bitumen	ST bitumen	LT bitumen
Softening point (°C)	48.2	56.3	63.3
Penetration (25°C, 0.1mm)	68.3	45.3	19.8
Ductility (15°C, cm)	>150	41.4	5.45

Dynamic viscosity (60°C, Pa • s)	235	408	1453
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118 In order to clarify the influence of rejuvenator's viscosity on the final performance of rejuvenated  
 119 aged binders, five rejuvenators were first designed with different viscosities. There are three  
 120 original materials which including aromatic oil, plasticizer and anti-stripping agent were selected  
 121 to prepare the primary formulation of rejuvenator [31]. The mass ratio of these three materials  
 122 was determined to be aromatic oil : plasticizer : anti-stripping agent = 100 : 10 : 2. In addition,  
 123 different dosages of 110 pen soft virgin bitumen was incorporated into the primary formula  
 124 rejuvenator to obtain rejuvenators with different viscosity level. The blending ratios of soft bitumen  
 125 in primary formula rejuvenator were determined to be 10%, 20%, 30%, 40% and 50%. Finally, the  
 126 viscosities of the designed rejuvenators are presented in Table 2.

127 Table 2. Viscosity of rejuvenators at different temperatures

Rejuvenator	R1	R2	R3	R4	R5
Brookfield viscosity (60°C, Pa • s)	0.1080	0.1500	0.2170	0.3200	0.5150
Brookfield viscosity (90°C, Pa • s)	0.0045	0.0095	0.0185	0.0615	0.0915

128 For using rejuvenators in the aged binder, they need to be incorporated and homogeneously mixed  
 129 with the aged bitumen to obtain rejuvenated binders. As the RAP materials collected from the  
 130 onsite road normally experiences a long period of service life, the long-term aged bitumen  
 131 conditioned by PAV was selected in this research. The rejuvenator's dosage was primary calculated  
 132 based on the Equation 1 (JTG F41-2008) before conducting any other tests. Then by adjusting, the  
 133 optimal dosage of rejuvenators was determined based on two experimental parameters  
 134 (penetration and Brookfield viscosity at 90°C) of the rejuvenated binder. Finally, the optimal  
 135 dosages of these five rejuvenators which can restore the long-term aged bitumen to the target  
 136 properties of the virgin bitumen were obtained, as shown in Table 3.

$$137 \lg \lg \eta_{mix} = (1 - \alpha) \lg \lg \eta_{old} + \alpha \lg \lg \eta_{new} \quad (1)$$

138 Where,  $\eta_{mix}$  is the viscosity of the rejuvenated binder at 60°C (Pa • s);  $\eta_{old}$  is the viscosity of the  
 139 aged binder at 60°C (Pa • s);  $\eta_{new}$  is the viscosity of the rejuvenator at 60°C (Pa • s);  $\alpha$  is the  
 140 dosage of the rejuvenator.

141 Table 3. Optimal dosage of rejuvenators to restore long-term aged binder

Rejuvenator	R1	R2	R3	R4	R5
Optimum dosage (%)	8	10	12	14	17

## 142 2.2 Experimental methods

### 143 2.2.1 Conventional bitumen performance tests

144 The softening points, penetration and ductility of the rejuvenated bitumen and virgin bitumen  
 145 were measured by the Ring & Ball test, needle penetration and ductility test (according to JTG E20-  
 146 2011). Brookfield rotational viscometer was used to evaluate the high-temperature viscosity of  
 147 bituminous binders before and after rejuvenating (ASTM D4402).

### 148 2.2.2 SARA test and colloidal index

149 SARA (Saturate, Aromatic, Resin and Asphaltene) fractioning method was used in this research to  
 150 characterize the chemical composition of the virgin bitumen, the aged bitumen as well as the

151 rejuvenated binders. Due to different solubilities of bitumen components in n-heptane, bitumen  
152 can be conveniently fractionated into maltenes and asphaltenes. The maltenes including saturates,  
153 aromatics and resins, can be further fractionated by liquid adsorption chromatography using alumina  
154 as the adsorbent and a solvent containing 1wt% distilled water. The detailed description of the  
155 SARA fractioning method can be found elsewhere [32]. Based on the steric colloidal model  
156 presented by Park [33], the asphaltenes exist in the form of suspended particles with some of the  
157 resins adsorbed on their surfaces to keep the asphaltenes in suspension. Other resins are dissolved  
158 in the oil phase to prevent the flocculation of the asphaltene structures.

159 With the view of estimating the structure stability of bitumen, the colloidal index (CI) was  
160 introduced to calculate the ratio between combined contents of asphaltenes and “floculent”  
161 agents and “peptizing” agents [34], as shown in Equation 2. Based on Lesueur [16], common  
162 bitumen tends to have CI values in the range between 0.5 and 2.7. In addition, binders with CI value  
163 less than 0.7 exhibit typical sol-type behavior, while they are evident gel-type if CI is higher than  
164 1.2.

$$165 \quad CI = \frac{X_{asphaltenes} + X_{saturates}}{X_{aromatics} + X_{resins}} \quad (2)$$

166 Where,  $X_i$  is the mass content of the bitumen fraction “i”.

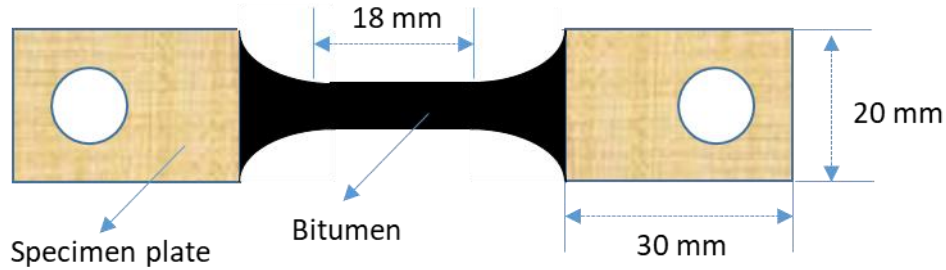
### 167 2.2.3 Dynamic shear rheometer test

