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

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

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

1. Introduction

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

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

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

More researches have investigated the feasibility of using rejuvenators to restore properties of the aged binder with the view of increasing the RAP usage in recycling asphalt mixtures. Normally, rejuvenators can be defined as softening additives or recycling agents, which help to restore mechanical properties of the aged binder [22][23]. The addition of rejuvenators softens the aged binder by increasing the maltenes content, which in turn reduces its stiffness and increases its ductility. Based on previous researches, several types of materials including plant oils, waste-derived oils as well as refinery-based oils have the possibility to be used as rejuvenators [10],[24]. Mangiafico et al. [25] investigated the influence of bio-based oil on properties of the recycled HMA, and their results indicated that the bio-based oil reduced the complex modulus and enhanced the fatigue performance of the recycled HMA with a high RAP content. Another study suggested that vegetable oil and maltene obtained similar effect on flowability improvement of highly aged binders, while the aged binder rejuvenated by vegetable oil has the best thermal behavior [26]. However, it should be noticed that the vegetable oil might cause high moisture susceptibility of the recycled HMA and adhesion enhancing additive might be necessary to be incorporated [27]. Recycled motor oils were also employed as rejuvenators and suggested that the recycled HMA rejuvenated by recycled motor oil reduced the mixing temperature and postponed the permanent deformation [28]. Asli et al. [29] investigated the novelty of using waste cooking oil to rejuvenate aged binders. The results indicated that the waste cooking oil not only reduced the ratio of Asphaltenes/Maltenes, but also rejuvenated physical properties of the RAP binder. Composite castor oil and pongamia oil were selected to restore properties of aged binder and revealed that the rejuvenated binder obtained similar rutting resistance and better fatigue resistance than that of the virgin binder [30]. In summary, it is a consensus that incorporating rejuvenators might be an effective method to promote the application of RAP materials in the HMA production. However, all the studies abovementioned mainly focused on the restoring effect of different rejuvenators on the properties of aged binders and recycled mixtures. A systematic exploration of the influence of the rejuvenator's viscosity on chemical compositions, rheological and mechanical properties of aged binders is still absent. Therefore, there is a need to explore the influence of rejuvenators with different viscosities on the comprehensive performance of aged binders.

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

2. Materials and experimental methods

2.1 Materials

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

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

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

Dynamic viscosity (60℃,Pa • s)	235	408	1453

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

Table 2. Viscosity of rejuvenators at different temperatures

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

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

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

Where, η_{mix} is the viscosity of the rejuvenated binder at 60℃(Pa • s); η_{old} is the viscosity of the aged binder at 60℃ (Pa • s); η_{new} is the viscosity of the rejuvenator at 60℃ (Pa • s); α is the dosage of the rejuvenator.

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

2.2 Experimental methods

2.2.1 Conventional bitumen performance tests

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

2.2.2 SARA test and colloidal index

SARA (Saturate, Aromatic, Resin and Asphaltene) fractioning method was used in this research to characterize the chemical composition of the virgin bitumen, the aged bitumen as well as the rejuvenated binders. Due to different solubilities of bitumen components in n-heptane, bitumen can be conveniently fractionated into maltenes and asphaltenes. The maltenes including saturates, aromatics and resins, can be further fractioned by liquid adsorption chromatography using alumina as the adsorbent and a solvent containing 1wt% distilled water. The detailed description of the SARA fractioning method can be found elsewhere [32]. Based on the steric colloidal model presented by Park [33], the asphaltenes exist in the form of suspended particles with some of the resins adsorbed on their surfaces to keep the asphaltenes in suspension. Other resins are dissolved in the oil phase to prevent the flocculation of the asphaltene structures.

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

$$\mathrm{CI} = \frac{X_{asphaltenes}+X_{saturates}}{X_{aromatics}+X_{resins}} \tag{2}$$

Where, X_i is the mass content of the bitumen fraction "i".

