Diffusion characteristics of surface treatment emulsion in aged asphalt mortar of porous asphalt mixture through SEM/EDS analysis

Bin Yang[a], Zhen Leng[a*], Jiwang Jiang[b], Ruiqi Chen[a], Guoyang Lu[c]

[a] *Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Kowloon, Hong Kong*

[b] *School of Transportation, Southeast University, Nanjing, Jiangsu, China*

[c] *Department of Architecture and Civil Engineering, City University of Hong Kong, Kowloon, Hong Kong*

*Corresponding author: Zhen Leng. Tel: +852-2766-6007; Fax: 852-2334-6389;

Email: zhen.leng@polyu.edu.hk

(Total word: 6159 words)

Diffusion characteristics of surface treatment emulsion in aged asphalt mortar of porous asphalt mixture through SEM/EDS analysis

Abstract: Spaying surface treatment (ST) asphalt emulsion can be an effective preventive maintenance method to alleviate the ravelling problem of porous asphalt (PA) pavement. The applied ST emulsion may gradually diffuse in and soften the aged asphalt mortar film in PA, which however still lacks quantitative evidence. This study aims to quantify the diffusion behavior of new ST emulsion residue in aged asphalt mortar of PA within 28 days of curing. The Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) was utilized to capture the spatial distribution of ST emulsion residue within PA under different curing temperature and duration conditions. Titanium dioxide was selected as a tracer for the ST emulsion. A new statistical index of diffusion degree (Dd), derived from the counting of Ti and S elements, was proposed to quantify the diffusion depth of ST emulsion residue in aged asphalt mortar. It was found that the SEM/EDS is an effective microscopic method to directly monitor the diffusion phenomenon at the mixture scale. Both the curing temperature and curing duration are important factors affecting the diffusion rate. The diffusion rate at 60 ºC is about 5 times faster than that at 25 ºC, indicating that spraying ST emulsion in hot weather can improve its diffusion efficiency. Besides, the existence of fine aggregates in mortar may increase the diffusion path due to the hindrance effect. The outcomes of this study shed more light on the diffusion of soft binder in aged asphalt mortar of PA at normal temperature but a longer time period.

Keywords: porous asphalt (PA); surface treatment (ST) emulsion; diffusion phenomenon; scanning electron microscopy (SEM); energy dispersive spectroscopy (EDS)

1 Introduction

Porous asphalt (PA), an open-graded asphalt mixture with a large air void content, has been widely used as an environmental-friendly pavement material (Stempihar *et al.* 2012, Ma *et al.* 2018, Zhong *et al.* 2018). However, compared with dense-graded and gap-graded asphalt mixtures, PA usually has a relatively shorter service life mainly due to the ravelling problem. Recently, the Dutch Ministry of Infrastructure and Environment found that spraying surface-treatment (ST) emulsion was a promising preventive maintenance technology to alleviate the ravelling problem of the in-service PA wearing courses (Van de Ven *et al.* 2013). Unlike the fog seal, which is usually applied to dense-graded and gap-graded asphalt pavements, the ST emulsion is expected to penetrate into the PA mixture without clogging air voids and compromising the functional properties. Zhang *et al.* (2012) revealed that applying rejuvenation materials to PA pavements could fill in micro-cracks and thicken asphalt binder film. They concluded that ST emulsions could rejuvenate the aged asphalt binder in the mortar via diffusion (Zhang 2015, Zhao *et al.* 2016, Zhang and Leng 2017). Xu *et al.* (2018) also investigated the improvement effect of different ST emulsions on ravelling resistance by conducting the single-sided Cantabro test. They found that one of the ST emulsions containing a rejuvenator exhibited a significant recovery effect on the ravelling resistance of PA. Braham *et al.* (2013, 2015) used beam mixtures to conduct the bending beam rheometer (BBR) test, and they found that the m-value was more sensitive than the stiffness to characterize the rejuvenation effect of asphalt emulsion on aged asphalt pavement.

Nowadays, many studies have been conducted to investigate the diffusion of soft virgin binder/rejuvenator in the aged binder of reclaimed asphalt pavement (RAP) at high construction temperatures. When the contact surfaces between virgin and aged binders are established during the mechanical mixing process, binder diffusion becomes the dominant process that governs the blending quality of RAP (Orešković *et al.* 2020, Pirzadeh *et al.* 2021). These studies ranged from the microscopic or rheological investigation of diffusion phenomenon in aged binder up to laboratory-prepared mixture specimens. One of the earliest studies of the diffusion in aged binder was performed by Oliver (1974), and the radioactive material was chosen to mark rejuvenators. It was found that adding more rejuvenators or increasing the temperature could increase the diffusion rate. Attenuated total reflectance-fourier transform infrared spectrophotometry (ATR-FTIR) was also used to characterize the diffusion of rejuvenator in aged binder (Karlsson and Isacsson 2003a, Karlsson and Isacsson 2003b), which indicated that temperature had a significant effect on the diffusion coefficient, which follows the Arrhenius-type relationship. Later on, the same researchers characterized the diffusion using the dynamic shear rheometer (DSR) and claimed that the diffusion phenomenon could be described by Fick's law (Karlsson *et al.* 2007), which is consistent with the findings of their early studies. For the characterization of diffusion in asphalt mixture in the laboratory, a multistep staged solvent washing and extraction method has been widely used for analyzing the different binder layers around RAP aggregate particles (Noureldin and Wood 1987, Huang *et al.* 2005). Then, the properties of different binder layers were characterized by various chemical and rheological tests such as gel permeation chromatography (GPC), DSR, and FTIR tests to evaluate the diffusion degree of virgin binder or rejuvenator in the aged binder of RAP (Kriz *et al.* 2014, Rad *et al.* 2014, Zhao *et al.* 2016). It was found that the diffusion of virgin binder in aged binder could be accomplished in hot mix asphalt (HMA) containing 50% RAP, which can also be improved by adding the warm mix additive (WMA) (Zhao *et al.* 2016). Besides, some researchers selected molecular dynamics simulations to investigate the diffusion between virgin binder/rejuvenator and aged binder (Ding *et al.* 2016, Ren *et al.* 2022). However, previous studies about the diffusion of virgin binder/rejuvenator in aged binder were mainly focused on RAP mixture at a higher temperature within a few hours. Very few studies have been conducted on the potential diffusion phenomenon at room temperature with a long duration, which is important to understand the interaction mechanism between ST emulsion residue and aged asphalt mortar of PA from a microscopic perspective.

