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Investigation of diffusion of rejuvenator in aged asphalt

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Abstract

Recycling asphalt pavement creates a cycle of reusing materials that optimize the use of natural resources. For optimal rejuvenation of the aged binder, the diffusion rate of the rejuvenator should be considered. However, the diffusion mechanism between the rejuvenator and aged asphalt is still far from understood. In this study, two experimental methods were conducted to research the diffusion of rejuvenator in aged asphalt. The two asphalt binders were identical in terms of asphalt A7 (60/80 pen) and asphalt A11 (100/120 pen) and two rejuvenators were identical in terms of RA (containing 90% alkyl aromatic oil and 10% saturate oil), and RS (containing 10% alkyl aromatic oil and 90% saturate oil). Experimental results indicated that two experimental methods are also an effective means to research the diffusion of rejuvenator in asphalt in spite of a slight difference. The effect of temperature on the diffusion coefficient is large and the effect of layer thickness of the rejuvenator on diffusion coefficient is obviously not. The rejuvenator RA has a high diffusion rate in asphalt over a wide range of temperatures. In addition, the diffusion coefficient of rejuvenator in asphalt A11 is larger than that in asphalt A7. The test data suggested that the use of rejuvenator with high diffusion is a viable option for recycling old asphalt mixture.

Keywords: Recycling; Rejuvenator; Diffusion; Asphalt; Fickian law

1. Introduction

Asphalt is used extensively as an adhesive material in many fields, especially in asphalt pavement construction. About 5.0% of asphalt in asphalt mixture is usually needed for acceptable pavement performance [1]. But asphalt binder is easy to age during applying and service, especially under thermal and/or ultraviolet radiation (UV) conditions [2–4]. In addition, asphalt pavement suffers from different kinds of distresses, such as cracking, deformation, fatigue. Existing asphalt pavement materials are commonly removed during resurfacing, rehabilitation, or reconstruction operations. Once removed and processed, those become waste asphalt mixture, which contains valuable asphalt binder and aggregate [5]. Compared with virgin asphalts, the asphalt in waste asphalt mixture is more brittle and has worse relaxation characteristics that make asphalt more prone to cracking. But incorporating the waste asphalt mixture into new pavements significantly reduces the usage of new asphalt and aggregate, conserves natural resources and solves disposal problems [6]. There has been renewed interest in increasing the amount of recycling asphalt pavement used in hot mix asphalt [7,8]. Thus, how to use this waste asphalt mixture is a major issue.

Over the past three decades, most research about recycling asphalt pavement (RAP) has led the different country, company, and local agencies to consider a variety of potentially recyclable materials for pavement applications. Initially, the use of reclaimed asphalt mixture in hot asphalt

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mixture is allowed with a percentage varying between 0 to 30%. Long term pavement performance (LTPP) program has been established that the performance of pavements containing RAP is similar to that of pavements constructed from virgin materials with no RAP [9–11]. Over the years, considerable experience has been gained; the recycling ratio may be close to 100%. However, ensuring confidence in the success of using reclaimed asphalt mixture would require low recycling ration, such as lower than 70%, and addressing much durability concerns related to the interaction between reclaimed asphalt and the new binder [12,13]. Collected data indicated that the use of new binder is a viable option for recycling asphalt mixture with high RAP material content. One major factor that remains unclear is the interaction between aged asphalt and new binder. The new binder goes by different names as rejuvenators, softening agent, modifiers, extender or recycling. Just for the sake of name, the term rejuvenator is used to denominate all products used for rejuvenation of aged asphalt [14–16]. Some hypothesized that the rejuvenator forms a very low viscosity layer that surrounds the aged asphalt binder and rejuvenator penetrates the aged asphalt layer [17]. After penetration, the aged asphalt binder is softened and the rejuvenator disappears into the asphalt binder. This process is the diffusion of a rejuvenator into aged asphalt. But previous research focuses on the rejuvenation process using extraction of the old asphalt binder from waste asphalt mixture [18]. Mixing the rejuvenator with extracted binder and the diffusion of the rejuvenator in the layers of aged binder on the exterior of aggregates is a separate process.

Diffusion is the process responsible for the movement of matter from one part of a system to another, and it is mainly due to random molecular motions. A good rejuvenator should not only have superior regeneration and anti aging properties, but also should have appropriate diffusion. Diffusion is deemed to depend on temperature, viscosity and time. In addition, the materials structure, molecules size, molecules shape and intermolecular forces also influence the diffusion rate. This study aims to understand the diffusion process between rejuvenators and aged asphalt binders because it is an ordinary process in reclaimed asphalt pavement materials during waste asphalt mixture recycling operations in pavement construction [19]. Two experimental methods were designed to research the diffusion of rejuvenators into asphalt, which is a simplistic and convenient method. The effects of diffusion rate, application of two methods, are illustrated by studies of parameters such as the rejuvenator film thickness, temperature, rejuvenator and the type of asphalt.

2. Basic concepts and theory

Asphalt is typically regarded as a colloidal system consisting of high molecular weight asphaltene micelles dispersed or dissolved in a lower molecular weight oily medium (maltenes). The micelles are considered to be asphaltene clusters together with an absorbed layer of high molecular weight aromatic resins which act as a stabilizing solvation medium. According to the colloidal nature of the asphalt, asphalt is divided into sol asphalt, gel asphalt and sol-gel asphalt. In practice, asphalt that is applied in pavement is sol-gel asphalt [20]. The aromatic and resin fraction of asphalt will decrease after aging and it lost the solvation power to fully peptize the asphaltenes. During asphalt aging, heat first promotes the migration of oils out of the asphalt. Then, some of these oils are volatilized, and others are washed away because of subsequent solubility in water. Finally, oxygen migrates into the system, leading to the formation of more polar molecules known as asphaltenes.

Diffusion in asphalt is complex and the diffusion rates should not be like those in liquids or in solids. It remains a challenge to understand, predict and control the diffusion of rejuvenators in old asphalt. It depends strongly on the concentration and degree of swelling of asphaltenes. But the theories and physical models of diffusion may help to realize the diffusion of rejuvenators in old asphalt systems. Fig. 1 shows the colloidal structure and the diffusion of rejuvenator in old asphalt.

