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Atomic force microscopy (AFM) based microstructural and micromechanical analysis of bitumen during ageing and rejuvenation

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ABSTRACT

Aging deteriorates the performance of bitumen whereas rejuvenation can partially restore these properties. Although the macroscale properties of bitumen ageing and rejuvenation have been well documented, the microscale mechanisms are still not well understood. Understanding the microscale properties is deemed critical to fully comprehend the mechanisms of ageing and rejuvenation. This study investigated the topographical, micromechanical, and micro-adhesion properties and their correlations of bitumen in terms of ageing and rejuvenation using an atomic force microscope (AFM). Two types of bitumen were aged to five different levels. Subsequently, one bitumen was rejuvenated using two rejuvenators, applied at five dosages. The 2D and 3D microscale properties of aged and rejuvenated bitumen were then comprehensively characterised. The results suggested that ageing altered the microstructures of bitumen while rejuvenation processes cannot recover these microstructures. Ageing initially increased the roughness and adhesion properties of bitumen, but these properties were seen to be later decreased. The modulus increased with ageing and decreased with rejuvenation. The correlation between adhesion force and rejuvenator dosage was material dependent while the microstructures and micromechanical properties of aged and rejuvenated bitumen were correlated.

1. Introduction

The performance of bitumen deteriorates progressively during its lifespan because of ageing. Ageing of bitumen happens under the multiple effects such as thermal, ultraviolet, and reactive oxygen species (ROS) etc. [1–3]. Ageing increases the stiffness and reduces the ductility of bitumen, which consequently weakens its cracking resistance [4,5]. Moreover, ageing reduces adhesion between bitumen and stones (aggregates), which is responsible for ravelling and moisture damage related distresses [6–8]. Based on the mechanism and severity, ageing of bitumen is commonly clarified into two categories, which are short-term ageing and long-term ageing, respectively. Short-term ageing of bitumen primarily occurs during manufacture of asphalt mixtures, transporting mixtures to field and construction of asphalt pavements processes, which can be simulated in laboratory using the rolling thin film oven (RTFO) tests. Long-term ageing of bitumen occurs during the entire lifespan of asphalt pavements, which can be simulated in laboratory using the pressure ageing vessel (PAV) tests [9].

Rejuvenation, also known as regeneration, is an effective way to recover the deteriorated performance of bitumen caused by ageing. In the process of rejuvenation of bitumen, rejuvenators are commonly employed. Rejuvenators are the additives to restore the deteriorated performance of aged bitumen, such as cracking resistance and adhesion performance. The lighter fractions, such as oily components within rejuvenators can replenish and rebalance the components within bitumen caused by ageing. Therefore, the physical properties of aged bitumen could be recovered [10].

The macroscale characterisation of bitumen ageing and rejuvenation has been well documented, such as the rheological and mechanical properties of bitumen and asphalt mixtures [11–15]. However, the

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microscale characterisation of bitumen ageing and rejuvenation has not yet been fully established. It has been reported that the microscale properties of bitumen are closely correlated with their macroscale properties and overall performance [16–18]. Microscale characterisation of bitumen provides an advanced understanding of the mechanisms underlying changes in bulk performance [19]. For instance, the microstructure of bitumen reveals insights into molecular mobility, which is influenced by interactions among various chemical species, and could indicate the effectiveness of recycling agents in diffusing into recycled bitumen [19,20]. Such understanding is critical when considering the design and optimising of future mixes.

There are several microscale characterisation methods for characterising bitumen, such as atomic force microscopy (AFM) [21,22], scanning electron microscopy (SEM) [23,24], environmental scanning electron microscopy (ESEM) [23,25], confocal laser scanning microscopy (CLSM)[26,27], optical microscopy [28], and fluorescence microscopy [29,30]. Among these methods, AFM is one of the most popular techniques as it can provide more comprehensive information—such as the microtopography, micromechanics, micro-adhesion, phase contrast, and dispersion—compared to other microscopies [31].

Based on the AFM results, it was reported that the micromorphological profiles of bitumen change considerably with ageing, resulting in the alterations of its microstructures, such as the formation of "bee-structures", and changes in the surface roughness [32,33]. Moreover, the Derjaguin-Muller-Toporov (DMT) modulus, which can also be measured using an AFM, changes with ageing and rejuvenation significantly. DMT modulus quantifies the stiffness of a material by considering both elastic deformation and adhesive interactions at the contact interface. It is particularly useful in characterising materials at the microscale, where surface forces can significantly influence mechanical behaviour [32]. Moreover, the adhesion force of bitumen also changes with ageing and rejuvenation, but the trends have been reported to be arbitrary [34–36].

In line with previous studies, AFM is considered a valuable tool for exploring the fundamental mechanisms underlying bitumen ageing and rejuvenation at the microscale [37]. However, current AFM-based investigations have produced contradictory results [31,38], with differing—and sometimes opposing—trends observed during the ageing and rejuvenation processes. These discrepancies may have stemmed from variations in sample preparation methods, material dependencies, and data analysis approaches, as reported in literature [39,40].

Although previous research has examined the microscale properties of both short-term and long-term aged bitumen, most long-term ageing studies have focused on standard PAV samples (20 hours) without considering extended ageing conditions [26,39,41]. Extended long-term ageing can affect bitumen properties in distinct ways, yet such studies remain scarce [42]. Furthermore, investigations into the microscale properties of rejuvenated bitumen are limited, particularly in regard to how rejuvenator dosage influences parameters such as microtopography and micromechanics. Moreover, while AFM can reveal various aspects of bitumen's microscale properties related to ageing and rejuvenation, studies that explore correlations between these aspects are rare.

Therefore, the present study aims to systematically investigate the impact of ageing and rejuvenation on the microscale properties of bitumen and to establish correlations between these properties. Various factors will be considered, including bitumen type, ageing protocol (short-term and long-term), ageing duration, rejuvenator type, and rejuvenator dosage. The study will evaluate the microscale properties of bitumen based on parameters such as microtopography, micromechanics, and micro-adhesion characteristics. By correlating the microstructural and micromechanical properties during ageing and rejuvenation, the underlying mechanisms governing these processes will be elucidated. Ultimately, the goal is to achieve a fundamental understanding of bitumen's microscale behaviour under varying ageing and rejuvenation scenarios, thereby providing key insights into the mechanisms of bitumen ageing and rejuvenation.

2. Materials and methods

2.1. Materials

Two types of penetration grade bitumen were employed in this study. The first bitumen was a penetration grade 40/60 bitumen, and the second was a penetration grade 70/100 bitumen. The technical properties of bitumens employed in this study are shown in Table 1 with their SARA fractions, which stand for the content of saturates, aromatics, resins and asphaltenes within the bitumen.