168 Rheological properties of bituminous binders can be expressed by a complex shear modulus  $G^*$   
169 which is composed of storage modulus ( $G'$ ) and loss modulus ( $G''$ ). The rheological parameters of  
170 bitumen can be evaluated through sinusoidal loading within a linear visco-elastic range by using  
171 dynamic shear rheometer (DSR). In this research, temperature sweep test was performed at a  
172 constant frequency of 10 rad/s in the temperature range of 30°C-70°C with an increment of 10°C.  
173 Following the procedure in JTG E20-2011, disc shaped bitumen samples with a diameter of 25 mm  
174 were first prepared by silicon moulds. The 25 mm parallel geometry plate with 1 mm gap was  
175 selected and the strain control mode was used for testing. Parameters including complex modulus  
176 ( $G^*$ ) and phase angle ( $\delta$ ) were measured and recorded with the temperature increase. The  $G^*$  is  
177 the ratio of maximum shear stress to maximum shear strain which represents the resistance of  
178 bitumen to deformation [35]. The  $\delta$ , is the time delay between the applied stress and the measured  
179 strain which represents the visco-elastic balance of the measured bitumen [36].

### 180 2.2.4 Direct Tension test

181 As previously mentioned, the ageing effect can make the RAP binder stiff and brittle, and the  
182 recycled mixtures containing RAP binder has potentially higher susceptibility to crack. So, it is  
183 essential to evaluate the fracture resistance of the rejuvenated binders and compared with the  
184 reference binder. The Direct Tension (DT) test was performed to evaluate the fracture properties  
185 of binders at low temperature (ASTM D6732-02). Figure 1 presents the schematic of the specimen  
186 used for DT test. Samples were prepared by pouring hot bitumen in aluminum molds, which is  
187 similar as the specimen preparation procedure for the bitumen ductility test. The DT test in this  
188 research was performed at -15°C with the temperature controlled by a cooling bath using methyl  
189 acetate solution. Before testing, the prepared samples were conditioned in the cooling bath for 1  
190 h to reach temperature balance. Subsequently, samples were installed on the loading rack by a

191 special clamp. Finally, a horizontal load was applied with a constant displacement of 1 mm/min till  
 192 the sample was fractured. Parameters such as elongation at break, breakdown stress as well as the  
 193 original stress-strain data can be automatically recorded by the equipment.



194  
 195 Figure 1. Schematic of the binder specimen used for DT test

196 2.2.5 Surface energy test and moisture damage evaluation

197 The ageing and rejuvenating process significantly influence the chemical composition of  
 198 bituminous binders, which in turn effect their surface energy components. The Sessile Drop  
 199 Method was applied to measure the contact angle of specific probe liquids on the bitumen surface  
 200 and the results were then used to calculate the surface energy of bitumen, as shown in Figure 2.  
 201 During testing, a small drop of liquid which has certain surface energy components was first  
 202 dispensed on the bitumen glass slide. Digital images of the drops were then captured and the  
 203 contact angle values were measured automatically with the help of inbuilt software. Three probe  
 204 liquids including water, glycerol and di-iodomethane were selected in this research to measure  
 205 their contact angle with the bitumen. The obtained contact angle values and the surface energy  
 206 components of probe liquid were then applied to the Young-Dupre equation for the work of  
 207 adhesion ( $W_{SL}$ ) between the two materials:

208 
$$W_{SL} = \gamma_L(1 + \cos\theta) = 2\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + 2\sqrt{\gamma_S^-\gamma_L^+} + 2\sqrt{\gamma_S^+\gamma_L^-} \quad (3)$$

209 where,  $\theta$  is the contact angle between probe liquid and bitumen, S represents the solid bitumen,  
 210 L represents the probe liquid,  $\gamma^{LW}$  is the Lifshitz-van der Waals component of the surface energy,  
 211  $\gamma^+$  is the Lewis acid component of surface interaction,  $\gamma^-$  is the Lewis base component of  
 212 surface interaction.

213 The three surface energy components ( $\gamma^{LW}, \gamma^+, \gamma^-$ ) of bitumen were finally determined by solving  
 214 three equations with known contact angle values and surface energy components of three probe  
 215 liquids.

216 In order to evaluate the adhesion property of aggregate-bitumen interface, the surface energy  
 217 components of two aggregates (Limestone and Granite) were cited from the other publication [37],  
 218 as shown in Table 4. The work of adhesion of the aggregate-bitumen interface, referred to the work  
 219 done to create a new unit area of fracture, can be calculated based on Equation 4.