Fickian law is the most popular approach to evaluate diffusion due to its simplicity. Fickian law actually has two forms. Fickian first law describes the correlation between the diffusive flux of a gas component and the concentration gradient under steady-state conditions.

$$J = -Aj = -AD\frac{\partial C}{\partial x} \tag{1}$$

where J is the flux, A is the area across which diffusion occurs, j is the flux per unit area, D is the diffusion coefficient, C is the concentration, x is the diffusivity distance. $\frac{\partial C}{\partial x}$ is the concentration gradient along the x direction.

In the case of diffusion without convection and a unitary area, Eq. (1) can be written as follows.

$$J = -D\frac{\partial C}{\partial x} \tag{2}$$

Most practical diffusion situations are nonsteady-state ones. The diffusion flux and the concentration gradient at some particular point in a solid vary with time, with a net accumulation or depletion of the diffusing species resulting. Fickian second law relates the unsteady diffusive flux to the concentration gradient.

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right) \tag{3}$$

If the diffusion coefficient is independent of composition, Eq. (3) simplifies to Eq. (4).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \tag{4}$$

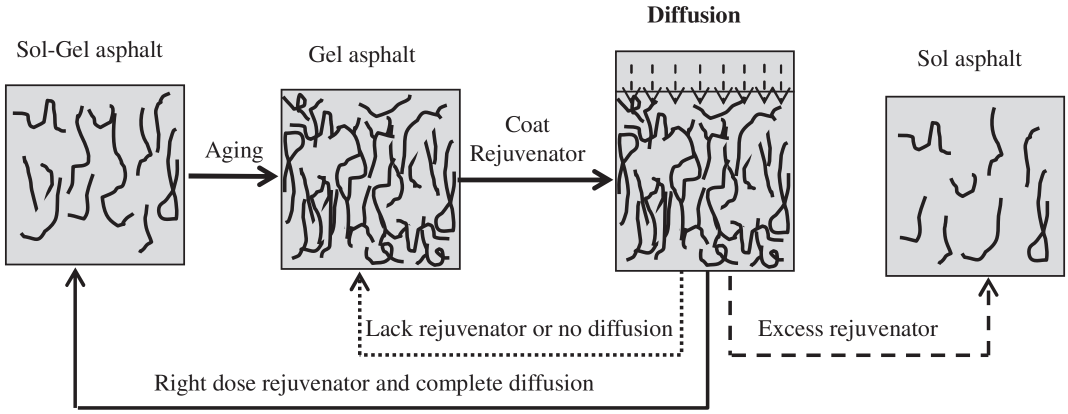

Fig. 1. The colloidal structure of asphalt and diffusion.

In order to evaluate the diffusion of rejuvenator on old asphalt, the semi-infinite surface was employed, which represents more general cases. The concentration of rejuvenator in old asphalt surface is held constant. Furthermore, the following assumptions are made:

a. Before diffusion, the rejuvenator in old asphalt is uniformly distributed with concentration of C_0.
b. The value of x at the surface is zero and increases with distance into the old asphalt.
c. The time is taken to be zero the instant before the diffusion process begins.

The boundary conditions are simply stated as follows:
For $t = 0$, $C = C_0$ at $0 \leqslant x \leqslant \infty$;
For $t > 0$, $C = C_s$ (the constant surface concentration) at $x = 0$ and $C = C_0$ at $x = \infty$.

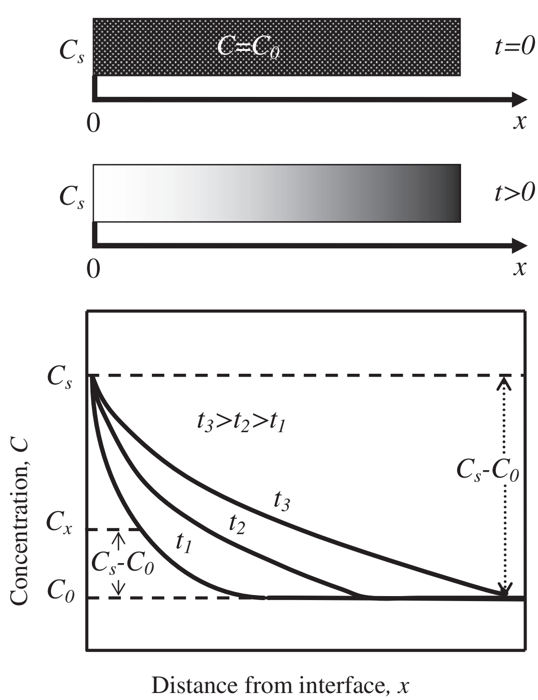

Fig. 2. Concentration profile for diffusion.

Fig. 2 shows the concentration profile for diffusion and application of these boundary conditions to Eq. (4) yields the solution as Eq. (5).

$$C(x,t) = C_s - (C_s - C_0)erf\left(\frac{x}{2\sqrt{Dt}}\right) \tag{5}$$

Sorption kinetics is one of the most common experimental techniques to study the diffusion of small molecules in polymers. In this technique the polymer film with t thickness is immersed into the infinite bath of penetration, then concentrations of rejuvenator at points distance x from the center of the film at some time t_d, C_t, was related to the concentration at equilibrium, C_∞, and the diffusion coefficient at this time, D, via the following equation for one dimensional diffusion Eq. (6).