Two bio-rejuvenators were used in this study. Their main technical properties are listed in Table 2. The dosages for rejuvenator 1 were 3 %, 4 %, 5 %, 6 % and 7 % respectively and for rejuvenator 2 were 1 %, 2 %, 3 %, 4 %, and 5 % respectively in accordance with previous studies [14].

2.2. Ageing and rejuvenation procedures

Each bitumen underwent short-term ageing using Rolling Thin Film Oven (RTFO) method at 163 °C for 75 mins in accordance with BS EN 12607–1 [43]. Afterwards, the short-term aged bitumen was long-term aged using Pressure Ageing Vessel (PAV) method at the temperature of 100 °C and the pressure of 2.1 MPa for 20 hours, 30 hours and 40 hours in accordance with BS EN 14769 [44]. The 20-hour PAV aged bitumen was subjected to rejuvenation using two rejuvenators. For each rejuvenator used, five dosages were applied. The bitumen was placed in an oven at 160 °C for 30 mins to ensure its fluidity was sufficient for blending. Then the bitumen was placed onto a laboratory hotplate at the same temperature. The rejuvenators at designed dosages were added to the aged bitumen and blended for 10 minutes using a laboratory mixer to assure the homogeneity of the rejuvenated bitumen.

2.3. Configuration of AFM

The schematic of the working principle of an atomic force microscopy is shown in Fig. 1. Fig. 1(a) shows the trajectory of the probe over a cycle. Path A to C and path C to E represent the approach and retraction phases, respectively. Initially, the probe is distant from the testing specimen without any force. As the probe approaches, attractive forces increase until the probe contacts at location B. Afterwards, the probe slightly deforms the testing specimen at point C. Upon retraction, the probe is momentarily held by adhesion at point D before returning to its original position. During the cycle, the force alters from attraction to repulsion. Fig. 1(b) displays the force-distance curve, the red lines illustrates the attraction phase and the blue lines represents the repulsion phase [45].

It has been reported that the surface roughness of bitumen changes with time initially while reaches an equilibrium and stable status after five days [46]. Therefore, the samples were stored in a dust-free closed container for five days prior to testing. The testing configuration is shown in Table 3.

3. Results and discussion

3.1. Topographical characterisation

3.1.1. The impact of ageing on micro-morphology of bitumen

Fig. 2 shows the 2D topography of 40/60 bitumen with varying ageing levels. Some alternating light and dark stripes could be observed from the 2D topography of bitumen, which is commonly described as "bee-structures". It is well recognised that the "bee-structures" of bitumen is related to ageing, as ageing induced chemical changes can be reflected by the change in the "bee-structures" [20].

It can be observed from Fig. 2 that in the 2D view, the morphological properties or microstructures of bitumen altered significantly with the progressively increased ageing levels. The length of bee-structures increased with ageing initially then decreased. Bitumen after 20 hours

Table 1
Technical properties of bitumen.

Penetration grade	Penetration (0.1 mm)	Softening point (°C)	PG	SARA	Viscosity (135 °C) (mPa·s)
40/60	43	51.5	PG 70–16	5:55:24:16	375
70/100	81	45.5	PG 64–22	4:59:21:16	306

Table 2
Technical properties of rejuvenators.

Code	Rejuvenator 1	Rejuvenator 2
Density (kg/l)	0.915	0.890
Viscosity at 25 °C (cP)	60	60
Appearance	Dark green liquid	Brown to yellow liquid
Image		

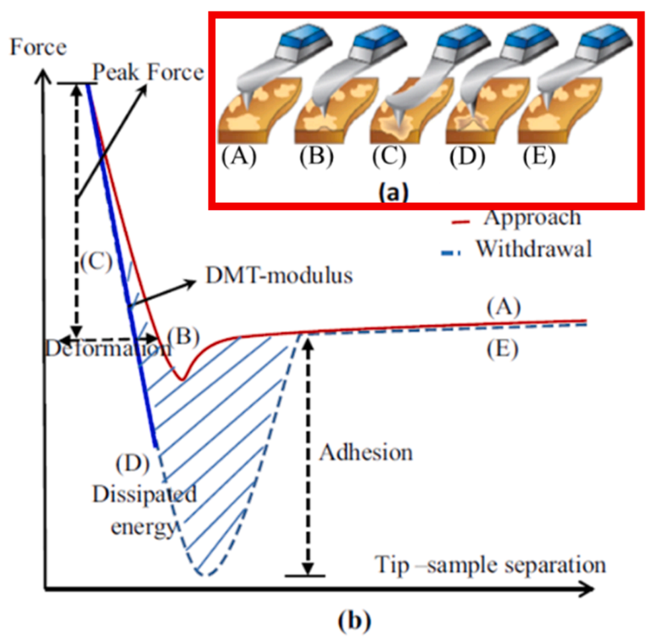


Fig. 1. Working principle of AFM (sourced from [45]).

Table 3
Testing setup.

Parameter	Unit	Setup
Mode	-	PF-QNM, tapping
Spring constant	N/m	5
Scan speed	Hz	1
Scan size	μm	20 × 20
Resolution	pixel	256 × 256
Temperature	°C	Room temperature

of PAV ageing had the longest length of bee-structures. Afterwards, the length of bee-structures reduced gradually and formed smaller bee-structures. During process, the bee-structures tended to agglomerate together, as circled in Fig. 2. For the virgin bitumen, the bee-structures distributed individually, however, with the progressively increased ageing, some bee-structures were associated with adjacent ones, forming obvious agglomerations. This observation could be attributed to the increase of polarity of bitumen during ageing. With the progressively increased ageing, bitumen tended to be more polar, resulting in the attraction of adjacent microstructures, which subsequently formed the agglomerations [19].

The 3D topographical images are shown in Fig. 3. The areas surrounding the bee-structures are termed as the “matrix phase”. As seen in Fig. 3, the surface of the matrix phase of virgin bitumen was relatively flat. Several large bee-structures were sparsely distributing on the surface. When it comes to the short-term aged bitumen, it showed similar pattern to the virgin bitumen, but more bee-structures could be observed. The topography of long-term aged bitumen changes dramatically, the matrix phase become rugged, with an increasing number of sunken areas as ageing progresses [47].