220 
$$W_{BA}^a = 2\sqrt{\gamma_B^{LW}\gamma_A^{LW}} + 2\sqrt{\gamma_B^+\gamma_A^-} + 2\sqrt{\gamma_B^-\gamma_A^+} \quad (4)$$

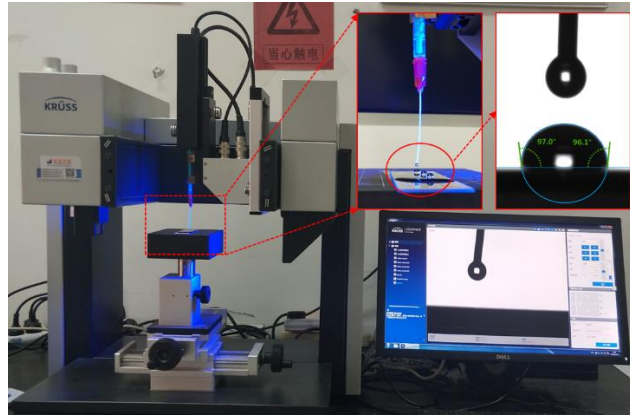
221 where  $W_{BA}^a$  is the work of adhesion between aggregate (A) and bitumen (B).

222 When water penetrated into the aggregate-bitumen interface, the work of adhesion for two

223 materials in contact with a third medium can be explained by Equation 5. This parameter  
 224 represents the reduction in bond strength of an aggregate-bitumen system when water displaces  
 225 the bitumen from the aggregate surface.

$$226 \quad W_{BWA}^a = -\Delta G_{BWA}^a = \gamma_{BW} + \gamma_{WA} - \gamma_{BA} \quad (5)$$

227 where subscript A, B and W represent aggregate, bitumen and water, respectively.



228  
 229 Figure 2. KRUSS Drop Sharp Analysis equipment

230 Table 4. Surface energy components of aggregates [23]

Aggregate	Surface energy component (mJ/m <sup>2</sup> )			
	$\gamma^{LW}$	$\gamma^+$	$\gamma^-$	$\gamma$
Limestone	82.2	6.7	59.3	122
Granite	68	163.9	122.7	351.6

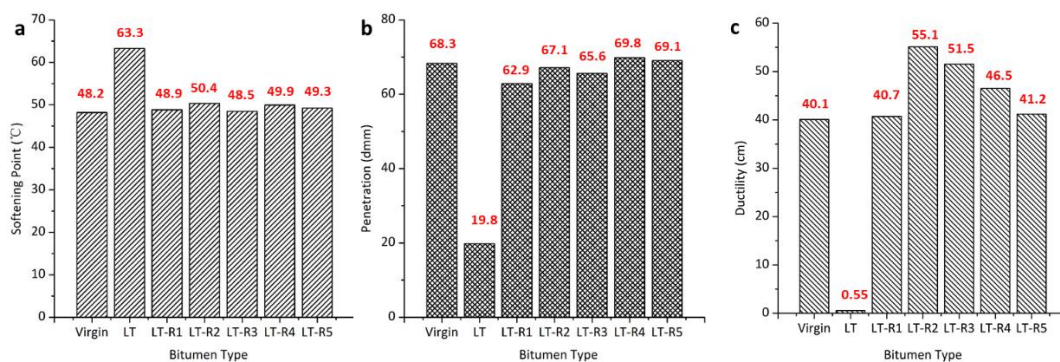
231 **3. Results and Discussion**

232 3.1 Conventional properties of virgin, aged and rejuvenated binders

233 The conventional physical parameters of bituminous binders including softening point, penetration  
 234 and ductility, were measured and the results are shown in Figure 3. As shown in Figure 3(a), the  
 235 long-terms ageing process increased the softening point of the virgin bitumen from 48.2°C to  
 236 63.3°C. By adding rejuvenators determined in Section 2, the softening point of the aged bitumen  
 237 was reduced and nearly restored to similar level as that of the virgin bitumen. It was noticed that  
 238 the long-term ageing declined the bitumen penetration from 68.3 dmm to 19.8 dmm, as shown in  
 239 Figure 3(b). The incorporation of rejuvenators changed the penetration grade of the aged bitumen  
 240 to resemble the virgin binder. It is known that the oxidation reaction makes the bitumen stiff and  
 241 incorporating rejuvenators can soften the aged binder. By comparing five rejuvenated binders, all  
 242 rejuvenators with different viscosities can reduce the stiffness of the aged bitumen and obtain  
 243 identical results. Because the ductility results of the virgin and rejuvenated binders are all greater  
 244 than 150 cm at 15°C, the ductility test was performed at 10°C in order to obtain different  
 245 responses as shown in Figure 3(c). The ductility of the aged bitumen dropped to only 0.55 cm due  
 246 to the long-term ageing, indicating brittle behavior of the aged bitumen. The addition of  
 247 rejuvenators improved the ductility of the aged bitumen and their ductility reached and even  
 248 surpassed that of the virgin binder. It is noticed that, with the increase of rejuvenator's viscosity,  
 249 the ductility of the rejuvenated binder first increased followed by declining after reaching the top

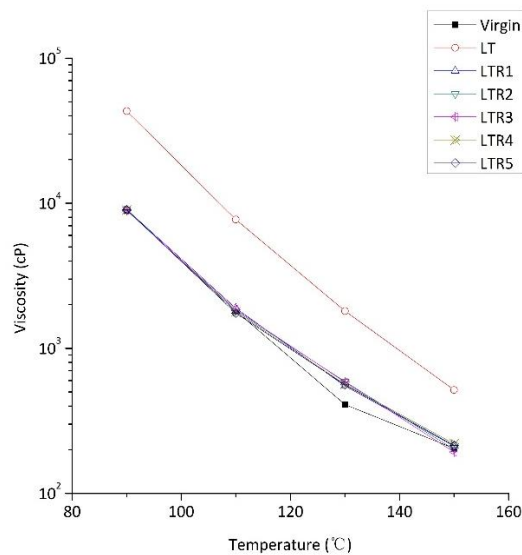
250 value at LT-R2. The rejuvenator with a proper viscosity can achieve better contribution to the  
 251 improvement of ductility.