Some recent studies showed that Scanning Electron Microscopy (SEM) with Energy Dispersive Spectroscopy (EDS) was an effective tool to investigate the blending efficiency between virgin and aged binders in RAP mixture (Castorena *et al.* 2016, Jiang *et al.* 2018). Titanium dioxide (TiO_2) was selected as a tracer to tag virgin binder to evaluate the binder mobilization, which provides an alternative way to characterize binder diffusion at room temperature. Although spraying ST emulsion is a potentially effective preventive maintenance method to alleviate the ravelling problem of PA, relevant studies or applications are still in the early stages. Little is known about whether the applied ST emulsion residue diffuses into aged asphalt mortar of PA or not, and there is no quantitative indicator available to characterize the diffusion behavior. To fill these knowledge gaps, this study aims to: 1) develop a specimen preparation method for observing the diffusion phenomenon by SEM/EDS; 2) investigate the diffusion of ST emulsion in aged asphalt mortar of PA under different curing conditions (e.g., temperatures and curing durations); and 3) propose a quantitative index for characterizing the diffusion degree. The findings are expected to provide guidance for applying ST to PA for preventive maintenance and promote its application.

2 Materials and Methodology

2.1 Laboratory testing program

2.1.1 Materials and mixture design

One PA mixture with a nominal maximum aggregate size of 13.2 mm (PA-13) was selected in this study. The asphalt binder was a SBS modified asphalt binder that fulfilled the Superpave performance grade of 76-16 (PG76-16). The aggregates used were granite. The hydrated lime with a content of 1.5% by mass of total aggregates was added into mixture to improve its moisture damage resistance. According to the Chinese standard JTG/T 3350-03-2020, the optimum asphalt content was determined as 3.9% by mass of the mixture, and the target air void content was 23%. The aggregate gradation of PA-13 is shown in Figure 1.

A cationic slow-setting (CSS-1) type asphalt emulsion was prepared as the ST emulsion. The ST emulsion was prepared by using a catatonic emulsifier, containing fatty amine derivatives. The contents of asphalt binder, emulsifier, deionized water, and stabilizer are 60%, 3%, 36.8%, and 2‰ by mass of ST emulsion, respectively. Firstly, a virgin asphalt binder with a penetration grade of 60/70 (Pen60/70) was heated to 135 ºC for later mixing. The emulsifier was mixed with deionized water at 60 ºC to prepare the soap solution. Calcium chloride powders were subsequently added to soap solution as the stabilizer. Then, the hydrochloric acid was gradually dropped into soap solution and a glass rod kept stirring the soap solution until the PH value reached 2.0-2.5. It should be noted that the well-prepared soap solution needs to be stored in oven at 60 ºC for several seconds. After that, the soap solution was poured into a colloid mill with a shearing rate of 2,870 rpm. Finally, the heated asphalt binder with a temperature of 135 ºC was gradually added into the soap solution and emulsified by the colloid mill within 2 minutes. Table 1 shows the basic information of the ST emulsion. TiO2 was selected as a tracer to tag the ST emulsion and its basic physical properties are shown in Table 2. As recommended by previous studies (Castorena *et al.* 2016, Pape and Castorena 2021), the tracer content is 10% by mass of virgin binder. TiO_2 was first mixed with virgin binder by a high-speed shear mixer and then the TiO_2 modified asphalt binder was emulsified by the soap to produce ST emulsion for spraying. In this study, each specimen was placed on a balance during the whole spraying period to precisely control the application dosage of ST emulsion. The emulsion was sprayed to specimen's surface via a spraying gun.

This device is commonly used in the coating field (Perše *et al.* 2013, Toma *et al.* 2013, Wang *et al.* 2022) and can simulate on-site spraying conditions on asphalt pavement in the field. Compressed air was used to atomize ST emulsion and direct its particles. Then ST emulsion could be uniformly sprayed to the specimen's surface. The application rate of 0.6 kg/m^2 for ST emulsion was used based on our previous works (Jiang *et al.* 2022, Yang *et al.* 2022).

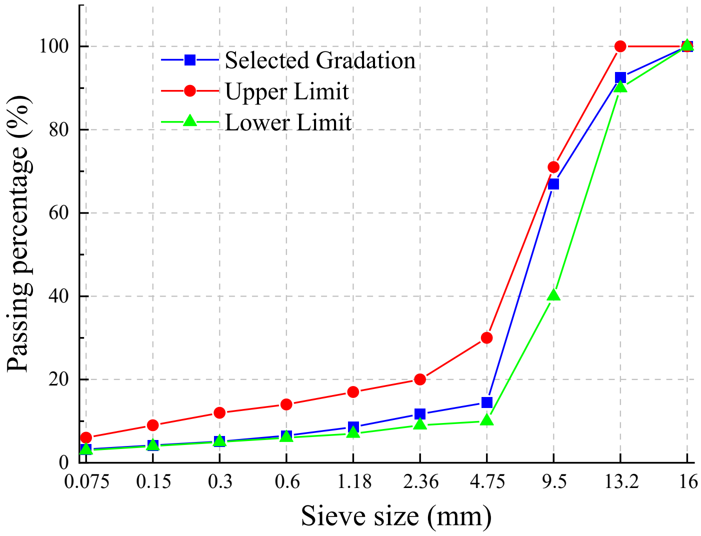


Figure 1. Aggregate gradation of PA-13

Table 1. Basic properties of ST emulsion

	Evaporated residue				Storage stability	
	Residue content (%)	Penetration (25 °C, 0.1 mm)	Softening point (°C)	Ductility (5 °C, cm)	1 day (%)	5 days (%)
ST emulsion	60	64	50	67.2	0.3	2.1

Table 2. Physical properties of TiO_2

Color	Appearance	Purity (wt%)	Specific surface area (m^2/g)	Granularity (nm)
White	Powder	99.90	78	500

2.1.2 PA Specimen preparation and performance test

All PA specimens were subjected to long-term aging (Zhang *et al.* 2021) and freezethaw conditioning (ASTM D7064) to artificially create internal micro-cracks. Then, ST emulsions were sprayed to those damaged PA specimens, which were cured for different durations at 25 °C or 60 °C. The mass loss ratio of the treated PA specimen was determined through the Cantabro Abrasion test in accordance with ASTM C131 to evaluate the effects of curing conditions (duration and temperature) on the recovery efficiency of ST emulsion. The mass loss ratio was calculated by Eq. (1). Three replicates were prepared for each condition.

$$Mass\ loss\ ratio = \frac{m_1 - m_2}{m_1} \times 100\% \qquad (1)$$

where m_1 and m_2 represent the original and final mass of the tested specimen before and after the Cantabro abrasion test, respectively, g.

Figure 2 shows the variations in mass loss ratio as a function of curing time at different curing temperatures. At the very beginning (without curing), the mass loss ratio is about 32%. With the increase of curing of ST emulsion, the mass loss ratios of PA specimens rapidly decreased and gradually flattened out. Specifically, a higher curing temperature may accelerate the demulsification and water evaporation of ST emulsions, so the specimens cured at 60 °C showed a lower value of mass loss ratio than that those at 25 °C at the early stage. After 14 days of curing, it could be speculated that all water in PA mixture has evaporated. Specimens cured at two different temperatures should have exhibited a similar recovery efficiency of ravelling resistance. But the mass loss ratio still indicated a relatively lower value at 60 °C than that at 25 °C, which is about 1%. It can be attributed to a more sufficient diffusion of ST residue in aged asphalt mortar at a higher curing temperature, which benefits the rejuvenation of aged asphalt binder in PA. It should be noted that the diffusion phenomenon might happen once the ST residue covered aged asphalt mortar or filled up micro-cracks inside PA mixture. Next, the SEM/EDS was adopted to investigate the potential diffusion of new ST emulsion residue in aged asphalt mortar from the microscopic perspective.