The numbers of bee-structures were quantified and the roughness or the surface were measured, as shown in Fig. 4. The number of bee-structures of 40/60 binder increased 13 %, 46 %, 68 %, and 72 % after short-term ageing, long-term ageing for 20, 30, 40 hours, respectively. The increment percentages for 70/100 binder were 16 %, 30 %, 39 % and 46 % respectively. Combined with Fig. 2, it was seen that the bee-structures were distributed randomly and independently within the matrix phase for virgin bitumen. After long-term ageing, the sizes of bee-structures were smaller, and more bee-structures appeared and were agglomerated, which aligned with previous studies [45]. There are several assumptions for this phenomenon, such as the result of asphaltenes and wax crystallisation [37], volatilisation and polymerisation [48], ageing induced change in aromatic fractions [35] etc. Among them, waxy crystallisation theory is currently the governing theory. Waxes are sensitive to temperature changes. When the solubility of waxes decreases due to aging, these waxes can crystallise, forming the bee-structures [31].

The roughness increased with ageing levels initially then decreased, as shown in Fig. 4(b), which was consistent for two bitumens. As illustrated in Fig. 3, the 3D topography images showed that the distance between the “peaks” and “valleys” of the microstructures in virgin bitumen was relatively greater. This indicates a more pronounced surface roughness in the virgin bitumen compared to other samples. However, the distances between the “peaks” and “valleys” for aged bitumen were smaller, which contributed to the decrease in roughness [39]. It has been reported that surface roughness has significant influence on the adhesion and self-healing properties of bitumen. Greater value of roughness corresponds to better adhesion and self-healing performance. The increase of adhesion performance caused by increased roughness could contribute to increased surface free energy, as reported in previous study [45]. Generally, the results suggested that short-term ageing increased the roughness of bitumen samples and thereby improved the adhesion and self-healing properties of bitumen. On the contrary, long-term ageing adversely impacted the adhesion and self-healing properties. More severe ageing resulted in more remarkable decrease in roughness and thereby more significant deterioration of adhesion and self-healing properties, which aligned with previous studies [42].

3.1.2. The impact of rejuvenation on micro-morphology of bitumen

The topographical images of rejuvenated bitumen using different rejuvenators with varying dosages are shown in Fig. 5.

As mentioned earlier, after ageing, the bee-structures tended to agglomerate together, forming clusters of bee-structures. The agglomerations of bee-structure clusters is assumed to be related to wax

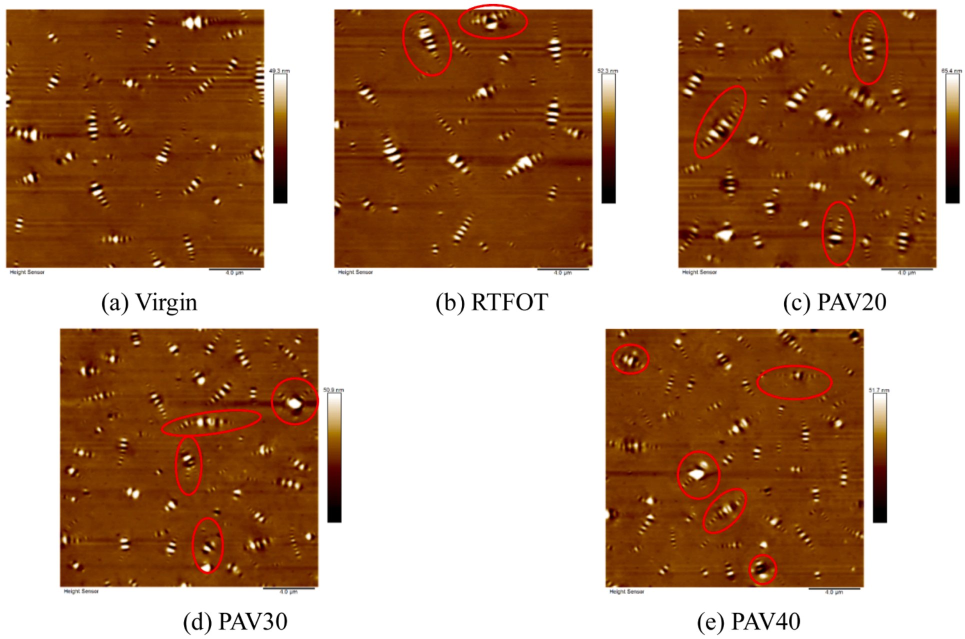


Fig. 2. 2D topography of bitumen with varying ageing levels.

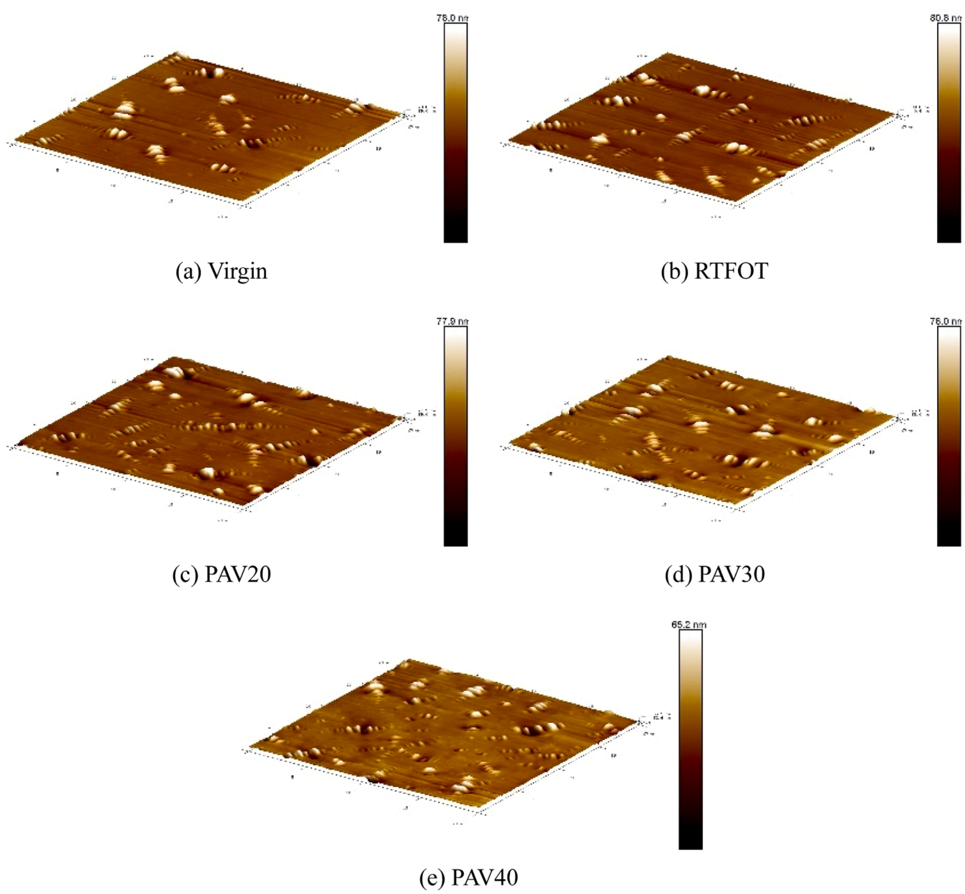


Fig. 3. 3D topography of bitumen with varying ageing levels.

crystallisation [49]. Ageing is thought to form a thin surface film caused by wax crystallization, which acts as a barrier preventing the micro-structures from floating freely. As a result, the bee-structures are compelled to cluster together [50].