$$\frac{C_t}{C_\infty} = 1 - \frac{4}{\pi}\sum\frac{(-1)^n}{2n+1}\exp\left[\frac{-D(2n+1)^2\pi^2 t_d}{t^2}\right] \times \cos\left[\frac{(2n+1)\pi x}{t}\right] \tag{6}$$

where n is an integer, t the film thickness for a semi-infinite film in a infinite bath. It was also assumed that the thickness of each sample was much smaller than the other dimensions for one-dimensional diffusion to be valid [21,22]. Considering that the distance from the center to the edge was given by $t/2 > x > 0$ and that the initial concentration of rejuvenator in the old asphalt was zero, then integration of Eq. (6) gave the total rejuvenator content as

$$(w_t - w_0)/w_0 = (4D^{1/2}t_d^{1/2})/(t\pi^{1/2}/2) = (4D^{1/2}/\pi^{1/2})(2t_d^{1/2}/t) \tag{7}$$

where W_t and W_0 is the weight of the asphalt at immersion time t_d and the initial weight, respectively. And t is the thickness of the sample. Eq. (7) indicates that a plot of mass uptake $(W_t - W_0)/W_0$ versus the parameter $2t_d^{1/2}$ should be initially linear. Results obtained from such plots confirmed the initial assumption that Fickian behavior was expected to occur and the diffusion coefficient was calculated from the gradients of the linear parts. The initial linear region was found to be followed by a clearly defined equilibrium plateau region. The diffusion coefficient was calculated from the slop of the linear region according to the Eq. (8).

$$\text{slope} = 4D^{1/2}/\pi^{1/2} \tag{8}$$

3. Material and experimental design

3.1. Raw materials

Two asphalts consisting of the typical A7 with 60/80 pen grade and A11 with 100/120 pen grade were used in this research. To study the diffusion of rejuvenator in asphalt, the two asphalts with obvious different contents of chemical compound are selected. The physical properties of asphalt have been presented in Table 1. To ensure the most conclusive diffusion insight, a middle ground material was considered. The rejuvenator selected for this study was the RA with 90% alkyl aromatic oil and 10% saturate oil, and RS with 10% alkyl aromatic oil and 90% saturated oil.

3.2. Preparation of aged asphalt

The aged asphalt was prepared after three aging processes. (1) The Rolling Thin Film Oven (RTFOT) was employed to simulate short term aging according to ASTM D2872. The oven is kept at 163 °C and the carriage is rotated in the oven at a rate of 15 rpm for 85 min. (2) The Pressure Aging Vessel (PVA) was used for the accelerated aging of asphalts. The temperature inside the PAV was within ±2 °C of the aging temperature (109 °C), an air pressure of 2.1 ± 0.1 MPa was applied and maintained for 20 h ± 10 min. (3) Ultraviolet (UV) aging tests were performed in an UV weathering oven. As soon as the time of PVA of asphalt binder was over, each asphalt sample was immediately poured into the market pans and the approximately 3 mm thickness film was obtained. Then the sample was placed together in the UV weathering oven to undergo UV aging. The UV lamp was 500 W with a main wavelength of 340 nm and the average intensity of UV irradiation on asphalt binder surface was about 0.45 W/m^2. Asphalt binders undergo UV irradiation 7 days under 60 °C in the UV weathering oven. The physical properties of aged asphalt were also presented in Table 1.

Table 1
Physical property and chemical composition of asphalts.

Physical properties	Measured values			
	A7	A11	Aged A7	Aged A11
Penetration (25 °C, 0.1 mm)	69	115	51	58
Softening point (°C)	48.5	45.3	55.7	54.1
Ductility (15 °C, cm)	123	182	–	–
Ductility (5 °C, cm)	15	25	–	–
Viscosity (135 °C, mPa·s)	450	270	835	580
Chemical composition (wt%)				
Saturates	15.05	14.57	15.37	15.11
Aromatics	27.78	46.29	21.29	39.14
Resins	51.21	29.76	52.87	30.44
Asphaltenes	5.90	9.37	10.46	15.32

3.3. Thin-layer chromatography with flame ionization detection (TLC-FID)

The samples were prepared by solution of 80 mg bitumen in 4 mL toluene and the concentration of solutions is 2% (w/v). The chromarods were cleaned and activated in the FID-flame before 1 μL of sample solution was spotted on them using a spotter. The separation of bitumen into four fractions (saturates, aromatics, resins and asphaltenes) was performed with a three-stage process. The first development was in *n*-heptane and expanded to 100 mm of the chromarods, the second stage in toluene/*n*-heptane (80/20 by volume) was developed to 50 mm, and the last development was in dichloromethane/methanol (95/5 by volume) and expanded to 25 mm. After the development solvents were evaporated in an oven at 80 °C, the chromarods were then scanned in the TLC-FID analyzer.

3.4. Methods of diffusion test

To evaluate the diffusion of rejuvenator in old asphalt, two experimental methods were designed.

The first experimental method (FM) adopts the change of weight to analyze the diffusion in old asphalt. The aged asphalt was poured into an aluminum tank (80 mm in diameter and 50 mm in height) and the height of aged asphalt is 10 mm. After cooling to ambient temperature (25 °C), the aluminum tank containing old asphalt was weighted. And the rejuvenator was coated on the aged asphalt. Ten samples were sealed and stored horizontally in an oven with a constant-temperature (experimental temperature) for each test. At various intervals, the aluminum tank containing the sample was removed without interference and cooled in a refrigerator at 0 °C for 4 h ± 5 min. The rejuvenator on top of aged asphalt was cleaned carefully, and afterward, the weight of the aluminum tank containing the sample was evaluated. Eq. (8) is applied to double-face diffusion. In this study, the single face diffusion was adopted to analyze. Thus, Eq. (8) now becomes Eq. (9).

$$\begin{aligned}(w_t - w_0)/w_0 &= (4D^{1/2}t_d^{1/2}/(t\pi^{1/2}/2) \\ &= (4D^{1/2}/\pi^{1/2})(t_d^{1/2}/t)\end{aligned} \tag{9}$$

The rejuvenator uptake $(W_t - W_0)/W_0$ % plotted against $t_d^{1/2}/t$ should be obtained by experiment.

The second experimental method (SM) adopts the change of composition's proportion to analyze the diffusion in old asphalt. The same preparation procedure is used as mentioned above. The rejuvenator on top of aged asphalt was cleaned carefully, and afterward, the sample that apart from about 10 mm of the aluminum tank was discard to eliminate possible effects of interface. Finally, 3 mm in thickness of asphalt in the sample was analyzed using TLC-FID. The distance from the middle of 3 mm of the specimen to the interface of asphalt/rejuvenator was measured. And the concentration of specimen's chemical compound was regarded as the concentration in the middle of the specimen. Fig. 3 shows the FM method. The effects of temperature and time on the diffusion were studied.