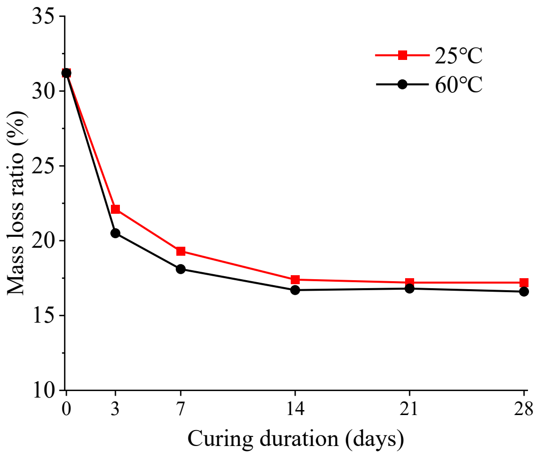


Figure 2. Temporal variations of mass loss ratios at 25 °C and 60 °C

2.1.3 SEM/EDS specimen preparation

A procedure with multiple steps was followed to prepare the specimens for the SEM/EDS test. The damaged PA specimens with a diameter of 150 mm and a height of 40 mm were first prepared by the Superpave gyratory compactor (SGC). Small PA specimens with a diameter of 30 mm were then drilled out from the SGC specimens (Figure 3a). After that, these small specimens were sawed into several slices with a thickness of 5 mm (Figure 3b). ST emulsion containing TiO_2 was sprayed on the surface of the thin slices, which penetrated into PA through the interconnecting pores (Figure 3c). After ST, the thin slices were dried in a vacuum drying oven for 24 hours of curing to accelerate the demulsification of emulsified asphalt and evaporation of water. Then, the specimens were immersed in epoxy resin under a vacuum of 90 kPa for 10 min. This process not only helps get a clear boundary between the epoxy and mortar film for the convenience of quickly locating the added ST emulsion, but also improves the strength of the whole mixture to avoid the dislodgement of aggregate particles and the slippage of mortar during specimen grinding and polishing. Subsequently, the specimens were ground and polished until the smooth surface was exposed (Figure 3d). The reason is that a sloping and rough surface may prevent the electronic signal from bombarding the specimen to form shadow areas or hinder the detector from collecting the excited electronic signal. Finally, the surface of each specimen was sputter-coated by Au to make it conductive for microscopic observation (Figure 3e). It's also recommended to draw some silver paints lines from the specimen surface to the carbon tape at the bottom of the specimen to improve the specimen's conductivity. Besides, pre-marking of the air void peripheries on the specimen surface can help locate the target test areas quickly.

The specimen preparation procedures shown in Figure 3 not only preserve the original morphology of PA specimen as much as possible but also allow direct in-situ observation of the diffusion of ST emulsion residue in aged asphalt mortar of PA.

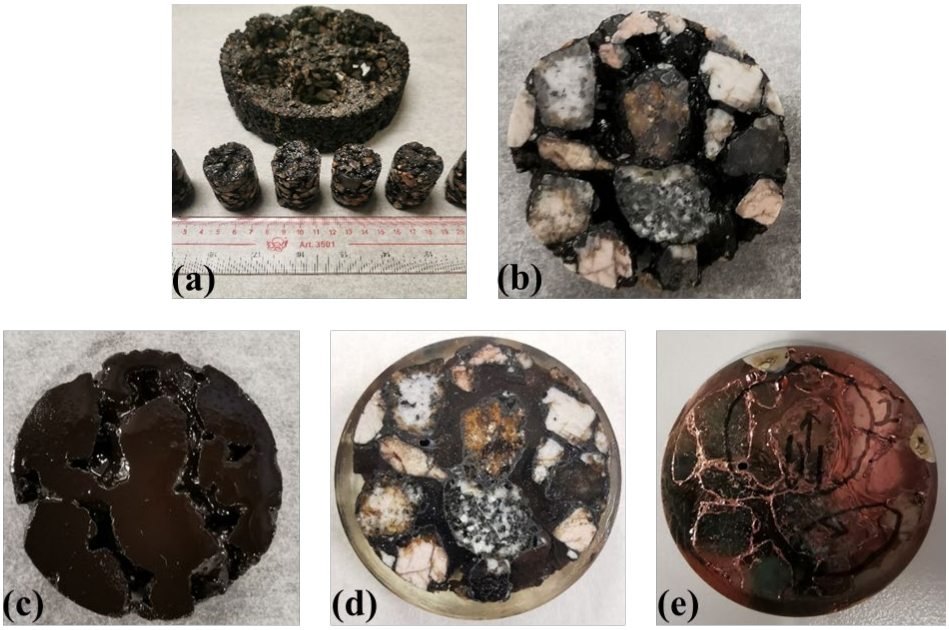
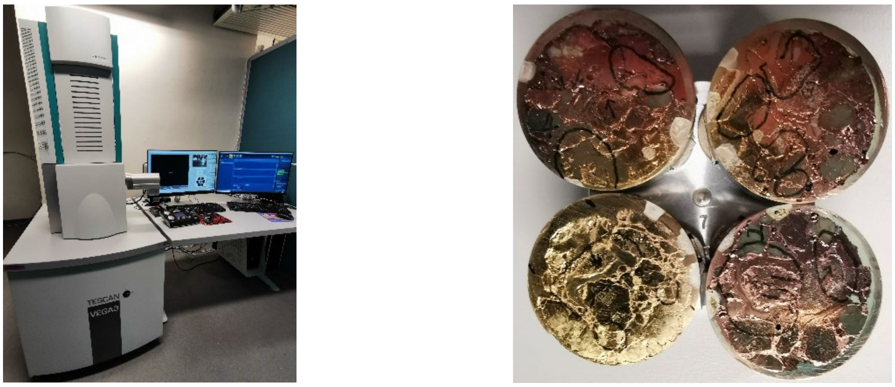


Figure 3. Procedures for specimen preparation: (a) Drilling cores; (b) A slice of PA; (c) Spraying ST emulsion; (d) Grinding and polishing; (e) Sputter coated by Au

2.2 Identification and analysis of characteristic elements

A TESCAN VEGA3 scanning electronic microscope (SEM) equipped with an Oxford energy-dispersive X-ray spectroscope (EDS) was used to investigate the diffusion of ST emulsion in aged asphalt mortar (Figure 4a). The accelerating voltage was 20 KV and the backscattered electron (BSE) imaging was performed on the PA specimen after ST.