After rejuvenation, there was no deagglomeration observed for rejuvenated bitumen with both rejuvenators, regardless of the dosages used. It has been reported that ageing results in the agglomeration of polar fractions [51]. Therefore, if the rejuvenation process can

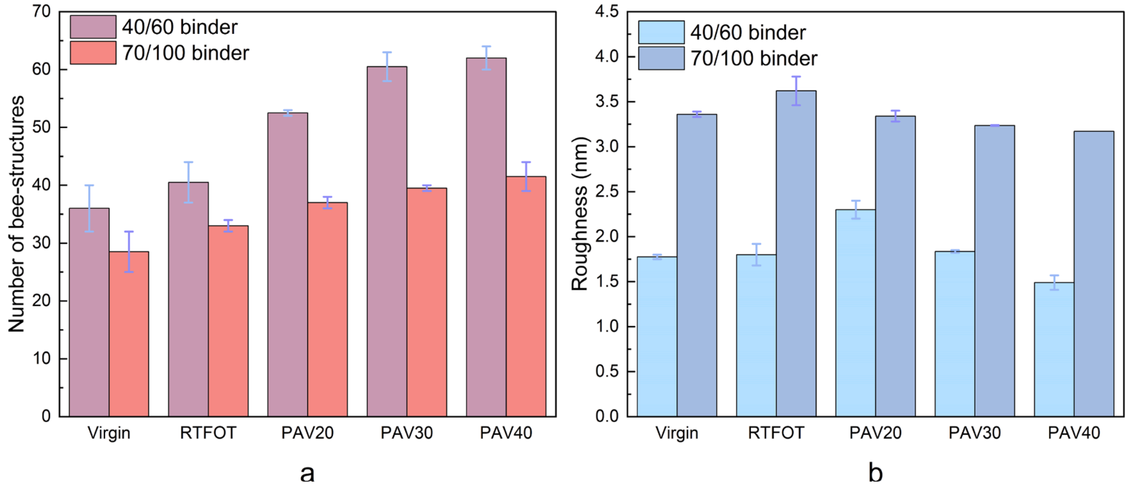
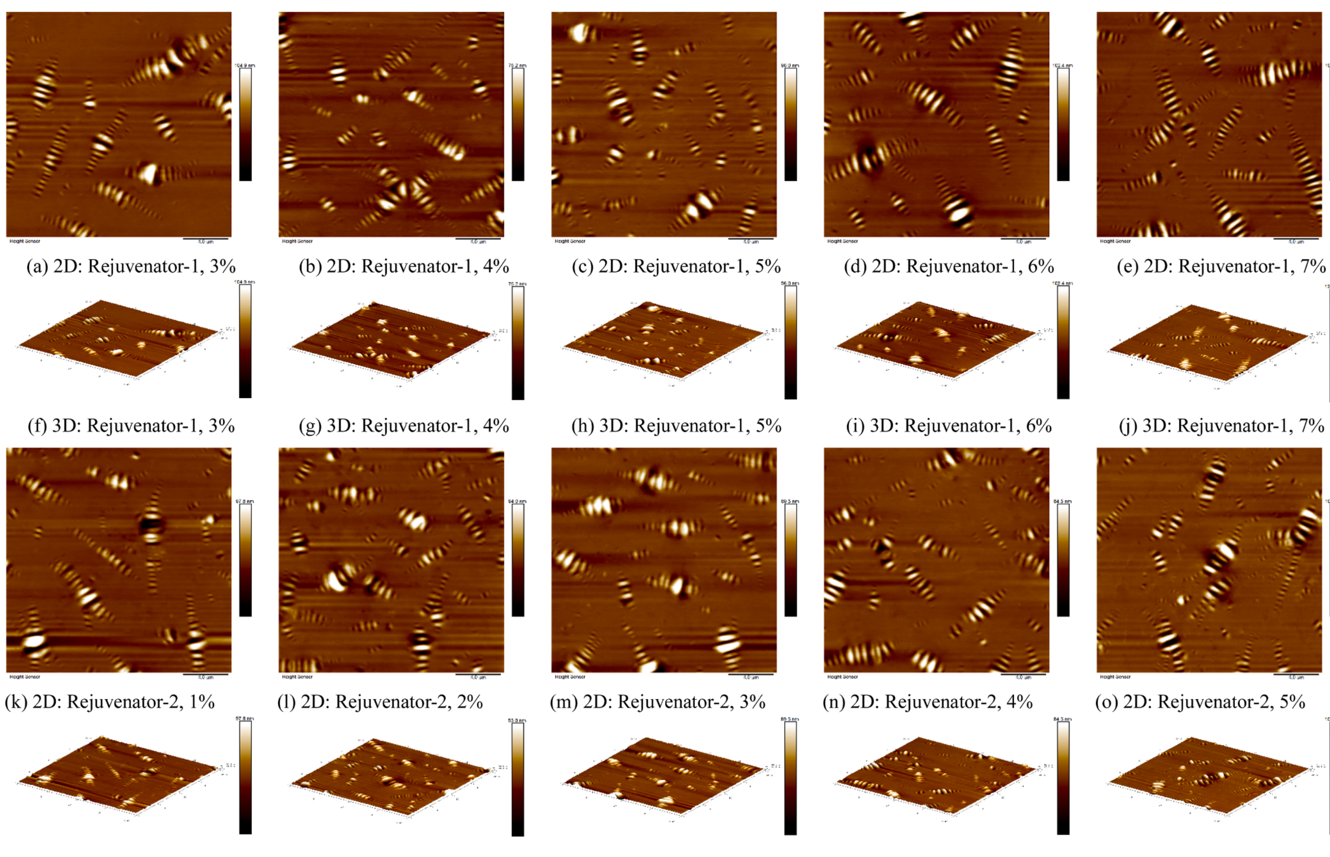


Fig. 4. Quantitative characteristics of micromorphology of bitumen in terms of ageing (a) Bee-structures and (b) Roughness.