4. Results and discussion

4.1. Effects of test components on diffusion coefficient

To evaluate the diffusion of rejuvenator on old asphalt, two experimental methods were designed in this paper. The second experimental method (SM) needs to test the components of asphalt before and after diffusion. But the asphalt contains the four chemical components (asphaltenes, resins, aromatics and saturates) and the rejuvenator contain the two components (aromatics and saturates). Fig. 4 shows the effects of the analysis group on the diffusion coefficient at 100 °C with 10 mm asphalt +9 mm rejuvenator. The results indicated that it does not seem to affect the diffusion using different component analysis. However, in the case of the sum of aromatics and saturates, the deviation is slightly lower than the other case. Thus, for decreasing the errors, the sum of aromatics and saturates was employed to investigate the diffusion rate when the second experimental methods were used.

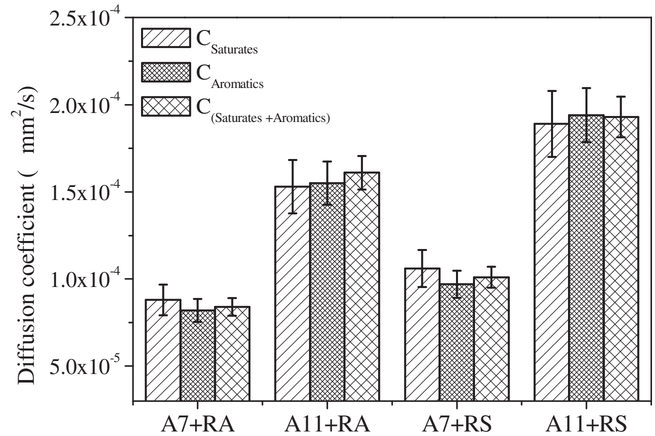

Fig. 4. Effects of analysis group on the diffusion coefficient at 100 °C (10 mm asphalt + 9 mm rejuvenator).

4.2. Effects of layer thickness on diffusion coefficient

To verify whether two experimental methods is valid and to investigate the influence of layer thickness on the diffusion coefficient, the aged asphalt A7 and rejuvenator RA were applied in five combinations of layer thickness (10 mm A7 + 3 mm RA, 10 mm + 6 mm, 10 mm + 9 mm, 10 mm + 12 mm and 10 mm + 15 mm) and diffused 15d at different temperatures. The mass of asphaltenes and aromatics was analyzed using TLC-FID when FM experimental methods were used. Fig. 5 presents the results of diffusion coefficient using statistical analysis for two experimental methods. The effect of temperature on diffusion coefficient is large. The results showed that the diffusion coefficient did not demonstrate any significant influence of layer thickness of rejuvenator for every test method. It is indicated that the self-diffusion in asphalt and rejuvenator is approximately of the same order of magnitude for same test methods. But the diffusion coefficient using the FM method is slightly larger than that of the test using SM methods. It maybe attributed to different investigation methods and calculations. In addition, Fig. 5 also indicated that the test with a comparatively larger proportion of rejuvenator shows slightly greater values than other tests at a lower proportion of rejuvenator. Thus, the concentration of rejuvenator has a negligible effect on the diffusion coefficient.

4.3. Effects of temperature on diffusion coefficient

Fig. 6 shows that the relationship of concentration versus $erf(\frac{x}{2\sqrt{Dt}})$ after 45d (64,800 min) diffusion at 100 °C and 60 °C. The results indicated that there was a good linear relationship between concentration and $erf(\frac{x}{2\sqrt{Dt}})$. It is according to the Fickian law as Eq. (5) showed. In addition, the temperature has a larger effect on the diffusion. Compared with the results of 100 °C, the diffusion distance is smaller than those of 60 °C. Thus, to get more diffusion

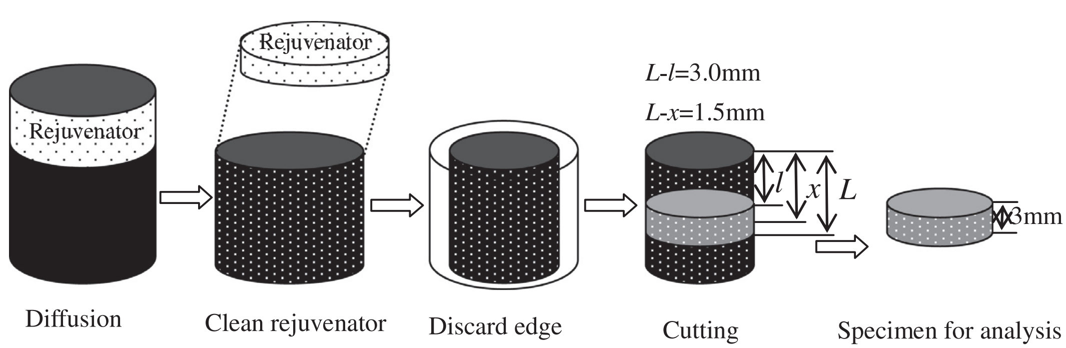

Fig. 3. The first experimental method (FM) for diffusion test.