Four specimens were prepared according to the aforementioned method (Figure 4b). Two curing temperatures (25 ºC and 60 ºC) and five curing durations (0d, 7d, 14d, 21d and 28d) were considered in this study. Two replicates were prepared at each temperature for periodic observation and three different locations were selected for each specimen to conduct the EDS tests.

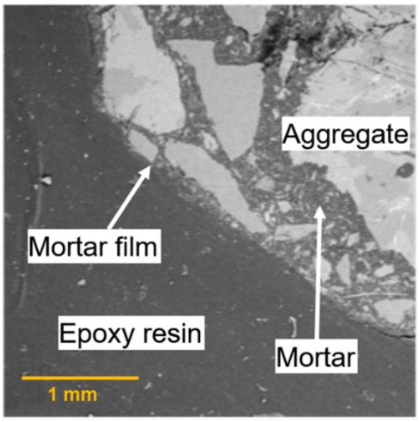


(a) (b)

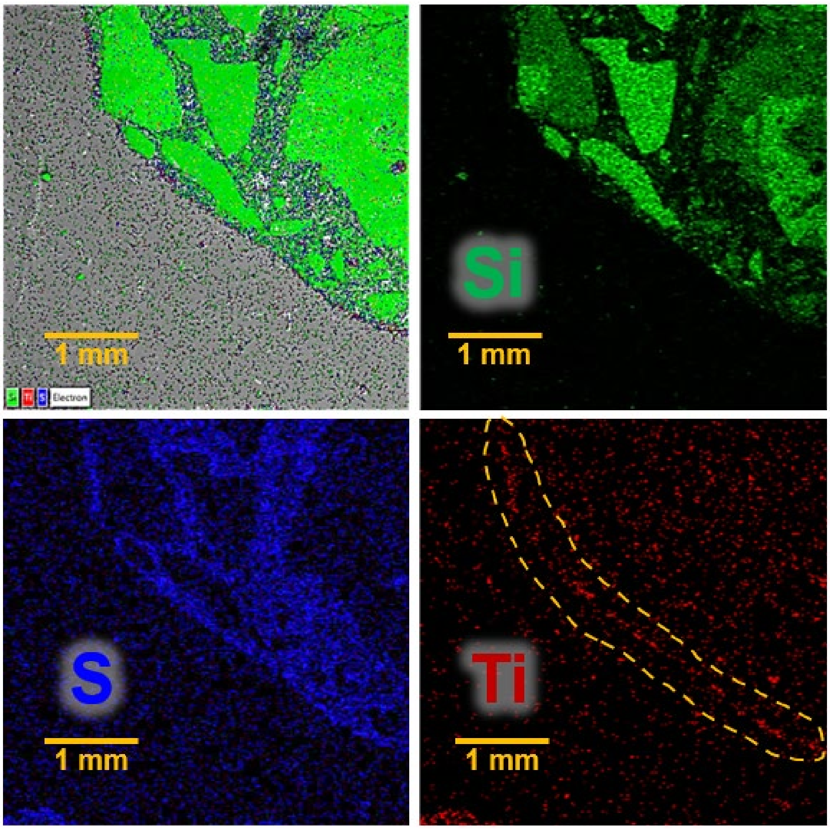
Figure 4. SEM/EDS testing: (a) SEM equipment; (b) Final prepared specimens

2.2.1 Selection of test areas and consistency verification

The morphology of a test area on a specimen's surface is shown in Figure 5(a). Fine aggregates, mortar and epoxy resins can be clearly distinguished in each SEM image based on their colors and relative positions. Meanwhile, the location of mortar film can be inferred according to the relative position of the other components of specimens, which is critical for the EDS line scanning test later. Because each component of PA mixtures has a unique characteristic element, chemical analysis of a test area by EDS allows the identification of mechanically similar but chemically distinct phases. The silicon (Si), titanium (Ti) and sulfur (S) are the characteristic elements of the aggregates, added ST emulsion and aged asphalt binder, respectively. Epoxy resin is an organic material consisting of carbon, hydrogen, and oxygen, which are also the main elements in asphalt binder. Therefore, no particular element can be selected to represent the epoxy resin in this study. Figure 5(b) shows the EDS map scanning results. The main distribution areas of the aggregates, new and aged asphalt binder are illustrated by green, red and blue colors, respectively. A red contour line was observed along the boundary between epoxy resin and PA, suggesting that the applied ST emulsion was distributed around the contact zone between epoxy and mortar.



(a)



(b)

Figure 5. Consistency verification of characteristic elements: (a) SEM image; (b) EDS map scanning images

2.2.2 Boundary identification of different components in PA specimen

Based on the EDS map scanning results, the EDS line scanning test was conducted around the areas of the applied ST emulsion to further identify different components. As shown in Figure 6, an EDS line scanning was performed from epoxy resin to aggregate to collect S/Ti/Si intensity data along the interesting line. The length of the line was controlled to be long enough to span the applied ST emulsion and old mortar film areas.

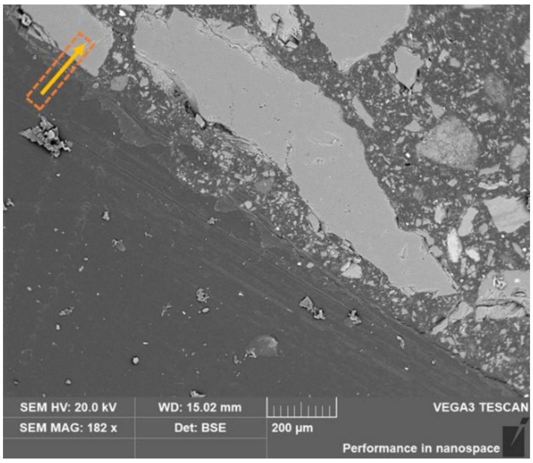


Figure 6. Example of an EDS line scanning test

Figure 7(a) shows the enlarged image of the test area. The EDS line was controlled to be as perpendicular as possible to the aggregate for the convenience of internal comparisons. Figure 7(b) illustrates the scanning results along the EDS line. The Y-axis unit, namely counts per second (cps), represents the intensity of each element, which is only related to the element content. The element intensities of Ti and S began with low value and rapidly grew as the line scanned from the epoxy resin to the ST emulsion residue. However, when the line scanned from the ST emulsion residue to the aged asphalt mortar, the intensity of Ti suddenly reduced to a similarly low level, but that of S remained at a peak level as before. Subsequently, when the line scanned from the aged asphalt mortar to aggregate, especially at the interfacial transition zone (ITZ), the intensity of Si dramatically increased to a very high level while that of S rapidly decreased to a low level. Therefore, three boundaries between epoxy resin, ST emulsion residue, aged asphalt mortar and aggregate can be clearly distinguished and identified at the ITZs based on the line scanning results of the three characteristic elements. It indicated that different components of PA specimens could be identified and demarcated by the EDS line scanning test, which makes it possible to continuously observe the potential diffusion of the ST emulsion residue in the aged asphalt mortar of PA.