(a) 2D: Rejuvenator-1, 3% (b) 2D: Rejuvenator-1, 4% (c) 2D: Rejuvenator-1, 5% (d) 2D: Rejuvenator-1, 6% (e) 2D: Rejuvenator-1, 7%

(f) 3D: Rejuvenator-1, 3% (g) 3D: Rejuvenator-1, 4% (h) 3D: Rejuvenator-1, 5% (i) 3D: Rejuvenator-1, 6% (j) 3D: Rejuvenator-1, 7%

(k) 2D: Rejuvenator-2, 1% (l) 2D: Rejuvenator-2, 2% (m) 2D: Rejuvenator-2, 3% (n) 2D: Rejuvenator-2, 4% (o) 2D: Rejuvenator-2, 5%

(p) 3D: Rejuvenator-2, 1% (q) 3D: Rejuvenator-2, 2% (r) 3D: Rejuvenator-2, 3% (s) 3D: Rejuvenator-2, 4% (t) 3D: Rejuvenator-2, 5%

Fig. 5. Topography images of rejuvenated bitumen.

deagglomerate the associated fractions, it could be assumed that rejuvenation chemically reverses ageing process. However, as no deagglomeration was observed, it is assumed that rejuvenation is most likely a physical softening process instead of chemical reversal of ageing [14, 52]. Some studies employed Fourier Transform Infrared Spectroscopy (FTIR) to identify the mechanism of rejuvenation of bitumen [14]. It has reported that there were no new molecular bonds being generated during rejuvenation process, which suggested that rejuvenation is more likely to be a physical softening process rather than chemical reversal of ageing [14,53].

From the 2D images, it was seen that two rejuvenators showed identical trend in terms of the 2D topography of rejuvenated bitumen. When it comes to the 3D images, it was observed that the continuous phase of bitumen was relatively flat, the heights of the bee-structures were similar for different dosages and different rejuvenators. Overall, it was seen that there was no significant differences could be identified based on the topography of rejuvenated bitumen. Therefore, rejuvenation could not recover the microstructures of aged bitumen, which aligned with previous studies [37].The number of bee-structures of rejuvenated bitumen was quantified and the roughness was calculated, as shown in Fig. 6. It was observed from Fig. 6(a) that the number of bee-structures was arbitrary with the dosages employed. The number of bee-structures in the rejuvenated bitumen treated with Rejuvenator 1 was higher than that in both virgin and aged bitumen, except in the case where a 7 % dosage of the rejuvenator was used. However, the number of bee-structures of rejuvenator 2 rejuvenated bitumen was higher than that of virgin bitumen while lower than that of aged bitumen.

It was seen that the addition of two rejuvenators increased the roughness of rejuvenated bitumen (except for rejuvenator 1 at 3 % of the dosage). However, the change of roughness with dosage showed opposite trend for two rejuvenators. The roughness of rejuvenator 1 rejuvenated bitumen increased −13.9 %, 0.1 %, 2.4 %, 21.4 % and 28.6 % at dosages of 3 %, 4 %, 5 %, 6 % and 7 %, respectively. However, the roughness of rejuvenator 2 rejuvenated bitumen increased 29.0 %, 26.5 %, 22.3 %, 18.4 %, and 9.7 % respectively. As previous studies have reported that the increase of surface roughness of bitumen can result in the increase of its adhesion performance. Moreover, the self-healing performance of bitumen is also positively correlated with the surface roughness of bitumen [54]. Therefore, these observations suggested that rejuvenators can improve the adhesion and self-healing performance of aged bitumen. However, the dosage of rejuvenators should be considered as inappropriate dosage of rejuvenators might adversely impact on the adhesion and self-healing properties of bitumen. The trends of the change of roughness with dosage were material dependent. Different trends might be attributed to the compatibility between rejuvenators and bitumen. If the rejuvenator is highly compatible with bitumen, their blends are believed to be homogeneous and stable. Therefore, the surface of the blend is expected to be less rough [55]. This assumption should be verified in the future studies by the compatibility characterisation methods such as using solubility science [56].

3.2. Micromechanical characterisation

3.2.1. The impact of ageing on micromechanics of bitumen

Based on the DMT modulus, the mechanical images can be mapped, as shown in Fig. 7. As the microstructure of bitumen is inhomogeneous, the images of DMT modulus showed similar “bee-structure” characteristics with topographical images. The moduli in dark areas were much lower than those in light areas, as indicated in Fig. 7.

This observation provided evidence that the “bee-structures” in the AFM images are not asphaltenes, contradicting to previous studies [57, 58]. The reason is straightforward, as it is well known that asphaltenes are stiffer than maltenes. If the “bee-structures” were asphaltenes, their modulus should be higher than their surrounding areas. However, opposite trends were observed, indicating that the “bee-structures” are seemingly not related to asphaltenes [50].

As shown in Fig. 8, ageing increased the DMT modulus of bitumen. For 40/60 binder, the DMT moduli increased 17 %, 121 %, 156 % and 164 % for short-term aged bitumen, long-term aged bitumen using PAV approach for 20 hours, 30 hours, and 40 hours, respectively. In terms of the DMT module for 70/100 bitumen, the increase percentages were 36 %, 76 %, 320 %, and 340 %, respectively. The DMT modulus suggested that the micromechanical properties of bitumen followed identical trend with the macro-mechanical properties in terms of ageing, as the complex modulus of bitumen increases continuously with ageing [8, 59]. Moreover, it was seen that the “bee-structures” resulted in significant variations in the DMT modulus of bitumen. The moduli in different areas varied considerably, suggesting that bitumen is an inhomogeneous material. When linking the micro properties of bitumen to the macro properties, the scale effect should be considered. For example, the selection of testing locations, as the selected location should be representatives of the whole sample rather than local representatives.

3.2.2. The impact of rejuvenation on the micromechanics of bitumen

The DMT moduli of rejuvenated bitumen are shown in Fig. 9. As expected, rejuvenators effectively softened the aged bitumen, denoted by gradually reduced DMT modulus.

The DMT moduli of rejuvenated bitumen using two types of rejuvenators were close to that of virgin bitumen at dosage 4, i.e. 6 % for rejuvenator 1 and 4 % for rejuvenator 2. This indicated that in terms of the DMT modulus, the optimal dosage for rejuvenator 1 was around 6–7 % while for rejuvenator 2 was around 3–4 %. The optimal dosage suggested that rejuvenator 2 was more efficient than rejuvenator 1 as less rejuvenator was required for rejuvenator 2 to get an equivalent softening effect with rejuvenator 1. Therefore, the DMT modulus is a promising metric when considering optimisation of the dosage of rejuvenators and addressing the mechanism of rejuvenation at the microscale level.