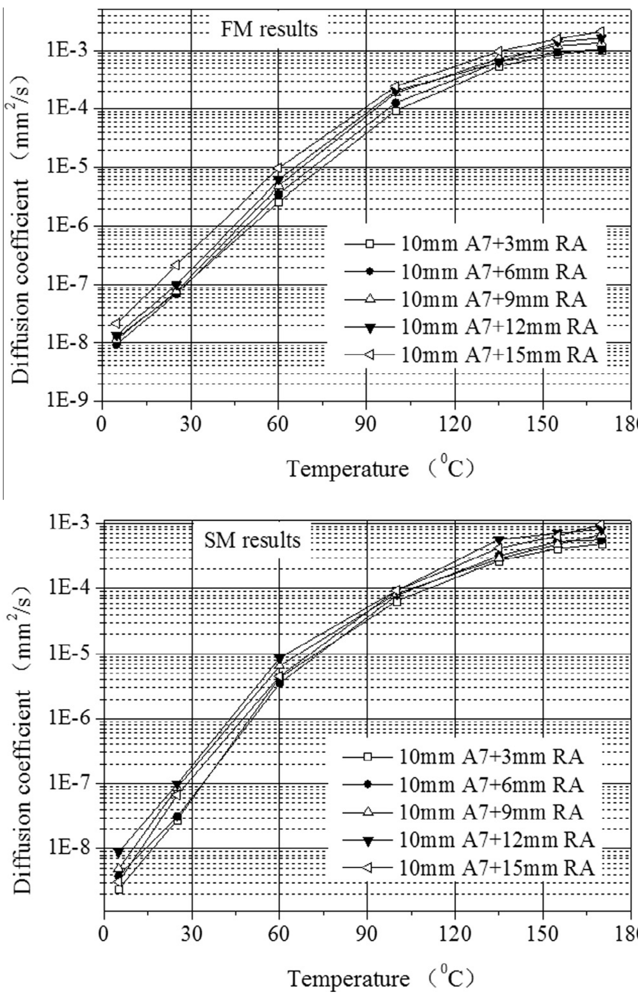

Fig. 5. Diffusion coefficient as function of temperature obtained from tests using two methods.

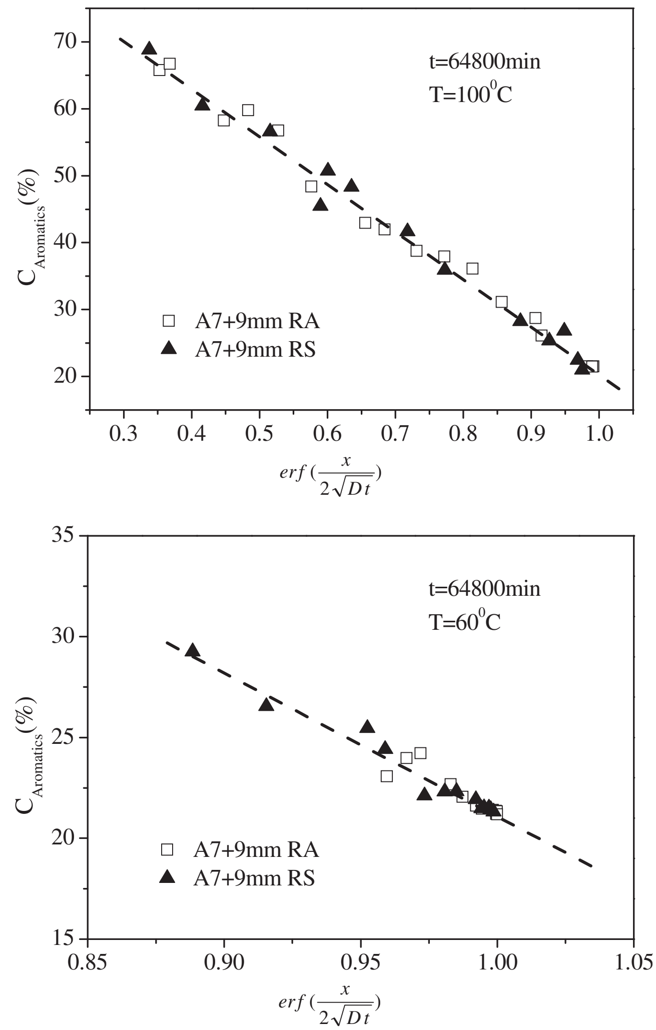

Fig. 6. Relative concentration versus $erf(\frac{x}{2\sqrt{Dt}})$ during diffusion at 100 °C and 60 °C.

depth, increase of temperature or prolonging the diffusion time is a better choice.

Fig. 7 shows that the relationship of $(W_t - W_0)/W_0$ versus $t_d^{1/2/t}$ during diffusion at 100 °C and 60 °C. The results also indicated that there was a good linear relationship between mass uptake of rejuvenator and the parameter $t_d^{1/2/t}$. It is satisfied by the relationship of Eq. (8). The results show differences in uptake of rejuvenator at different temperatures or rejuvenators. The RA diffusing in asphalt A7 exhibited rejuvenator uptake profiles that plotted higher than that of RS at the same temperature. It is denominated that the diffusion rate of RA in asphalt A7 is larger than that of RS. Also, the results suggest rejuvenator uptake at 100 °C are larger compared to that of at 60 °C in test cases. It is indicated that the temperature is an important factor affecting the diffusion rate.

Generally, the diffusion coefficient–temperature relationship of materials can be represented well by an Arrhenius equation:

$$D = D_0 \exp\left(-\frac{E_a}{RT}\right) \quad (10)$$

where D_0 is the pre-exponential factor, obtained from the relationship $\ln D$ and $1/T$, E_a is the activation energy for diffusion per mole (J·mol^{-1}), T is the absolute temperature and $R = 8.314$ J·mol^{-1}·K^{-1}. From the Eq. (10), the activation energy can be calculated from the Eq. (11):

$$E_a = \text{slope}\left(\ln D \frac{1}{T}\right) R \quad (11)$$

The activation energy (E_a) presents a strong correlation with the diffusion rate of materials. The higher the activation energy, the lower the diffusion rate the rejuvenator has, that is, more time to diffusion at the same temperature. The slope for each rejuvenator diffusing in different old asphalt using two test methods is shown in Fig. 8. It can be observed that the slope of the line for the A11 + RS was greater than that of other samples indicating that the uptake process is influenced obviously by temperature. From plots of $\ln D$ with $1/T$, the values of E_a for each rejuvenator diffusing in different old asphalt were calculated, and the results are given in Table 2. As can be observed,