(a)

(b)

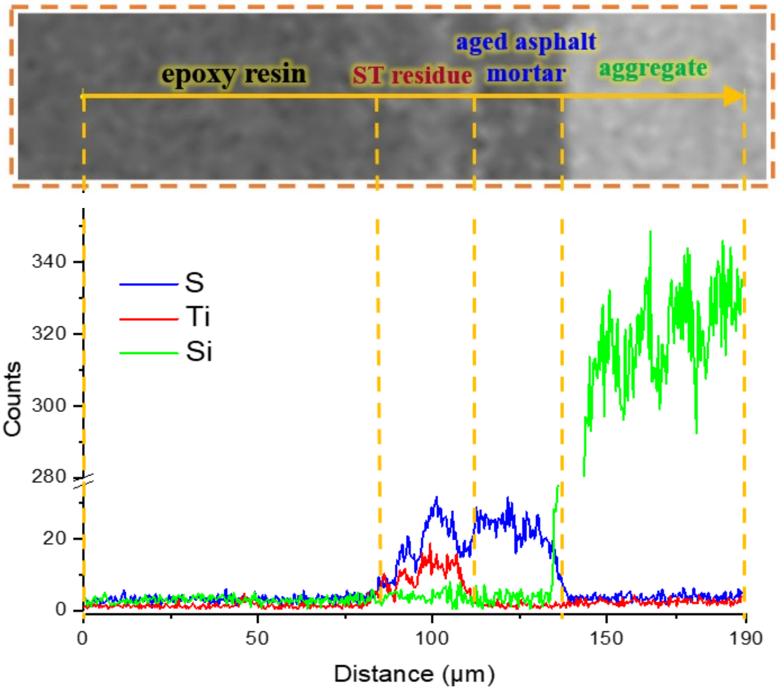


Figure 7. EDS line scanning results: (a) Test area; (b) Intensity distribution of elements

2.2.3 Diffusion degree of ST emulsion residue in aged asphalt mortar

Since the mass of the applied ST emulsion is fixed, the mass of the added tracer TiO_2

is also a constant. In the asphalt binder area containing tracers, the tracer content is expected to alter as the curing condition changes, representing the diffusion phenomenon. A new statistical indicator, namely the diffusion degree (D_d), was proposed and calculated using Eq. (2) to quantify the diffusion of ST emulsion residue in aged asphalt mortar. It is defined as the average ratio of Ti count number to S count number at each point in the asphalt binder area containing tracers. The line scanning test was repeated three times for each test area. At least 80 points per line were included in the calculation of D_d. It should be noted that the sulfur content of asphalt binder used in ST emulsion is similar to the sulfur content of asphalt binder used in the mixture based on the EDS line scanning test results.

$$D_d = \frac{1}{n}\sum_{i=1}^{n}\frac{C_{Ti}^{i}}{C_{S}^{i}} \tag{2}$$

where n is the number of points in the asphalt binder area containing TiO_2; C_{Ti}^{i} represents the count number of the Ti at the point of number i; and C_{S}^{i} is the count number of the S at the point of number i. A lower D_d indicates that more ST emulsion residues diffuse into the aged asphalt mortars.

3 Results and Discussions

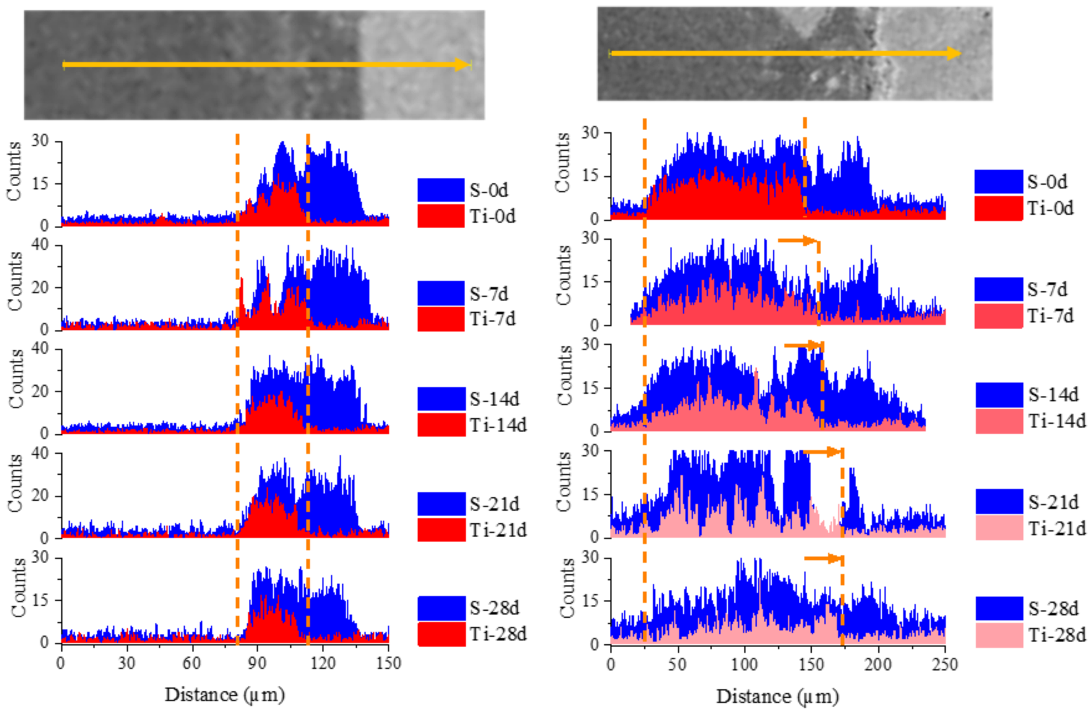
3.1 Diffusion phenomenon at different curing conditions

When applying ST emulsion to PA pavement, the pavement surface temperature may affect the ravelling resistance recovery of PA pavement. The climate of Hong Kong is subtropical, with mild winter and hot summer. In this study, the curing temperatures of 25 °C and 60 °C were selected to represent room temperature and higher temperature for the road surface, respectively (Yang *et al.* 2020). It should be noted that although the actual pavement surface cannot maintain a higher temperature, e.g. 60 °C, all day long, it is meaningful to investigate the effect of curing temperature on the diffusion efficiency of ST emulsion in aged mortar, which can help guide the selection of maintenance environment. Besides, considering that the diffusion phenomenon in asphalt mixture might be a very slow process at aforementioned temperatures, the EDS line scanning test is repeated every 7 days until no visible signs of diffusion occurred.