3.3. Micro-adhesion characterisation

3.3.1. The impact of ageing on micro-adhesion of bitumen

The adhesion properties of bitumen with varying ageing situations are shown in Fig. 10. In AFM testing, the adhesion force refers to the force required to separate the AFM probe from the surface of samples being examined. This force is indicative of the interactions between the probe and the specimen, including van der Waals forces, electrostatic

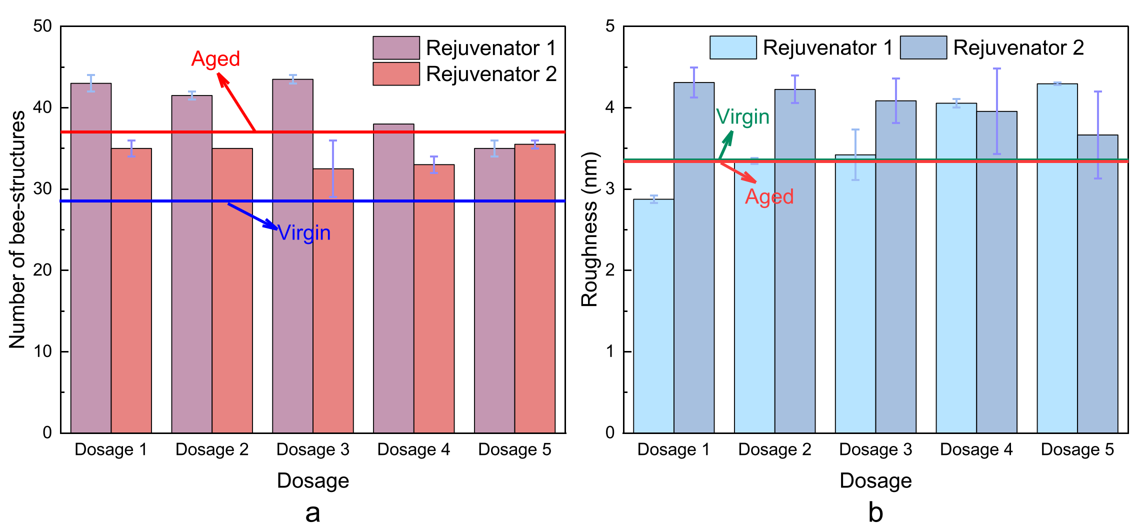


Fig. 6. Quantitative characteristics of micromorphology of bitumen in terms of rejuvenation (a) Bee-structures and (b) Roughness.

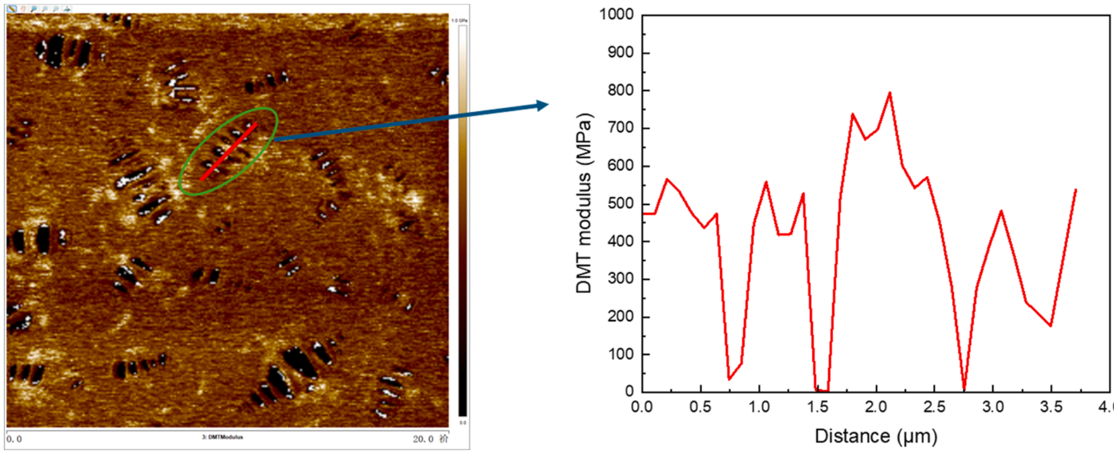


Fig. 7. 2D DMT modulus image (left) and DMT modulus mapping (right).

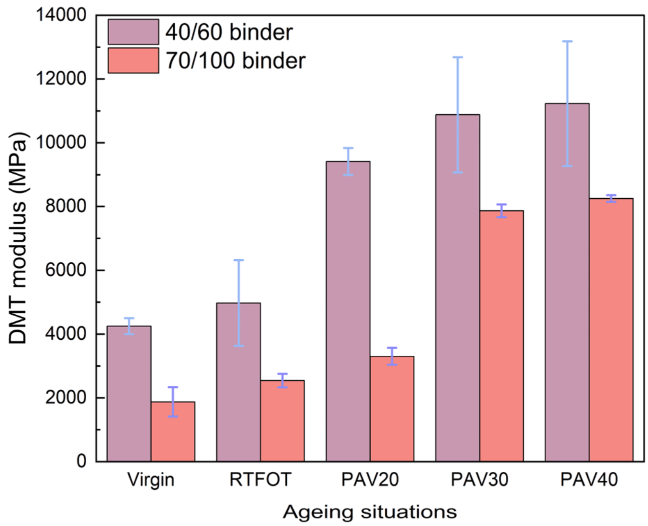


Fig. 8. DMT modulus of bitumen with different ageing levels.

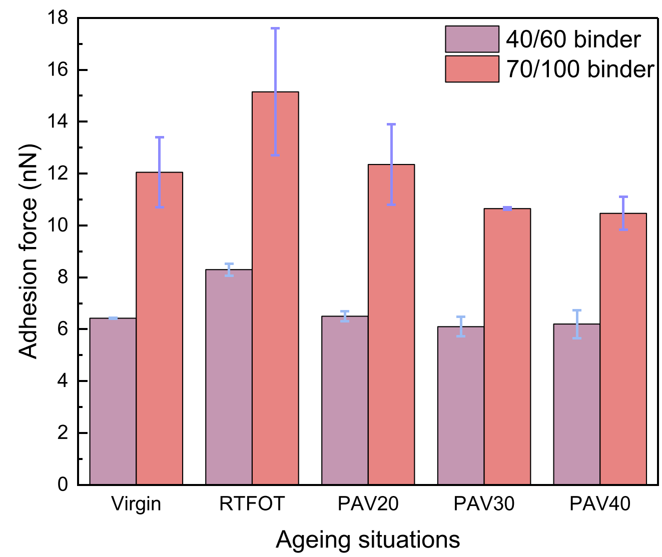


Fig. 10. Adhesion properties of bitumen in terms of ageing.