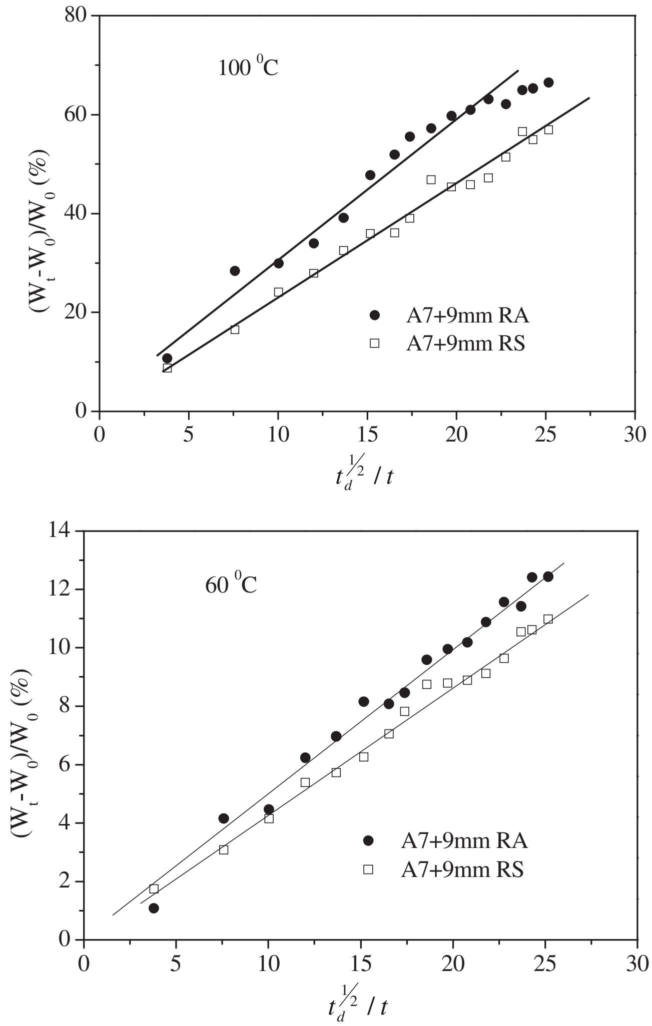

Fig. 7. Relative $(W_t - W_0)/W_0$ versus $t_d^{1/2/t}$ during diffusion at 100 °C and 60 °C.

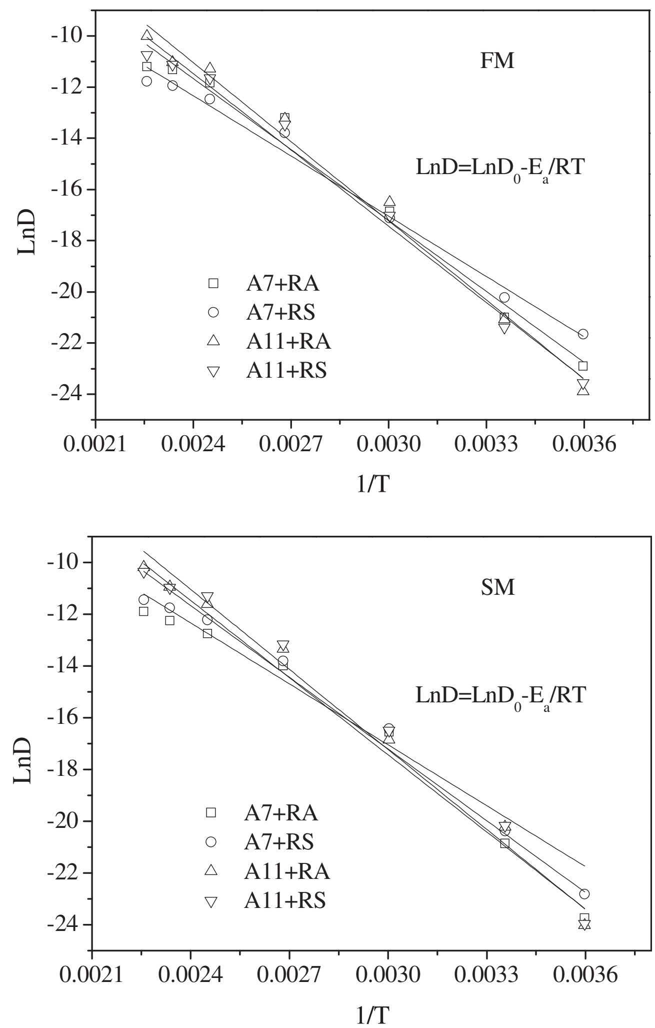

Fig. 8. Plots of $\ln D$ with $1/T$ with two test methods.

Table 2
Active energy of diffusion with two test methods.

Test method		A7 + RA	A7 + RS	A11 + RA	A11 + RS
E_a (J·mol^{-1})	FM	1111	944	1239	1195
	SM	1056	1034	1204	1095

the activation energy for this test sample ranges from around 940–1240 J·mol^{-1}. The results indicated that the difference of diffusion coefficient is small for the change of E_a is not large, and the activation energy for every sample is of the same order of magnitude. From the results of activation energy, the rejuvenator RS is diffused in asphalt A7 is more easy than others, and the RS is that diffused in A11 is difficult.

4.4. Effects of rejuvenator on diffusion coefficient

As Fig. 7 showed, the uptake of rejuvenator of RA in asphalt A7 is larger than that of RS. It is indicated that the diffusion coefficient of RA is great. But the effect of rejuvenator on the diffusion coefficient or the diffusion rate cannot be obtained from the Fig. 6. Thus, the diffusion coefficient was calculated from experimental data. The results are showen in Fig. 9 for different rejuvenators diffusing in two asphalts. The diffusion coefficient increases with the temperature increasing and the diffusion coefficient is very small when the temperature is lower than 60 °C. It is according to the study results about the effect of temperature on diffusion. The diffusion coefficient of the rejuvenator into asphalt A7 is larger using FM research methods than that using SM. Furthermore, the results of two research methods show the same conclusion that the rejuvenator RA diffusion rate faster than RS in asphalt A7. The trend of the increment of diffusion coefficient is more and more obvious with temperature increasing. The same tendency is also shown when rejuvenator diffusion occurs in asphalt A11 using FM research method. However, it displays the irregular result using the SM research method. Overall analysis on the effect of rejuvenator on diffusion coefficient, the rejuvenator RA diffusion rate is larger than