2.2.3 Dynamic shear rheometer test

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

2.2.4 Direct Tension test

As previously mentioned, the ageing effect can make the RAP binder stiff and brittle, and the recycled mixtures containing RAP binder has potentially higher susceptibility to crack. So, it is essential to evaluate the fracture resistance of the rejuvenated binders and compared with the reference binder. The Direct Tension (DT) test was performed to evaluate the fracture properties of binders at low temperature (ASTM D6732-02). Figure 1 presents the schematic of the specimen used for DT test. Samples were prepared by pouring hot bitumen in aluminum molds, which is similar as the specimen preparation procedure for the bitumen ductility test. The DT test in this research was performed at -15℃ with the temperature controlled by a cooling bath using methyl acetate solution. Before testing, the prepared samples were conditioned in the cooling bath for 1 h to reach temperature balance. Subsequently, samples were installed on the loading rack by a special clamp. Finally, a horizontal load was applied with a constant displacement of 1 mm/min till the sample was fractured. Parameters such as elongation at break, breakdown stress as well as the original stress-strain data can be automatically recorded by the equipment.

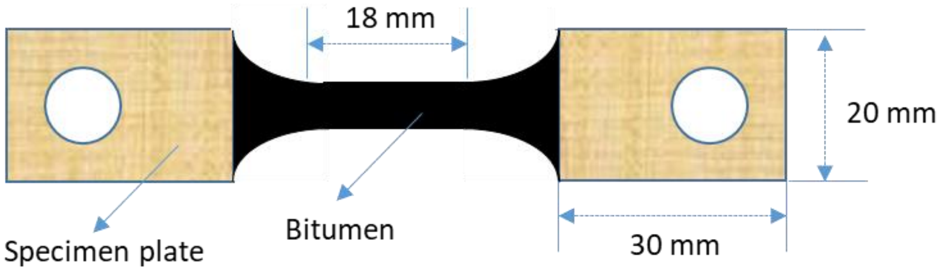

Figure 1. Schematic of the binder specimen used for DT test

2.2.5 Surface energy test and moisture damage evaluation

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

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

where, θ is the contact angle between probe liquid and bitumen, S represents the solid bitumen, L represents the probe liquid, γ^{LW} is the Lifshitz-van der Waals component of the surface energy, γ^{+} is the Lewis acid component of surface interaction, γ^{-} is the Lewis base component of surface interaction.

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

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

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

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

When water penetrated into the aggregate-bitumen interface, the work of adhesion for two materials in contact with a third medium can be explained by Equation 5. This parameter represents the reduction in bond strength of an aggregate-bitumen system when water displaces the bitumen from the aggregate surface.

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

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

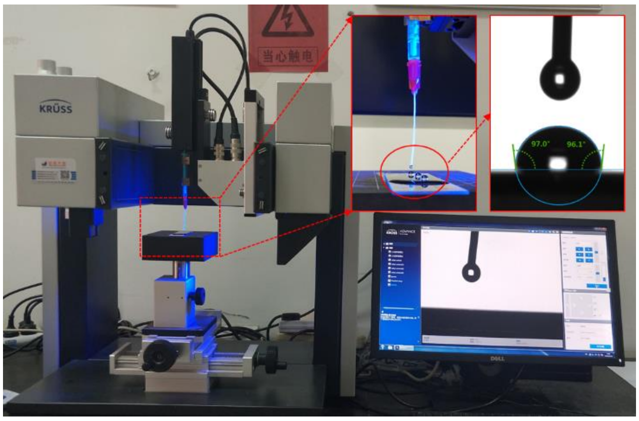

Figure 2. KRUSS Drop Sharp Analysis equipment

Table 4. Surface energy components of aggregates [23]

Aggregate	Surface energy component (mJ/m^2)			
	γ^{LW}	γ^{+}	γ^{-}	γ
Limestone	82.2	6.7	59.3	122
Granite	68	163.9	122.7	351.6