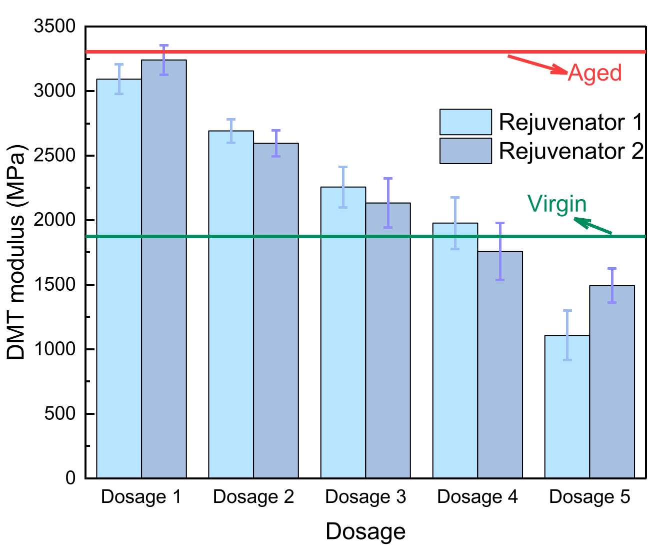


Fig. 9. DMT modulus of rejuvenated bitumen using different rejuvenators.

forces, capillary forces, and chemical bonding [60].

The adhesion related properties of bitumen is closely related to the ravelling resistance and moisture damage resistance of asphalt pavements [61,62]. Ageing has significant influence on the adhesion properties of bitumen, which adversely affect the adhesion performance [36, 63]. Controversy exists how prolonged ageing duration affects the adhesion performance of bitumen, at both macro and micro scales. Some studies have reported that ageing has positive influence on the adhesion performance of bitumen based on the pull-off tests. However, other studies have reported opposite observation [39,60].

As shown in Fig. 10, short-term ageing enhanced the adhesion force of bitumen while long-term ageing did not necessarily improve the adhesion properties. Prolonged ageing durations were seen to progressively reduced the adhesion forces and this trend was identical for both types of bitumen. After around 20 hours of PAV ageing, the adhesion forces of long-terms bitumen were close to that of virgin bitumen. This trend aligned with the adhesion properties of bitumen at the macro scale. Previous studies have reported that short-term ageing contributes to the bond strength of bitumen while long-term ageing reduced it gradually [42]. It is believed that the decrease of adhesion performance is related to the wettability of bitumen i.e., bond strength and nanoscale adhesion simulated by molecular dynamics simulation [42,64]. Moreover, it was observed that the alteration of adhesion force followed the same trend with the alteration of roughness, as analysed in the topographical properties subsection.

3.3.2. The impact of rejuvenation on micro-adhesion of bitumen

The adhesion properties of rejuvenated bitumen are shown in Fig. 11. Interestingly, the adhesion forces of rejuvenated bitumen decreased with dosage, suggesting that the increased dosage of rejuvenators adversely impacted the adhesion properties of rejuvenated bitumen.

It should be noted that when the dosage of rejuvenators was relatively low, the adhesion forces of rejuvenated bitumen were greater than those of both virgin and aged bitumen. However, when the dosages were relatively high, i.e. greater than 6 % for rejuvenator 1 and greater than 5 % for rejuvenator 2, the adhesion forces of rejuvenated bitumen were significantly lower than those of virgin bitumen. This reduction of adhesion forces might result in severe moisture damage due to the poor adhesion between bitumen and aggregates with the presence of water [65]. Therefore, in the perspective of adhesion properties, the dosage of rejuvenators should be designed carefully to assure the adhesion properties meet the practical requirements. Overall, the adhesion properties suggested that rejuvenators could improve the adhesion performance of bitumen. However, the dosage of rejuvenators should be designed carefully, as excessive dosage could adversely affect the adhesion performance [12].

3.4. Correlations between microscale properties of bitumen in terms of ageing and rejuvenation

The microscale properties of bitumen were characterised in previous subsections. Overall, correlations were observed between different microscale properties, such as roughness and adhesion force. The correlations between these properties during the ageing processes are illustrated in Fig. 12.

Fig. 12 suggested that there were strong correlations between DMT modulus and number of bee structures, and between adhesion force and roughness. The correlation coefficients were 0.86 and 0.85 respectively. DMT modulus was linearly and positively correlated with number of bee structures, indicating that the alteration in microstructures of bitumen could impact its micromechanical properties during ageing process. Moreover, the adhesion force was positively and linearly correlated with roughness, which aligned with previous studies [42]. This observation implied that the change in microstructures, such as surface roughness of bitumen could contribute to the change in the adhesion performance, as previous studies have reported that the micro properties of bitumen is closely correlated with its bulk properties [16]. There are some assumptions that could be used to explain the correlation between the roughness and adhesion performance. Firstly, as surface roughness increases, the total surface area available for adhesion also increases. This can enhance the mechanical interlocking between bitumen and the substrate, thereby improving adhesion at the microscale. Moreover, the increase of roughness leads to the increase of surface free energy, which contributes to the increase of the wettability of bitumen and subsequently the increase of adhesion properties and moisture damage resistance [66]. There were also linear correlations between roughness and bee-structures, adhesion and bee-structures, and adhesion and DMT modulus. However, these correlations were weak, denoted by the relatively lower correlation coefficients. DMT modulus was not correlated with roughness, the correlation coefficient was only 0.31. Therefore, the roughness has significant influence on the adhesion performance rather than on the stiffness of bitumen. Overall, these correlations indicate that based on microscale properties measured by AFM, selection of rejuvenators, and dosages can be optimised.

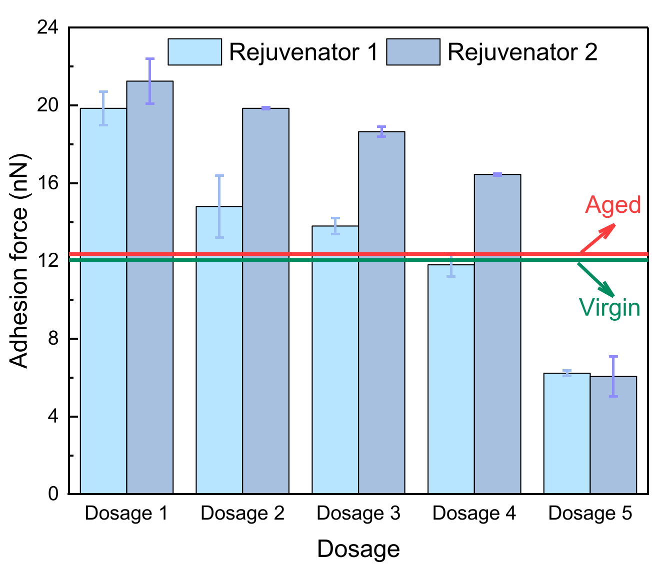


Fig. 11. Adhesion properties of rejuvenated bitumen.