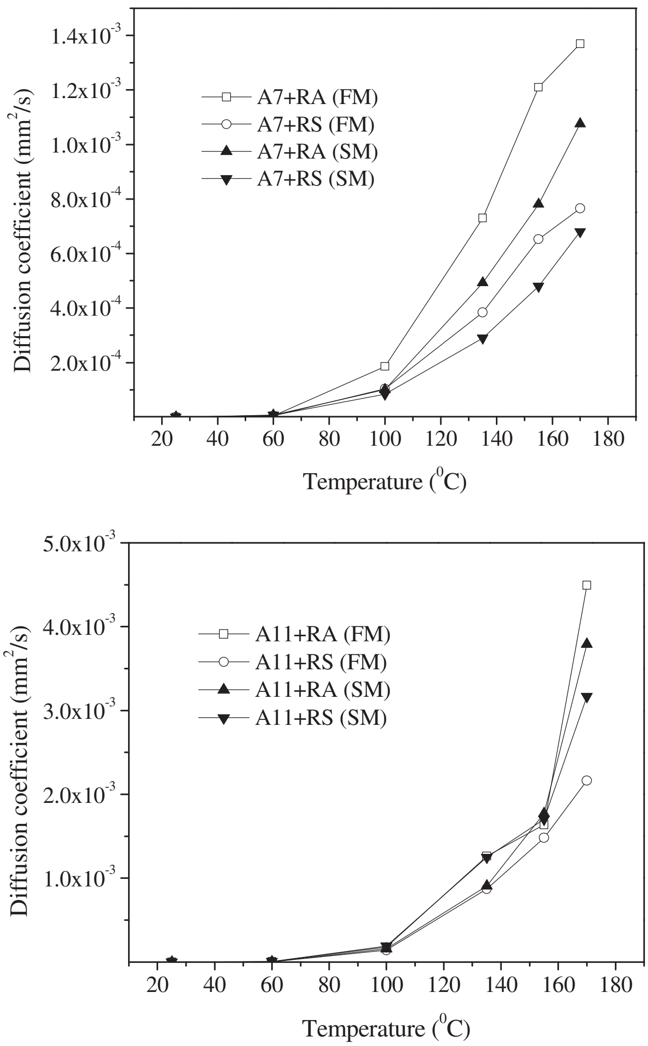

Fig. 9. Effects of rejuvenator on diffusion coefficient.

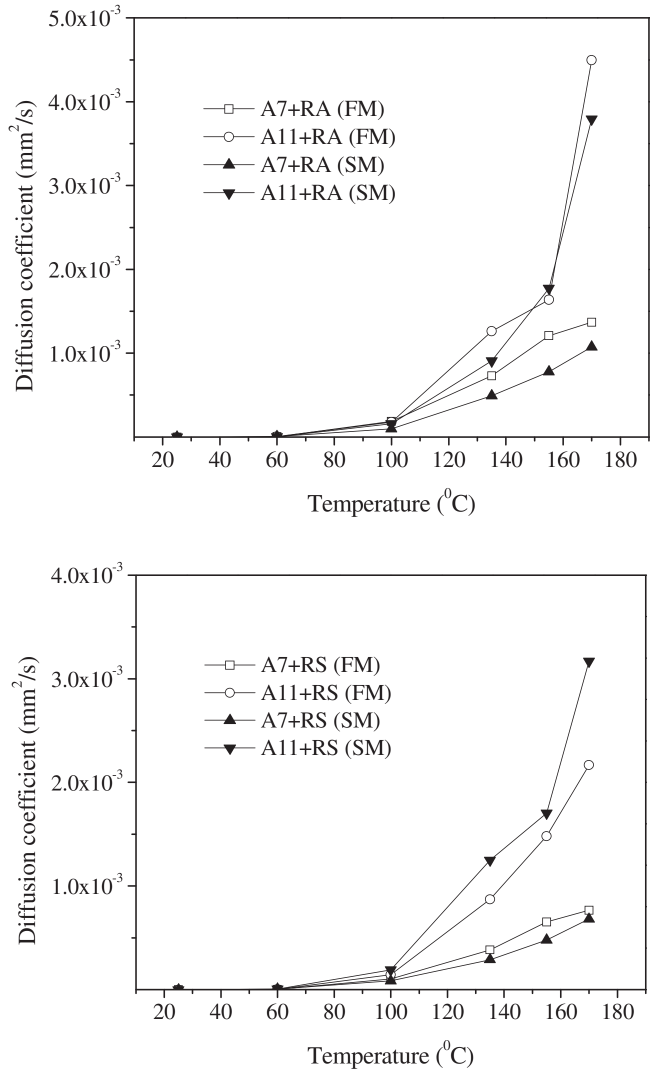

Fig. 10. Effects of asphalt on diffusion coefficient.

that of RS. Thus, the rejuvenators can influence remarkably the diffusion rate in asphalt.

4.5. Effects of asphalt on diffusion coefficient

The mass of asphaltene and resin content, which mainly differentiates the two grades of asphalt, has seemed to affect the diffusion and uptake of rejuvenator. Fig. 10 shows the effect of asphalt type on the coefficient. Two rejuvenator applications to asphalts are compared and analyzed. The diffusion coefficient in asphalt A11 is larger than that in asphalt A7 whichever research method is employed. And the diffusion coefficient of rejuvenator in asphalt A7 is small, especially the SM researching results. It may be attributed to the slightly lower mass of asphaltene and resin content. The asphaltenes and resins are higher molecular weights than saturates and aromatics found in asphalt. Molecular weights can play two roles in this case. The high molecular weights can reduce the ability of molecular motion. It leads to a decrease in the diffusivity and also can affect the ability of a molecular fragment from the rejuvenator to diffuse into the asphalt. This suggests that the rejuvenator in old asphalt could be diffused when it contains the aromatics or saturates. It is important to emphasize that asphalt is also a complex colloidal mixture of various components such as saturates, aromatics, resins and asphaltenes with different molecular weights. Hence, it is probable that one or more components could migrate into the rejuvenator, depending on the diffusion rate of asphalt components. The diffusion coefficients are likewise different for the two rejuvenators, indicating differences in the size of the diffusing molecule.