Figure 8 depicts two SEM images labeled with the yellow line scanning areas and the variations of two characteristic elements along the test path at two different curing temperatures. The asphalt binder area contains element S and the ST emulsion residue region contains element Ti. Based on the intensity variation of Ti along the scanning distance, the asphalt binder area containing the TiO2 tracer was illustrated between two vertical dark dash lines in each figure. Figure 8(a) shows that when the curing temperature is 25 °C, neither the intensity of Ti nor the length of the asphalt binder area containing tracers changed significantly over the whole continuous observation, indicating that there is no apparent diffusion of new ST emulsion residue in aged asphalt mortar. However, Figure 8(b) illustrates that when the curing temperature is 60 °C, the shapes of red and blue patterns were constantly changing, especially the length of the red region representing element Ti gradually increased. Their boundaries also became blurred at 60 °C as the curing duration increased. In other words, the length of the asphalt binder area containing TiO_2 gradually extended toward the aged asphalt mortar region as the curing duration increased, suggesting that the ST emulsion residue gradually diffused into and fused with aged asphalt binder. Such disparities between two different curing temperatures indicate that the curing temperature significantly affects the diffusion of ST emulsion residue in aged asphalt mortar. A higher curing temperature can promote the diffusion efficiency and further rejuvenate the aged asphalt binder, which is helpful to improve the ravelling resistance of PA pavement. This also provides an explanation for the relatively lower mass loss ratio of treated PA specimen at 60 °C as presented in Figure 2. Therefore, it is recommended to spray ST emulsion on PA pavement in hot weather (e.g. summer) to achieve better maintenance efficiency. Due to the low reflectivity of road surface and the moderate heat conductivity of asphalt, the region near the pavement surface area usually has a relatively higher temperature than the air temperature (Asaeda *et al.* 1996). And the average temperature of pavement surface area in summer is higher than in other seasons, which is helpful to promote the diffusion efficiency of those penetrated ST emulsion residues near the top of road surface.

Furthermore, as shown in Figure 8(b), because the mass of added tracer is a certain value, the distribution of element Ti disperses with the diffusion of ST emulsion residue in aged asphalt mortar, resulting in a decrease in the intensity of Ti. Thus, the red color representing the Ti gradually fades from crimson to light red with the increase of the curing duration. These variations once again confirmed the existence of the diffusion of new ST residue in aged asphalt binder.

Besides, it was also found that the diffusion phenomenon is difficult to observe after curing for 21 days. One possible explanation is that due to the physisorption, chemisorption, and mechanical interlock, the adhesion between asphalt and aggregate is stronger as it gets closer to the aggregate surface area (Zhu *et al.* 2017). Thus, the diffusion phenomenon can hardly be observed on the side close to the aggregate surface.



(a) (b)

Figure 8. Effect of curing temperatures on diffusion: (a) 25 °C; (b) 60 °C

3.2 Diffusion degree of ST emulsion residue in aged asphalt mortar

As shown in Figure 9, the diffusion behaviors within the treated PA were further statistically analyzed by the D_d values under different curing conditions. The D_d values at 25 °C and 60 °C were similar at the beginning, which are around 0.54. But they exhibited different changing trends at two curing temperatures as the curing duration increased. When the curing temperature is 25 ºC, although no obvious diffusion behavior showed in Figure 8(a) from a qualitative perspective, D_d presented a slightly decreasing trend from 0.54 to 0.49 throughout the curing duration. Meanwhile, when the curing temperature is 60 ºC, D_d gradually decreased with the extension of diffusion area and then flattened out around 0.28 after 21 days of curing. The reductions in D_d over the entire test period at 25 ºC and 60 ºC are 0.05 and 0.25, respectively. Thus, the diffusion rate at 60 ºC is around 5 times faster than that at 25 ºC, which again proves that a higher curing temperature can accelerate the diffusion of ST emulsion residue in aged asphalt mortar.

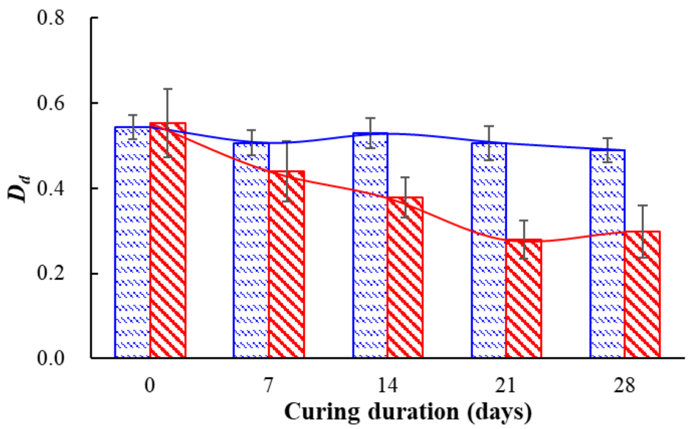


Figure 9. D_d under different curing conditions

3.3 Hindrance effect of fine aggregate on diffusion behavior

Asphalt mortar consists of fine aggregates, fillers and asphalt binders, which adheres to the coarse aggregate surface and interconnects with other aggregates. The actual diffusion condition of the applied ST residue in aged asphalt mortar is not as simple as that in pure aged asphalt binder. As shown in Figure 10(a), the intensity of S decreased sharply, while the intensity of Si increased dramatically near the regions containing fine aggregates. Due to the hindrance effect of fine aggregates, the diffusion of the ST emulsion residue in aged asphalt mortar could be obstructed even at the high curing temperature of 60 °C. In other words, the existence of fine aggregates in aged asphalt mortar may increase the diffusion path of new ST residue in aged asphalt mortar. Therefore, no obvious diffusion phenomenon was observed in Figure 10(b). Besides, the variations of D_d with and without fine aggregates in the diffusion path at 60 °C are illustrated in Figure 11. The D_d remained relatively stable over the whole observation period when fine aggregates existed in the test area, indicating that the existence of fine aggregates in the diffusion path could significantly decrease the diffusion efficiency. Thus, the diffusion behavior in mortar is more complex than that in asphalt binder, which needs further study.