4. Conclusions

This study investigated the topographical, micromechanical, micro-adhesion properties and their correlations of bitumen in terms of ageing and rejuvenation. Based on the results, the following conclusions could be drawn.

- Ageing increased the number of “bee-structures” while rejuvenation showed minimal relation with this metric. Ageing increased the roughness of bitumen initially, then decreased it. The roughness of rejuvenated bitumen was material dependent.
- Ageing increased the DMT modulus of bitumen while rejuvenation decreased it. The micromechanics of bitumen in terms of ageing and rejuvenation aligned with the macroscale mechanical properties.
- Ageing initially increased the adhesion forces of bitumen then decreased it gradually with prolonged ageing durations. Rejuvenating the bitumen with appropriate content of rejuvenators could improve the adhesion properties of aged bitumen. However, the adhesion forces decreased with dosages.
- Different aspects of microscale properties of bitumen were interlinked. Bee-structures were arbitrary in terms of ageing and rejuvenation. However, surface roughness of bitumen is likely closely related to its adhesion properties.

This study only used two types of bitumen and two types of rejuvenators. It is suggested that more diversity of materials should be used for future studies, and binders with varying ageing levels should be used for rejuvenation. It is also suggested that future studies link these results with the macroscale properties, such as the rheological properties of bitumen by comparing the microscale indicators with the rheological parameters. Additionally, scaling down the investigation to the nanoscale, i.e., molecular scale, is recommended to gain a more fundamental understanding of the mechanisms and behaviours of bitumen ageing and rejuvenation, and to link nanoscale properties with microscale properties.

CRediT authorship contribution statement

Singh Bhupendra: Writing – review & editing. **Kaya Özdemir Derya:** Writing – review & editing. **Airey Gordon D.:** Writing – review & editing, Supervision. **Li Bo:** Writing – review & editing. **Sreeram Anand:** Writing – review & editing, Supervision, Methodology, Formal analysis. **Si Wei:** Writing – review & editing, Resources, Funding acquisition. **Hu Yongping:** Writing – original draft, Software, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Yin Yike:** Writing – review & editing, Methodology,

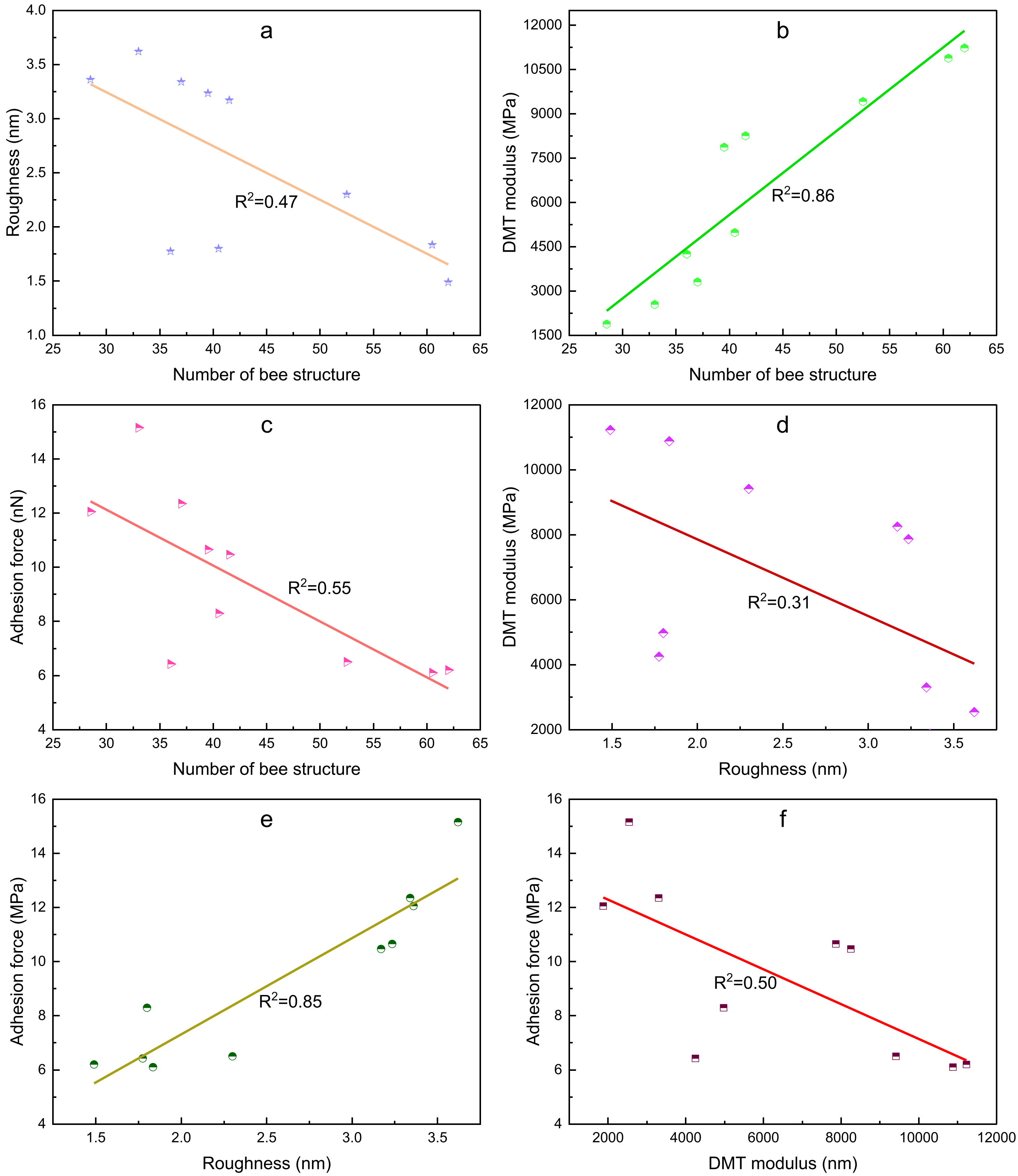


Fig. 12. Correlations of different microscale properties.

Investigation, Data curation. **Zhou Lu:** Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data Availability

Data will be made available on request.

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