252 Figure 4 presents the viscosity results of the bituminous binders in the temperature range of 90 °C  
 253 -150 °C, which were determined by the Brookfield rotational viscometer. As this temperature range  
 254 is correlated with the mixing and paving temperature of the HMA, the viscosity of binders at this  
 255 temperature directly affects the performance of asphalt pavement. As shown in Figure 4, the  
 256 viscosity of the long-term aged binder was obviously higher than that of the virgin binder. If RAP  
 257 materials were incorporated to produce recycled HMA, the aged binder with a higher viscosity  
 258 must influence the flowability and compaction of hot mixture. Overlapped curves of the virgin  
 259 bitumen and rejuvenated binders implies that different viscous rejuvenators had same effect to  
 260 restore the viscosity of bituminous binders.



261

262 Figure 3. Conventional properties of bitumen: (a) Softening point; (b) Penetration; (c) Ductility



263

264 Figure 4. Viscosity of bituminous binders at different temperatures

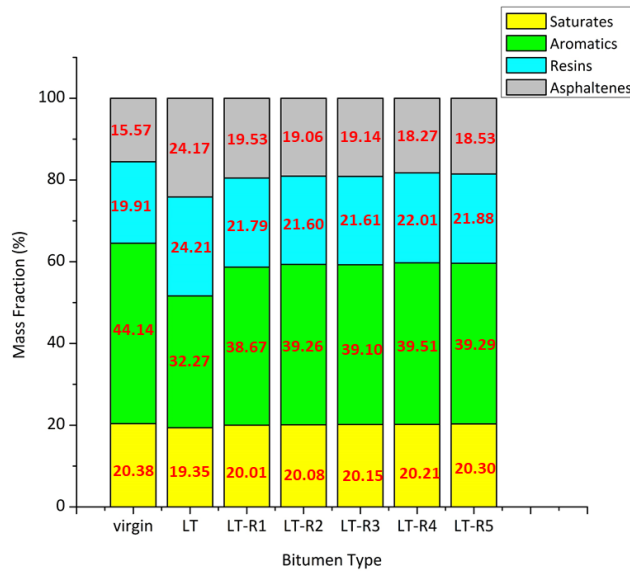
### 265 3.2 Chemical composition of virgin, aged and rejuvenated binders by SARA fractionation

266 In order to explore how the ageing and rejuvenating process influence the overall chemical  
 267 composites and their contribution to mechanical properties of bitumen, SARA fraction test was  
 268 conducted. Chemical fractions of virgin, aged and rejuvenated binders are shown in Figure 5. After



269 long-term ageing, the aromatic fraction was decreased from 44.14% to 32.27%, while the resin and  
 270 asphaltene fraction contents increased with values increased by about 4.5% and 9.5%, respectively.  
 271 This phenomenon is consistent with Dehouche's research [32] that ageing reduces the content of  
 272 aromatics which are in turn converted to resins and asphaltenes. However, the saturates content  
 273 is almost constant even after long-term ageing. The chemical variations, including decrease of  
 274 aromatics and increase of asphaltenes, are responsible for the stiffening and hardening effect of  
 275 the aged bitumen. Adding rejuvenators lowered the fractions of asphaltenes and resins in  
 276 comparison with the aged binder, while it can increase the fractions of aromatics, to some extent.  
 277 The recovery in chemical composition of the aged bitumen results in the restoring of mechanical  
 278 properties. It should be noticed that none of these five rejuvenators can recover the SARA fractions  
 279 of the aged binder to the same levels as in the virgin bitumen. Also, they had same effect on  
 280 recovering SARA components.

281 With respect to the colloidal index, the CI of the virgin bitumen was 0.561 and the ageing effect  
 282 increased this value to 0.771. This means that the long-term ageing changed the colloidal system  
 283 of the virgin bitumen from more gel-type behavior to be more sol-type behavior. This phenomenon  
 284 also explained the stiffening result of bitumen after ageing. CI values of the rejuvenated binders  
 285 declined from 0.771 to around 0.64 due to the incorporation of rejuvenators. It is noticeable that  
 286 the rejuvenator with a higher viscosity resulted in slightly lower CI value of the rejuvenated binder,  
 287 which behaves more gel-type.



288

289 Figure 5. Influence of rejuvenator's viscosity on chemical components of the aged bitumen

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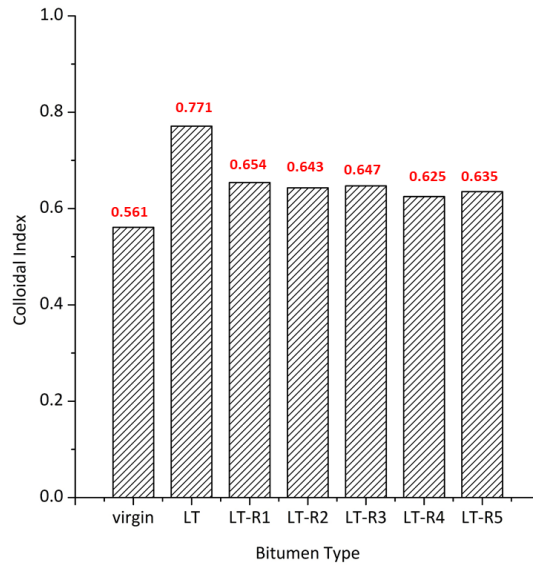
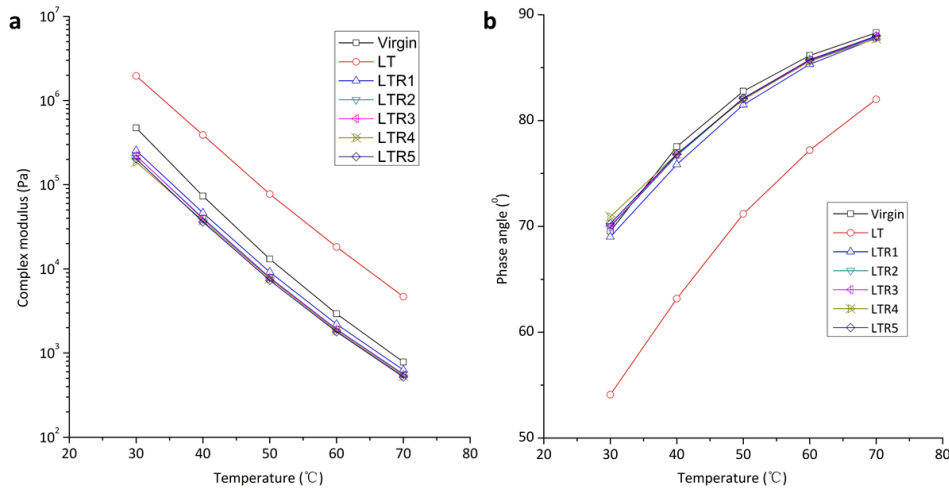