3. Results and Discussion

3.1 Conventional properties of virgin, aged and rejuvenated binders

The conventional physical parameters of bituminous binders including softening point, penetration and ductility, were measured and the results are shown in Figure 3. As shown in Figure 3(a), the long-terms ageing process increased the softening point of the virgin bitumen from 48.2℃ to 63.3℃. By adding rejuvenators determined in Section 2, the softening point of the aged bitumen was reduced and nearly restored to similar level as that of the virgin bitumen. It was noticed that the long-term ageing declined the bitumen penetration from 68.3 dmm to 19.8 dmm, as shown in Figure 3(b). The incorporation of rejuvenators changed the penetration grade of the aged bitumen to resemble the virgin binder. It is known that the oxidation reaction makes the bitumen stiff and incorporating rejuvenators can soften the aged binder. By comparing five rejuvenated binders, all rejuvenators with different viscosities can reduce the stiffness of the aged bitumen and obtain identical results. Because the ductility results of the virgin and rejuvenated binders are all greater than 150 cm at 15℃, the ductility test was performed at 10℃ in order to obtain different responses as shown in Figure 3(c). The ductility of the aged bitumen dropped to only 0.55 cm due to the long-term ageing, indicating brittle behavior of the aged bitumen. The addition of rejuvenators improved the ductility of the aged bitumen and their ductility reached and even surpassed that of the virgin binder. It is noticed that, with the increase of rejuvenator's viscosity, the ductility of the rejuvenated binder first increased followed by declining after reaching the top value at LT-R2. The rejuvenator with a proper viscosity can achieve better contribution to the improvement of ductility.

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

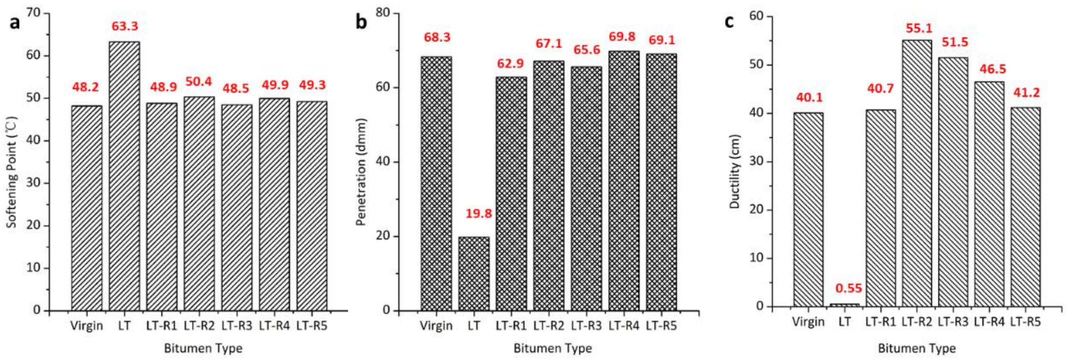

Figure 3. Conventional properties of bitumen: (a) Softening point; (b) Penetration; (c) Ductility

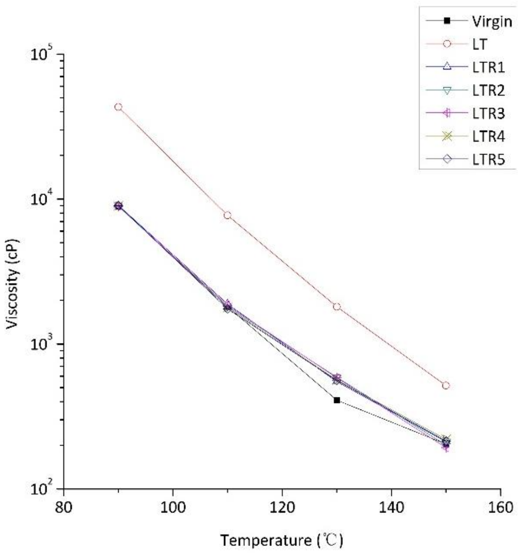

Figure 4. Viscosity of bituminous binders at different temperatures

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

In order to explore how the ageing and rejuvenating process influence the overall chemical composites and their contribution to mechanical properties of bitumen, SARA fraction test was conducted. Chemical fractions of virgin, aged and rejuvenated binders are shown in Figure 5. After long-term ageing, the aromatic fraction was decreased from 44.14% to 32.27%, while the resin and asphaltene fraction contents increased with values increased by about 4.5% and 9.5%, respectively. This phenomenon is consistent with Dehouche's research [32] that ageing reduces the content of aromatics which are in turn converted to resins and asphaltenes. However, the saturates content is almost constant even after long-term ageing. The chemical variations, including decrease of aromatics and increase of asphaltenes, are responsible for the stiffening and hardening effect of the aged bitumen. Adding rejuvenators lowered the fractions of asphaltenes and resins in comparison with the aged binder, while it can increase the fractions of aromatics, to some extent. The recovery in chemical composition of the aged bitumen results in the restoring of mechanical properties. It should be noticed that none of these five rejuvenators can recover the SARA fractions of the aged binder to the same levels as in the virgin bitumen. Also, they had same effect on recovering SARA components.