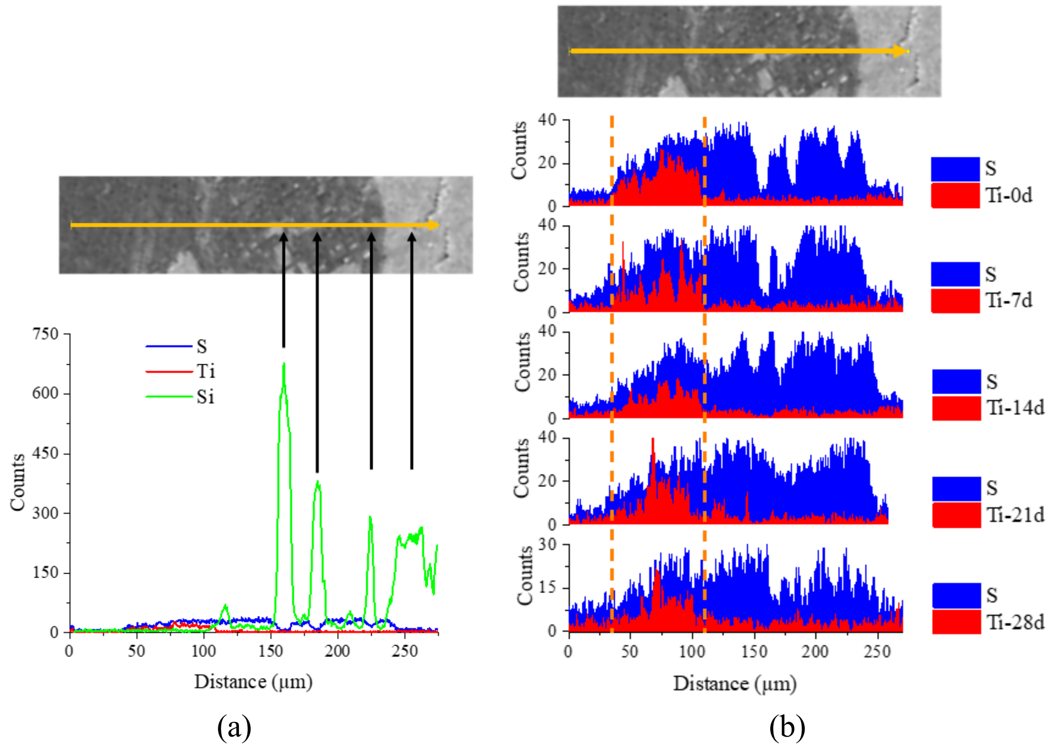


Figure 10. Hindrance effect of fine aggregates on diffusion: (a) Intensity distribution of element; (b) EDS line scanning test results at 60 °C

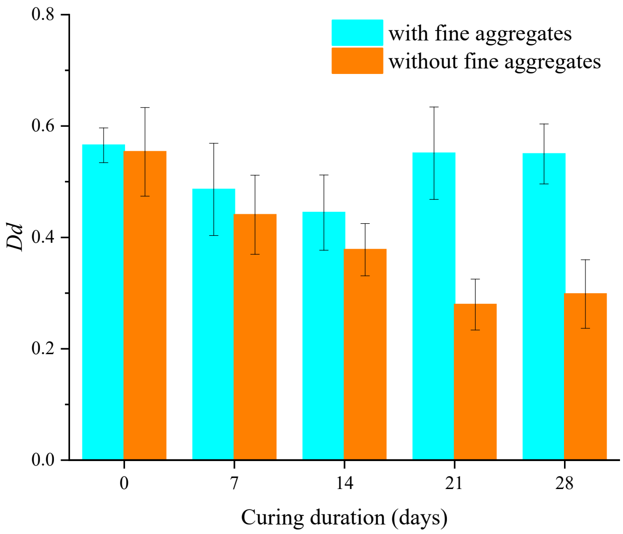


Figure 11. Variations of D_d with and without fine aggregates

4 Findings and Conclusions

In this study, a multi-step procedure was developed to prepare the treated PA specimens for the SEM/EDS test. The diffusion behavior was traced by the characteristic elements of different components in PA. The complex diffusion phenomena of the applied ST emulsion residues in aged asphalt mortars were investigated under different curing conditions. Moreover, a statistical indicator, D_d, was proposed to quantify the diffusion degree. The main findings and conclusions of this study are summarized as follows:

- The boundaries between the applied ST emulsion residues and other components of PA can be clearly distinguished through the SEM/EDS, which is an effective microscopic technique to directly observe the diffusion phenomenon within the PA mixture by careful specimen preparation.
- Curing temperature has a significant effect on the diffusion phenomenon and a higher curing temperature can accelerate this process based on the indoor test

results. Considering that the average temperature near the pavement surface area in summer is higher than in other seasons, it is recommended to spray ST emulsions on PA pavement in hot weather (e.g. summer) to enhance the efficiency of this preventive maintenance technology in the field.

- The diffusion phenomenon was obvious after curing for 21 days at 60 °C, while it was not apparent after 28 days at 25 °C.
- D_d can quantify the diffusion degree of the ST emulsion residue in aged asphalt mortar. A lower D_d value indicates a better diffusion status. The diffusion rate at 60 °C was about 5 times faster than that at 25 °C for the case investigated in this study.
- The diffusion phenomenon of ST emulsion residue in aged asphalt mortar is complex. The existence of fine aggregates in mortar may increase the diffusion path due to the hindrance effect.

It is worth noting that only one type of ST emulsion was selected in this study to investigate its diffusion in aged asphalt mortar of PA mixture in the laboratory. More ST emulsions containing different rejuvenators will be considered in the future to compare their diffusion rates in PA specimens. And the field data are necessary to further verify whether hot weather is helpful in enhancing the maintenance efficiency of ST emulsion.

Acknowledgments

The work described in this paper was fully supported by grants from the Research Grants Council of the Hong Kong Special Administrative Region, China (GRF projects No. 15209920 and No.15220621). The authors also thank Ingevity Corp. for providing emulsifiers for this study.

Disclosure statement

The authors report there are no competing interests to declare.

References

Asaeda, T., Ca, V.T. & Wake, A., 1996. Heat storage of pavement and its effect on the lower atmosphere. *Atmospheric environment,* 30 (3), 413-427.

Braham, A., Howard, I.L. & Barham, J., 2013. Exploration of a performance test for emulsion treated asphalt surfaces. *Journal of Testing and Evaluation,* 41 (2).

Braham, A., Howard, I.L., Barham, J. & Cox, B.C., 2015. Characterising emulsion effects on aged asphalt concrete surfaces using bending beam rheometer mixture beams. *International Journal of Pavement Engineering,* 16 (7), 620-631.

Castorena, C., Pape, S. & Mooney, C., 2016. Blending measurements in mixtures with reclaimed asphalt: Use of scanning electron microscopy with x-ray analysis. *Transportation Research Record,* 2574 (1), 57-63 Available from: https://journals.sagepub.com/doi/abs/10.3141/2574-06.

Ding, Y., Huang, B., Shu, X., Zhang, Y. & Woods, M.E., 2016. Use of molecular dynamics to investigate diffusion between virgin and aged asphalt binders. *Fuel (Guildford),* 174, 267-273.

Huang, B., Li, G., Vukosavljevic, D., Shu, X. & Egan, B.K., 2005. Laboratory investigation of mixing hot-mix asphalt with reclaimed asphalt pavement. *Transportation research record,* 1929 (1929), 37-45.

Jiang, J., Leng, Z., Yang, B., Lu, G., Tan, Z., Han, M. & Dong, Z., 2022. Penetration mechanism of the emulsion-based rejuvenator in damaged porous asphalt mixture: Microstructure characterization and 3d reconstruction. *Materials & design,* 221, 111014.