Figure 6. Colloidal index of different binders

### 3.3 Rheological behavior of virgin, aged and rejuvenated binders

In order to characterize the influence of ageing and rejuvenating on rheological properties of bitumen, temperature sweep tests was conducted at a constant frequency by using DSR, and the results are shown in Figure 7. As can be seen, the rheological properties of bituminous binders showed significant temperature dependence, with the complex modulus reducing and the phase angle increasing as the growth of testing temperature. The long-term aged binder has the highest complex modulus and the lowest phase angle in comparison with other binders. It is suggested that the bitumen after ageing condition behaves elastic and stiff. By adding rejuvenators, the complex modulus decreased and the phase angle increased for all rejuvenated binders, indicating a recovery of rheological properties of the aged binder. Complex modulus curves of rejuvenated binders are nearly overlapped and their values are slightly lower than that of the virgin bitumen. With respect to phase angle, the plots of rejuvenated binders were nearly overlapped with the virgin bitumen. This phenomenon indicated that the viscosity of the used rejuvenator had less effect on recovery of the rheological properties of the aged bitumen at moderate and high in-service temperatures.

The rheological development shown in Figure 7 can be explained by the change of chemical components in the rejuvenated bitumen. Due to long-term ageing, the reduced aromatic fractions and increased asphaltene fractions (as shown in Figure 5) resulted in the increase of stiffness and elasticity. After incorporating rejuvenators, the SARA fractions were supplemented to a certain extent, which in turn lead to recovery of rheological performance. However, as SARA fractions and colloidal index cannot recovered to the same level as that of the virgin binder, the rheological properties of the rejuvenated binders can be also affected.



315

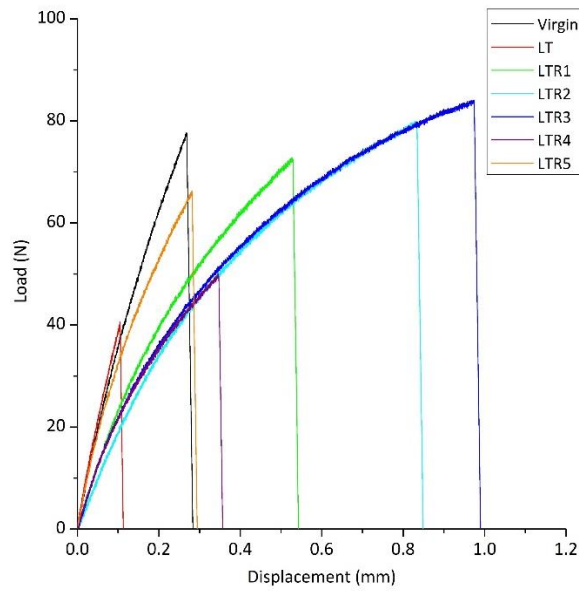
316 Figure 7. Rheological properties of different binders: (a) complex modulus; (b) phase angle

317 3.4 Fracture behavior of virgin, aged and rejuvenated binders at low-temperature

318 Due to the ageing effect, bituminous binders shift from ductile to brittle behavior, and this would  
 319 increase the risk of crack initiation. The fracture resistance of the rejuvenated binder at low in-  
 320 service temperature would thus be a vital parameter to predict the cracking resistance of recycled  
 321 asphalt pavement containing RAP materials. In this section, the direct tension (DT) test was  
 322 conducted to evaluate the fracture resistance of bituminous binders at -15°C. Figure 8 presents  
 323 the force-displacement curves of different binders obtained from the DT tests. The loading force  
 324 first rose gradually with the displacement followed by a cliff descent to crack once the peak loading  
 325 was reached. This indicates that the brittle fracture behavior happens for all binders at this  
 326 temperature level. By comparing virgin and aged binders, the curve of the aged binder shifted to  
 327 the left towards to lower elongation, which suggests less ductility than that of virgin binder. In  
 328 addition, all the curves of the rejuvenated binders shifted to the right indicating recovery of  
 329 ductility of the aged binders.