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

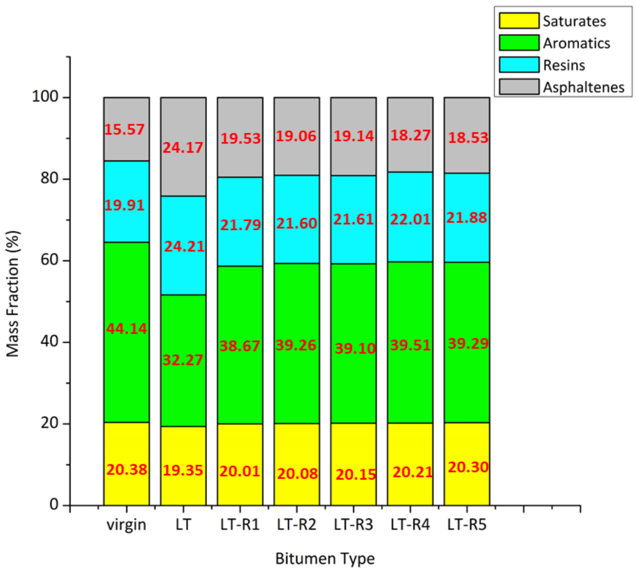

Figure 5. Influence of rejuvenator's viscosity on chemical components of the aged bitumen

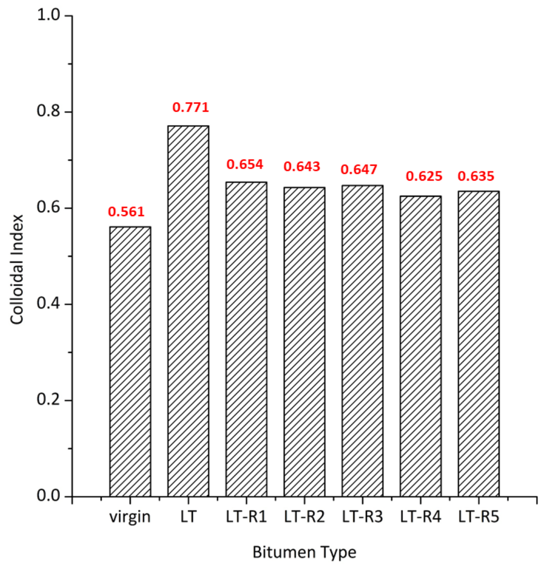

Figure 6. Colloidal index of different binders

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.

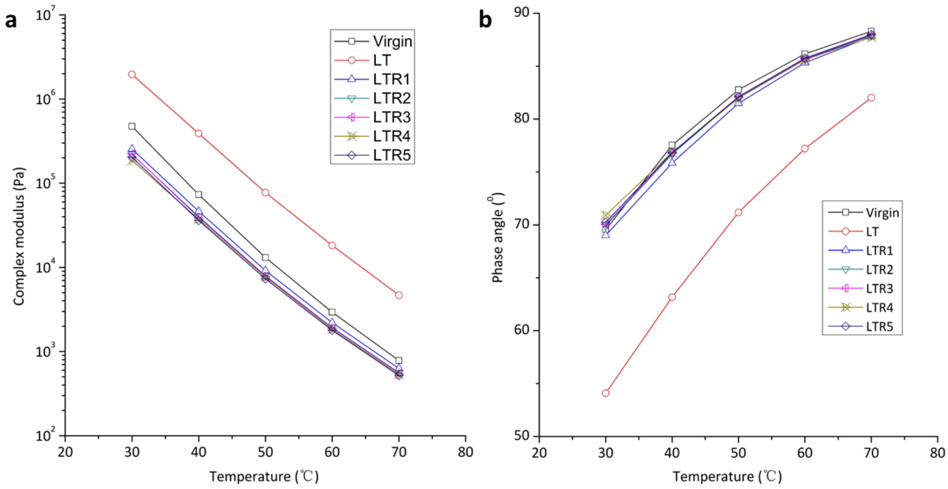

Figure 7. Rheological properties of different binders: (a) complex modulus; (b) phase angle