Jiang, Y., Gu, X., Zhou, Z., Ni, F. & Dong, Q., 2018. Laboratory observation and evaluation of asphalt blends of reclaimed asphalt pavement binder with virgin binder using sem/eds. *Transportation Research Record,* 2672 (28), 69-78 Available from: https://journals.sagepub.com/doi/abs/10.1177/0361198118782023.

Karlsson, R. & Isacsson, U., 2003a. Application of ftir-atr to characterization of bitumen rejuvenator diffusion. *Journal of materials in civil engineering,* 15 (2), 157-165.

Karlsson, R. & Isacsson, U., 2003b. Laboratory studies of diffusion in bitumen using markers. *Journal of materials science,* 38 (13), 2835-2844.

Karlsson, R., Isacsson, U. & Ekblad, J., 2007. Rheological characterisation of bitumen diffusion. *Journal of materials science,* 42 (1), 101-108.

Kriz, P., Grant, D.L., Veloza, B.A., Gale, M.J., Blahey, A.G., Brownie, J.H., Shirts, R.D. & Maccarrone, S., 2014. Blending and diffusion of reclaimed asphalt pavement and virgin asphalt binders. *Road materials and pavement design,* 15 (1), 78-112.

Ma, X., Li, Q., Cui, Y.-C. & Ni, A.-Q., 2018. Performance of porous asphalt mixture with various additives. *International Journal of Pavement Engineering,* 19 (4), 355-361 Available from: https://doi.org/10.1080/10298436.2016.1175560.

Noureldin, A.S. & Wood, L.E., 1987. Rejuvenator diffusion in binder film for hot-mix recycled asphalt pavement. *Transportation research record,* (1115).

Oliver, J.W., 1974. Diffusion of oils in asphalts. *Industrial & Engineering Chemistry Product Research and Development,* 13 (1), 65-70.

Orešković, M., Menegusso Pires, G., Bressi, S., Vasconcelos, K. & Lo Presti, D., 2020. Quantitative assessment of the parameters linked to the blending between reclaimed asphalt binder and recycling agent: A literature review. *Construction and building materials,* 234, 117323.

Pape, S.E. & Castorena, C., 2021. Assessment of the impacts of sample preparation on the use of eds for analysing recycled asphalt blending. *Journal of Microscopy,* 283 (3), 232-242.

Perše, L.S., Bizjak, A. & Orel, B., 2013. The role of rheological properties and spraying parameters on the spectral selectivity of thickness insensitive spectrally selective (tiss) paint coatings. *Solar energy materials and solar cells,* 110, 115-125.

Pirzadeh, P., Kapilan, S. & Kriz, P., 2021. Blending between aged and virgin asphalt binders in recycled pavements: A review study. *IOP conference series. Materials Science and Engineering,* 1075 (1), 12006.

Rad, F.Y., Sefidmazgi, N.R. & Bahia, H., 2014. Application of diffusion mechanism: Degree of blending between fresh and recycled asphalt pavement binder in dynamic shear rheometer. *Transportation Research Record,* 2444 (2444), 71-77.

Ren, S., Liu, X., Lin, P., Erkens, S. & Gao, Y., 2022. Chemical characterizations and molecular dynamics simulations on different rejuvenators for aged bitumen recycling. *Fuel (Guildford),* 324, 124550.

Stempihar, J.J., Pourshams-Manzouri, T., Kaloush, K.E. & Rodezno, M.C., 2012. Porous asphalt pavement temperature effects for urban heat island analysis. *Transportation Research Record,* 2293 (1), 123-130 Available from: https://journals.sagepub.com/doi/abs/10.3141/2293-15.

Toma, S.L., Bejinariu, C., Baciu, R. & Radu, S., 2013. The effect of frontal nozzle geometry and gas pressure on the steel coating properties obtained by wire arc spraying. *Surface and Coatings Technology,* 220, 266-270.

Van De Ven, M., Qiu, J. & Zhang, Y., Year. Increasing the functional service life of porous surfacings: Development of test methods to study the effect of rejuvenating bindersed.^eds. *Proceeding of 15th International Flexible Pavements Conference of AAPA, Australian Asphalt Pavement Association, Queensland, Australia*.

Wang, Q., Liu, J., Liu, J. & Li, J., 2022. Experimental research on the impact of annular airflow on the spraying flow field: A source control technology of paint mist. *Building and Environment,* 207, 108444.

Xu, B., Li, M., Liu, S., Fang, J., Ding, R. & Cao, D., 2018. Performance analysis of different type preventive maintenance materials for porous asphalt based on high viscosity modified asphalt. *Construction and Building Materials,* 191, 320-329 Available from: https://www.sciencedirect.com/science/article/pii/S0950061818324012.

Yang, B., Leng, Z., Jiang, J., He, Z. & Li, D., 2022. Recovery efficiency of the damaged porous asphalt mixture with emulsion-based surface treatment: Material optimization and performance verification. *Construction and Building Materials,* 347, 128530 Available from: https://www.sciencedirect.com/science/article/pii/S0950061822021900.

Yang, J., Wong, M.S., Ho, H.C., Krayenhoff, E.S., Chan, P.W., Abbas, S. & Menenti, M., 2020. A semi-empirical method for estimating complete surface temperature from radiometric surface temperature, a study in hong kong city. *Remote sensing of environment,* 237, 111540.

Zhang, Y., 2015. *Extending the lifespan of porous asphalt concrete*. Delft University of Technology.

Zhang, Y., Chen, H. & Bahia, H.U., 2021. Extended aging performance of high rap mixtures and the role of softening oils. *International Journal of Pavement Engineering*, 1-12 Available from: https://doi.org/10.1080/10298436.2020.1870115.

Zhang, Y. & Leng, Z., 2017. Quantification of bituminous mortar ageing and its application in ravelling evaluation of porous asphalt wearing courses. *Materials & Design,* 119, 1-11 Available from: https://www.sciencedirect.com/science/article/pii/S0264127517300692.

Zhang, Y., Ven, M.F.C.V.D., Molenaar, A.a.A. & Wu, S., 2012. Increasing the service life of porous asphalt with rejuvenators. *Sustainable construction materials 2012.* 318-330.

Zhao, S., Huang, B., Shu, X. & Woods, M.E., 2016. Quantitative evaluation of blending and diffusion in high rap and ras mixtures. *Materials & design,* 89, 1161-1170.

Zhong, R., Leng, Z. & Poon, C.-S., 2018. Research and application of pervious concrete as a sustainable pavement material: A state-of-the-art and state-of-the-practice review. *Construction & building materials,* 183, 544-553.

Zhu, X., Yuan, Y., Li, L., Du, Y. & Li, F., 2017. Identification of interfacial transition zone in asphalt concrete based on nano-scale metrology techniques. *Materials & Design,* 129, 91-102 Available from: https://www.sciencedirect.com/science/article/pii/S026412751730480X.