5. Conclusions

Two test methods have been established to study the diffusion of rejuvenator into asphalt. This allowed determination of the diffusion and recycling rate of the rejuvenator in old asphalt from waste asphalt mixture. The aim of this study was to develop a fundamental understanding on diffusion in old asphalts that can contribute to the user moving away from the empirical tests that can lead to erroneous conclusions. Based on the investigation of the effects of the rejuvenator film thickness, temperature, rejuvenator and asphalt type using two research methods, the following conclusions can be obtained:

a. The effects of research methods on the diffusion rate of the rejuvenator in old asphalt are little and diffusion is approximately of the same order of magnitude. But the sum of aromatics and saturates is best to research the diffusion rate for decreasing the errors.
b. The diffusion coefficient did not show any significant influence of layer thickness of the rejuvenator. It is indicated that the diffusion of the rejuvenator in asphalt is self-diffusion. But the research with a comparatively larger proportion of rejuvenator shows slightly greater values than other's in the low proportion of rejuvenator.
c. The diffusion of the rejuvenator in asphalt can be described by Fickian's law. Temperature and time are two important factors that influence the diffusion rate. To obtain more diffusion depth, increase of temperature or prolonging the diffusion time is the best choice.
d. The rejuvenator with high aromatic content shows good permeability to asphalt using the FM research methods. However, the rejuvenator RS with high saturates content shows irregular results.
e. The diffusion coefficient of the rejuvenator in asphalt A11 is larger than that in asphalt A7. The mass of asphaltenes and resin contents in asphalt can decrease the diffusion of rejuvenator into asphalt.

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References

[1] P.R. Herrington, Effect of concentration on the rate of reaction of asphaltenes with oxygen, Energy Fuels 18 (2004) 1573–1577.
[2] M. Le Guern, E. Chailleux, F. Farcas, S. Dreessen, I. Mabille, Physico-chemical analysis of five hard bitumens: identification of chemical species and molecular organization before and after artificial aging, Fuel 89 (2010) 3330–3339.
[3] P. Cong, J. Wang, K. Li, S. Chen, Physical and rheological properties of asphalt binders containing various antiaging agents, Fuel 97 (2012) 678–684.
[4] F. Durrieu, F. Farcas, V. Mouillet, The influence of UV aging of a styrene/butadiene/styrene modified bitumen: comparison between laboratory and on site aging, Fuel 86 (2007) 1446–1451.
[5] P. Cong, P. Xu, S. Chen, Effects of carbon black on the anti aging, rheological and conductive properties of SBS/asphalt/carbon black composites, Constr. Build. Mater. 52 (2014) 306–313.
[6] V. Mouillet, F. Farcas, S. Besson, Ageing by UV radiation of an elastomer modified bitumen, Fuel 87 (2008) 2408–2419.
[7] S. Lee, S.N. Amirkhanian, K.W. Kim, Laboratory evaluation of the effects of short-term oven aging on asphalt binders in asphalt mixtures using HP-GPC, Constr. Build. Mater. 23 (2009) 3087–3093.
[8] D.M. Brewis, J. Comyn, S.T. Tredwell, Diffusion of water in some modified phenolic adhesives, Int. J. Adhesion Adhesives 7 (1987) 30–32.
[9] John W. Larsen, D. Lee, Effect of solvent swelling on diffusion rates in bituminous coal, Fuel 62 (1983) 1351–1354.
[10] S.H. Carpenter, J.R. Wolosick, Modifier influence in the characterization of hot-mix recycled material. Transportation Research Record 777, 1980, Transportation Research Board, Washington, DC, pp. 15–22.
[11] M.N. Siddiqui, M.F. Ali, Investigation of chemical transformations by NMR and GPC during the laboratory aging of Arabian asphalt, Fuel 78 (1999) 1407–1416.
[12] R. Karlsson, U. Isacsson, Application of FTIR-ATR to characterization of bitumen rejuvenator diffusion, J. Mater. Civ. Eng. 15 (2003) 157–165.
[13] M.N. Siddiqui, M.F. Ali, Studies on the aging behavior of the Arabian asphalts, Fuel 78 (1999) 1005–1015.
[14] Philip R. Herrington, Diffusion and reaction of oxygen in bitumen films, Fuel 94 (2012) 86–92.
[15] L. Masaro, X.X. Zhu, Physical models of diffusion for polymer solutions, gels and solids, Prog. Polym. Sci. 24 (1999) 731–775.
[16] R. Karlsson, U. Isacsson, Rheological characterisation of bitumen diffusion, J. Mater. Sci. 42 (2007) 101–108.
[17] S.C. George, S. Thomas, Transport phenomena through polymeric systems, Prog. Polym. Sci. 26 (2001) 985–1017.
[18] P. Cong, S. Chen, J. Yu, S. Wu, Effects of aging on the properties of modified asphalt binder with flame retardants, Constr. Build. Mater. 24 (2010) 2554–2558.
[19] S. Upadhyay, V. Mallikarjunan, V.K. Subbaraj, S. Varughese, Swelling and diffusion characteristics of polar and nonpolar polymers in asphalt, J. Appl. Polym. Sci. 109 (2008) 135–143.
[20] P. Frantzis, Environmental attack on adhesive joints. Part III. Mechanisms of failure, JSME Int J. Ser. A 41 (3) (1998) 405–415.
[21] P. Frantzis, Crumb rubber–bitumen interactions: diffusion of bitumen into rubber, J. Mater. Civ. Eng. 16 (2004) 387–390.
[22] R. Karlsson, U. Isacsson, Laboratory studies of diffusion in bitumen using markers, J. Mater. Sci. 38 (2003) 2835–2844.