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

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

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

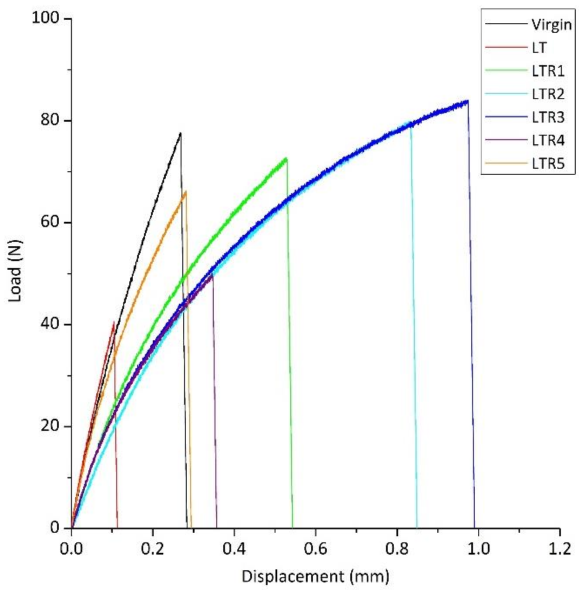

Figure 8. Force-displacement curves of different binders at -15℃

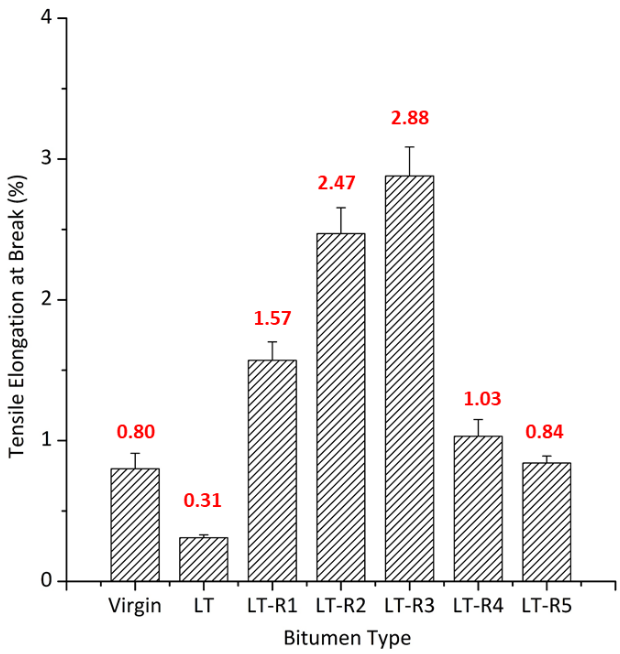

Figure 9. Tensile elongation at break of different binders at -15℃

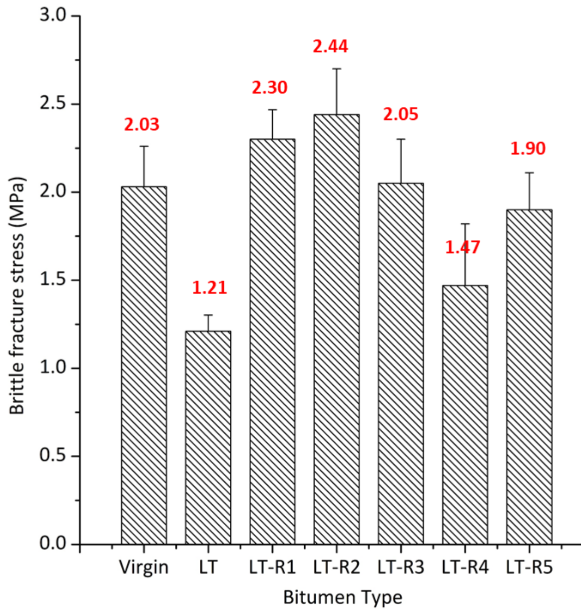

Figure 10. Brittle fracture stress of different binders at -15℃

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 γ^{LW} from 31.69 mJ/m^2 to 32.56 mJ/m^2, and nearly doubled the γ^{-}value. However, the γ^{+}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 (γ^{LW}), while the aged bitumen incorporating R3, R4 and R5 resulted in an obvious increase of γ^{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^2 to 37.84mJ/m^2. 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 aggregate, interface combinations with virgin bitumen obtained the lowest work of adhesion and the long-term ageing increased this value. As for rejuvenated binders, their work of adhesion seen further increase, with LT-R2-granite and LT-R3-limestone obtained the highest value. The increased work of cohesion and work of adhesion indicated that the rejuvenator with an appropriate viscosity listed in Table 2 can increase the stickiness between the aged bitumen and aggregates, which in turn had the positive effect on the mechanical properties of recycled asphalt mixture with RAP incorporated.