330 In order to discriminate fracturing resistance of binders at low temperature, a performance index  
 331 - tensile elongation at break - was introduced, and the results are presented in Figure 9. The long-  
 332 term ageing condition reduced the tensile elongation at break of the virgin binder from 0.8% to  
 333 only 0.31%, which made the aged binder more susceptible to low temperature cracking. After  
 334 incorporating rejuvenators, the tensile elongation of rejuvenated binders resulted in varying  
 335 degrees of growth with all of their values higher than that of the virgin binder. In particular, LT-R2  
 336 and LT-R3 obtained relatively higher tensile elongation at break than other rejuvenated binders.  
 337 This implies that under such viscosity, the rejuvenator can be helpful to restore the low-  
 338 temperature fracture behavior. With respect to the fracture stress as shown in Figure 10, the aged  
 339 binder showed lower value than that of the virgin bitumen. The reduced fracture stress could be  
 340 due to the embrittlement of the aged binder, in which stress concentration was more likely to occur.  
 341 The rejuvenated binder obtained increased fracture stress with some of their values higher than  
 342 the virgin binder. It is suggested that fracture strength of the aged binder can be restored by  
 343 selecting a rejuvenator with a proper viscosity, such as R1, R2 and R3. By comprehensive  
 344 considering the results in Figure 9 and Figure 10, it can be deduced that the rejuvenator with too

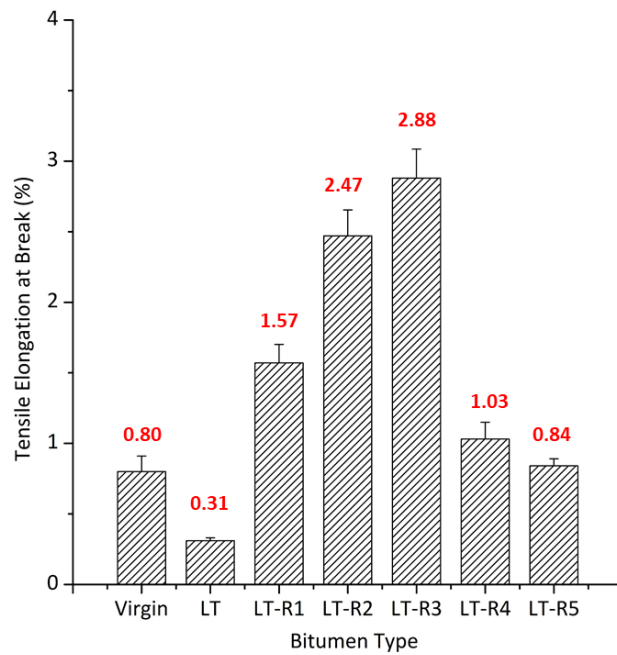
345 high or too low viscosity seems difficult to restore the low temperature properties of the aged  
 346 binder. Based on the DT test, it can be summarized that R2 and R3 resulted in better performance  
 347 in restoring the low temperature performance of the aged binder.



348

349 Figure 8. Force-displacement curves of different binders at -15°C

350



351

352 Figure 9. Tensile elongation at break of different binders at -15°C

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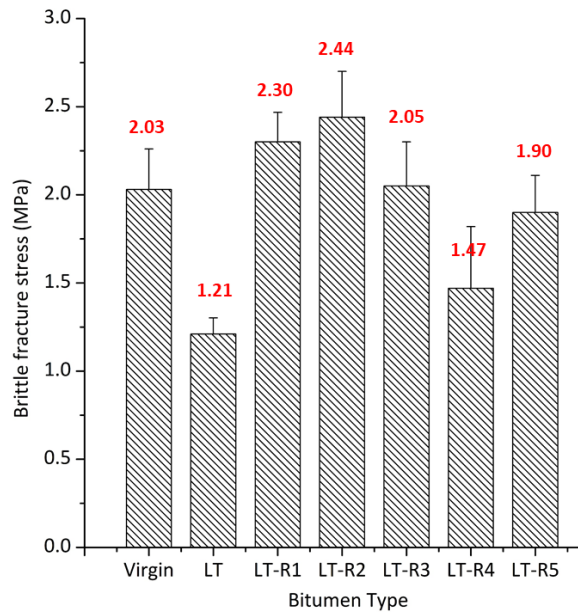


Figure 10. Brittle fracture stress of different binders at -15°C

### 3.5 Surface energy and adhesion property

The contact angle of probe liquids on the binder surface were measured by using the Sessile Drop Method, and then the surface energy components of bituminous binders were calculated based on Young-Dupre equation as shown in Table 5. It can be seen that the long-term ageing slightly increased the  $\gamma^{LW}$  from 31.69 mJ/m<sup>2</sup> to 32.56 mJ/m<sup>2</sup>, and nearly doubled the  $\gamma^-$  value. However, the  $\gamma^+$  had no obvious change with the value declined from 1.50 to 1.29. This is because the ageing process improved the polarity component of the bitumen, as shown in Figure 5, which in turn doubled the Lewis base component of surface interaction.

For the rejuvenated binders, rejuvenators with a lower viscosity (R1 and R2) were difficult to influence the Lifshitz-van der Waals component of the surface energy ( $\gamma^{LW}$ ), while the aged bitumen incorporating R3, R4 and R5 resulted in an obvious increase of  $\gamma^{LW}$  due to relatively higher viscosity of these rejuvenators. The Lewis acid and base components of the rejuvenated binders showed similar trend with increasing the rejuvenator's viscosity, and the highest value existed for LT-R2. The total surface energy values of different binders were calculated and shown in Figure 11. It can be seen that the virgin bitumen had the lowest total surface energy and ageing effect increased this value from 35.75mJ/m<sup>2</sup> to 37.84mJ/m<sup>2</sup>. The addition of rejuvenators improved the total surface energy of the aged binder in varying degrees and the rejuvenated binder LT-R3 obtained the highest value. Based on Equation 4, the work of cohesion of bitumen was twice than the total surface energy of the virgin bitumen. The ageing process can theoretically improve the fracture resistance of bitumen at moderate temperature. Moreover, the incorporation of rejuvenators resulted in further increment in work of cohesion, and LT-R3 exhibited the greatest potential. Such viscosity of rejuvenator is recommended.

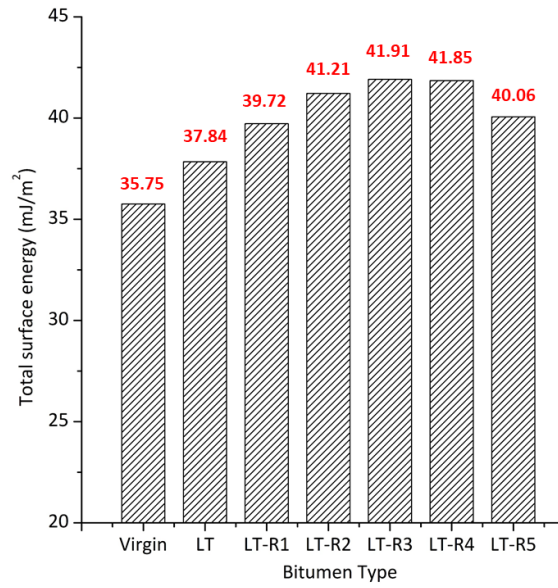
The work of adhesion of aggregate-bitumen interface was calculated with results presented in Figure 12. It can be seen that the work of adhesion was obviously aggregate dependent, in which the granite obtained higher work of adhesion than that of limestone. With respect to the same

381 aggregate, interface combinations with virgin bitumen obtained the lowest work of adhesion and  
 382 the long-term ageing increased this value. As for rejuvenated binders, their work of adhesion seen  
 383 further increase, with LT-R2-granite and LT-R3-limestone obtained the highest value. The increased  
 384 work of cohesion and work of adhesion indicated that the rejuvenator with an appropriate viscosity  
 385 listed in Table 2 can increase the stickiness between the aged bitumen and aggregates, which in  
 386 turn had the positive effect on the mechanical properties of recycled asphalt mixture with RAP  
 387 incorporated.

388 Work of debonding values of different aggregate-bitumen system in the presence of moisture were  
 389 calculated by using Equation 5, and the results are shown in Figure 13. The aggregate-bitumen  
 390 systems with positive work of debonding value means there is no bond strength reduction in wet  
 391 condition, which indicating a better moisture damage performance of that system. With respected  
 392 to negative values, smaller magnitude values indicate better moisture resistance. From this figure  
 393 it can be seen that the work of debonding was aggregate type dependent, with limestone obtained  
 394 positive results while granite resulted in much lower negative values. It is suggested that the  
 395 asphalt mixtures prepared with limestone would be expected to be more stable under moisture  
 396 attack than that of prepared with granite, and this phenomenon is in agreement with previous  
 397 research [37]. The physico-chemical behavior of aggregates plays a fundamental role in the  
 398 moisture resistance of aggregate-bitumen system. In terms of the systems prepared with limestone,  
 399 the ageing and rejuvenating process have limited influence on their moisture resistance, as all of  
 400 them obtained positive results. With respect to the aggregate-bitumen system prepared with  
 401 granite, the long-term ageing reduced the magnitude of work of debonding value, which indicating  
 402 improved resistance to moisture damage, theoretically. The addition of rejuvenators into aged  
 403 binder also influenced the work of debonding, and the values first reduced and followed by a rapid  
 404 growth with the increase of rejuvenator's viscosity. The rejuvenator R2 obtained the lowest work  
 405 of debonding value, which indicating its potential to improve the moisture resistance of aged  
 406 binder – granite systems. It can be summarized that rejuvenators with proper viscosity can  
 407 theoretically guarantee the moisture resistance of related recycled asphalt mixtures.

408 Table 5. Surface energy components of different binders

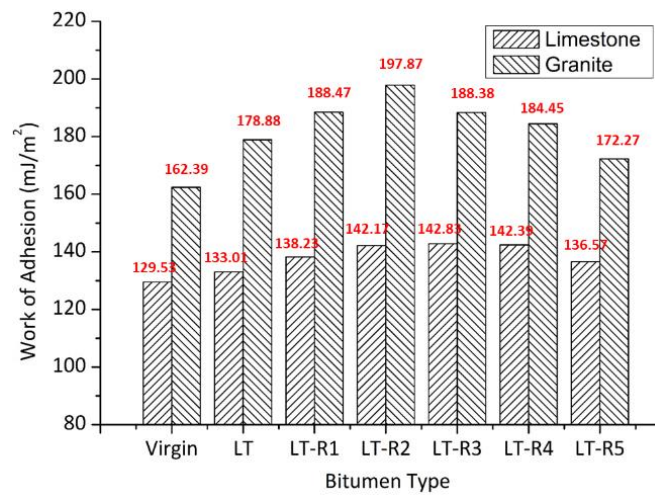
Surface energy (mJ/m <sup>2</sup> )	Virgin	LT	LT-R1	LT-R2	LT-R3	LT-R4	LT-R5
$\gamma^{LW}$	31.69	32.56	32.82	32.67	35.05	35.61	35.56
$\gamma^+$	1.50	1.29	1.98	2.59	2.46	2.37	1.53
$\gamma^-$	2.74	5.42	6.03	7.04	4.78	4.12	3.31



409

410

Figure 11. Total surface energy of different binders



411

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Figure 12. Work of adhesion between aggregate and different binders