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

Table 5. Surface energy components of different binders

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

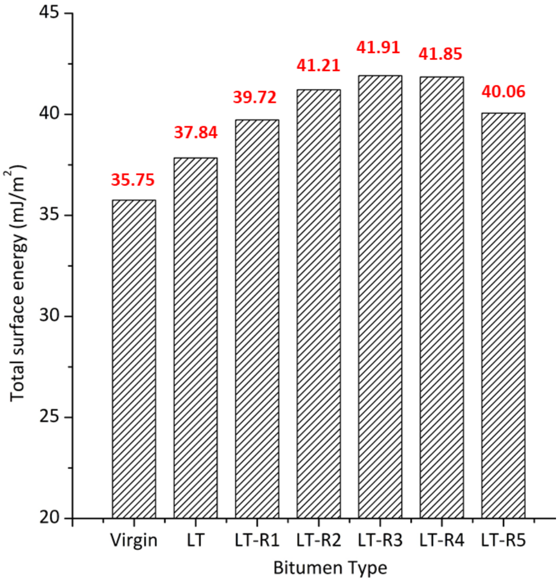

Figure 11. Total surface energy of different binders

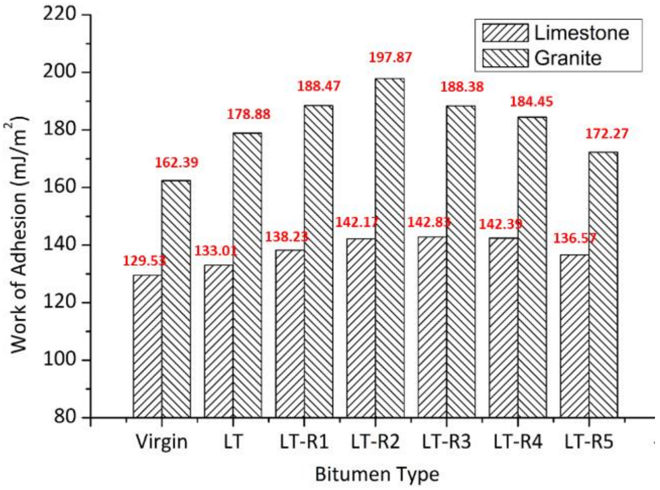

Figure 12. Work of adhesion between aggregate and different binders

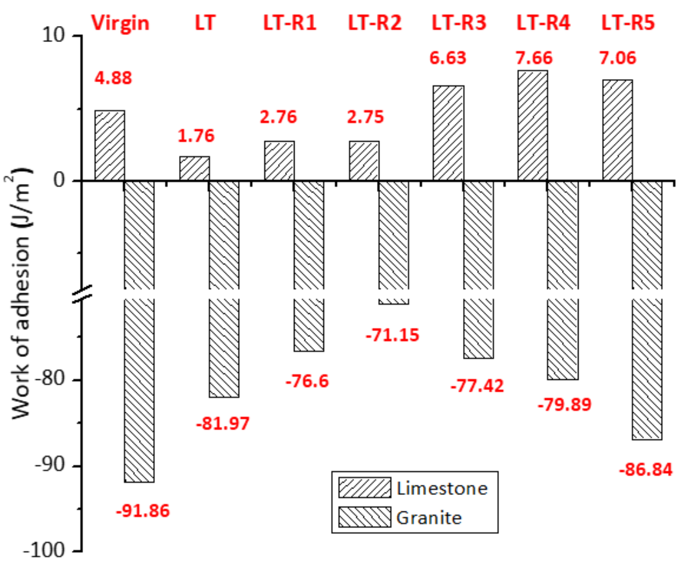

Figure 13. Work of debonding between aggregate and binders in wet condition

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

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

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