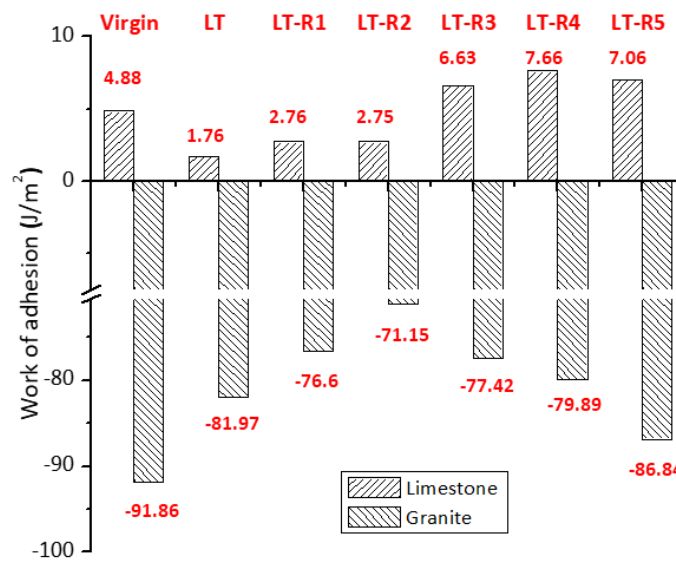


Figure 13. Work of debonding between aggregate and binders in wet condition

#### 4. Discussion

Based on experimental results in Section 3, the high-temperature performance of aged bitumen such as: softening point, penetration, viscosity, complex modulus and phase angle, can be easily recovered by adding rejuvenators. It demonstrated that the high-temperature behavior of rejuvenated bitumen is not sensitive to the viscosity of rejuvenators.

However, properties of rejuvenated bitumen related to low-temperature and cracking, such as ductility, cracking elongation and moisture debonding, were affected by the viscosity of rejuvenators. The property ranking of five parameters related to cracking and moisture resistance were summarized and presented in Table 6. It can be seen that the rejuvenated binder LT-R2 obtained four top-ranking out of five parameters, while the last ranking of these parameters belongs to LT-R4 and LT-R5. It demonstrated that the rejuvenator with proper viscosity level, such as R2, tend to obtain good performance in terms of cracking and moisture resistance.

Table 6. Property ranking of rejuvenated binders related to low-temperature and cracking

Parameters related to low-temperature and cracking	Property ranking				
	LT-R1	LT-R2	LT-R3	LT-R4	LT-R5
Ductility	5	1	2	3	4
Tensile elongation at break	3	2	1	4	5
Brittle fracture stress	2	1	3	5	4
Work of adhesion (Granite)	2	1	3	4	5
Work of debonding (Granite)	2	1	3	4	5

Note: The ranking level is from 1 to 5 and the ranking 1 level is the best.

#### 5. Conclusions

Service performance of recycled asphalt mixtures in pavements is strongly influenced by the chemical, rheological and mechanical properties of the rejuvenated binders in RAP. The ageing effects as well as the restoring effectiveness of different viscous rejuvenators were evaluated by a



433 series of experimental tests. The main findings were summarized below:

- 434 • The long-term ageing process deteriorated the conventional properties of the virgin bitumen,  
435 while incorporating rejuvenators can restore these parameters. When adopting an optimal  
436 viscous rejuvenator, ductility of the rejuvenated bitumen even surpassed that of the virgin  
437 bitumen.
- 438 • The increased viscosity of the aged binder showed the decrement of the flowability of asphalt  
439 mixture containing RAP materials, which in turn might have adverse impact on mixing and  
440 compaction effect of recycled asphalt mixtures. All rejuvenators designed with different  
441 viscosities in this research can restore the viscosity of the aged binder, which had positive  
442 effect on the workability of recycled asphalt mixtures.
- 443 • The ageing process also influenced the chemical components of bitumen, which had lower  
444 aromatic fraction that was converted to resins and asphaltenes. Incorporating rejuvenators  
445 supplemented the lost light fractions of the aged binder to some extent and this is responsible  
446 for the recovery of mechanical properties.
- 447 • Based on the rheological behavior, the bitumen after ageing behaves more elastic and stiffer.  
448 The five rejuvenators designed with different viscosities in this research had a similar effect in  
449 recovery of rheological properties of the aged bitumen. However, it seems difficult to  
450 rehabilitate rheological properties of the aged bitumen to exactly the same as that of the  
451 virgin binder.
- 452 • The long-term ageing condition reduced the tensile elongation and made the aged binder  
453 more susceptible to low-temperature cracking. After incorporating all rejuvenators, the  
454 tensile elongation of the rejuvenated binders was higher than that of the virgin binder. An  
455 optimal viscosity of rejuvenator was more effective to restore the tensile elongation and  
456 brittle fracture stress.
- 457 • The ageing effect increased the surface energy components of the virgin binder and  
458 incorporating rejuvenators resulted in further increment in these parameters. The increased  
459 work of cohesion and work of adhesion indicated that the rejuvenator with an appropriate  
460 viscosity can increase the stickiness between the aged bitumen and aggregates. Rejuvenators  
461 with proper viscosity can theoretically guarantee the moisture resistance of related recycled  
462 asphalt mixtures.
- 463 • In summary, the stiffness of the aged binder at relatively high temperature, such as viscosity,  
464 complex modulus and phase angle, can be recovered to similar level as that of the virgin  
465 binder by adding rejuvenators. However, the ductility, fracture resistance, adhesion as well as  
466 moisture resistance of the rejuvenated binders strongly depended on the rejuvenator's  
467 viscosity.

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