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ORIGINAL ARTICLE

Investigation on maximum packing fraction of bitumen particles during emulsion drying

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Abstract A good quality bitumen emulsion is a key prerequisite for a bitumen emulsion material with good performance. However, current evaluation methods of bitumen emulsion cannot distinguish the quality of bitumen emulsions with the similar grade of chemical stability but different bitumen particles size distribution. The maximum packing fraction of bitumen particles (ϕ_m) formed during drying, which affects the chemical stability, drying process and film properties of emulsion, is firstly proposed to evaluate the quality of different bitumen emulsions. Then, the mechanism influencing the ϕ_m of bitumen emulsions is discussed. Results indicate that although the same emulsifier type and dosage are used to produce bitumen emulsions, the ϕ_m of different bitumen emulsions can still differ greatly if their particle size distributions are different. The ϕ_m of bitumen emulsion is related to the motion ability of bitumen particles in emulsion due to particle Brownian motion, which is mainly dominated by the bitumen particle size and emulsion viscosity. The smaller bitumen particle size and emulsion viscosity can lead to a higher ϕ_m. Based on the ϕ_m results of bitumen emulsions, an empirical prediction model relating ϕ_m to the essential properties of bitumen emulsion (bitumen particle size and emulsion viscosity) is established. The empirical model can give a good quantitative relation of ϕ_m with the two essential properties of bitumen emulsion. It can be used to rapidly judge the quality of bitumen emulsion and help to quantitatively understand the effect of bitumen particle size and emulsion viscosity on the quality of bitumen emulsion.

Keywords Bitumen emulsion · Prediction model of maximum particle packing fraction · Drying · Bitumen particle size · Emulsion viscosity

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1 Background

With the growing awareness of health, safety, and environmental issues worldwide, sustainable development policy is being strongly encouraged in various industries. In pavement industry, due to the merits of low energy consumption, low carbon emissions and good workability [1], cold asphalt technologies based on a low-viscosity aqueous bitumen emulsion are now widely applied in pavement maintenance, preservation and rehabilitation [2–4]. The properties of bitumen emulsion, such as chemical stability, drying behaviour, properties of residue and film formation structure, can greatly affect the workability, hardening rate and mechanical properties of bitumen emulsion materials. A good quality bitumen emulsion is a key prerequisite for bitumen emulsion materials with good performance. In this regard, how to judge the quality of bitumen emulsion is a critical issue in the field of cold bitumen emulsion technologies.

In recent years, significant efforts have been placed on evaluating the quality of bitumen emulsion. These works mainly focused on the properties of residue and chemical stability of bitumen emulsion. Similarly to conventional bitumen, penetration and performance grade methods are used to test the properties of residue [5–7]. Recovery methods of residue can greatly affect its properties, which were gained many concerns in the engineering. Common residue recovery method is the direct heating method [8]. This method requires high temperatures (about 163 °C) which may degrade residue due to ageing. To minimize the ageing effect, evaporation methods at much lower temperatures are more preferred by researchers in recent years. Consequently, some specifications are proposed, such as ASTM D7497-09 [9] and AASHTO PP [10]. In these specifications, bitumen emulsion is dried at 25 °C for 24 h followed by an additional 24 h at 50–60 °C. Although the ageing effect can be weakened, there is still a relative high-temperature curing history for bitumen emulsion at these low-temperature evaporation methods. In this curing condition, the residue can have no-pores structure, which is similar to hot bitumen. Thus the properties of residue are equal to those of the original bitumen modified with emulsifier. However, the real emulsion residue dried under the application temperature may have many micro-pores due to water evaporation [11]. Because of this difference in structure, current residue evaluation methods ignore the effect of micro-pores formed during drying on the properties of emulsion residue.

The chemical stability of bitumen emulsion is another important property which can greatly affect the workability and mechanical properties of bitumen emulsion materials. To better utilize bitumen emulsion, the interaction between bitumen emulsion and mineral filler in fresh state was extensively studied. Generally, the chemical stability of bitumen emulsion is related to the reactivity of mineral filler with emulsifier [12–17]. To obtain a good workability of bitumen emulsion mixture, two common alternative ways are to reduce the reactivity of mineral filler (i.e. changing mixing sequence [18] and adding surfactant [18, 19]) and improve the chemical stability of emulsifier by employing nonionic emulsifier as co-emulsifier in emulsion production [12]. These previous studies are very meaningful to the workability control of bitumen emulsion materials. Besides, scholars recently realized that the demulsifying behaviour of bitumen emulsion could affect its coating ability on aggregate [20] and bitumen membrane structure [3], further affecting the mechanical properties of bitumen emulsion materials. However, previous works on the chemical stability of bitumen emulsion as well as its relation with the mechanical properties of bitumen emulsion materials are still qualitative studies. Besides, the effect of bitumen particle size distribution is also ignored in these studies. In fact, if two slow-setting bitumen emulsions with the same emulsifier or the similar breaking grade but different bitumen particles size distribution are employed to produce bitumen emulsion mixture, the workability and mechanical properties of two bitumen emulsion mixtures may differ greatly. Therefore, the chemical stability of bitumen emulsion still cannot efficiently judge the quality of bitumen emulsion.

In summary, previous studies cannot efficiently judge the quality of bitumen emulsion. Specifically, the current evaluation methods of bitumen emulsion cannot distinguish the quality of bitumen emulsions with the similar grade of chemical stability but different bitumen particles size distribution. Thus, a more reasonable index for evaluating the quality evaluation of bitumen emulsion is still urgently required.

2 Significance of maximum packing fraction of bitumen particles

An ideal bitumen emulsion mixture should feature considerable workable time, rapid hardening rate and good mechanical properties. Accordingly, a high-quality bitumen emulsion should have good chemical stability, short drying process and good film properties after drying. An index for evaluating the quality of bitumen emulsion should affect all these properties.

Fortunately, if reviewing the basic mechanisms of the drying and film formation process of latex, it can be found that the chemical stability, drying process and film properties of bitumen emulsion can be all related to the maximum packing fraction of bitumen particles formed during drying. As illustrated in Fig. 1, the film formation process of latex during drying can be described by a mechanism of consecutive stages which consist of dispersion, particle contact and deformation, and particle coalescence [21–23]. The drying process can be roughly divided into two stages according to the particles evolution process [24]. The evaporation rate of emulsion can be equal to that of the pure water before particles contact, however, it is significantly decreased after particles deformation and coalescence [25]. Particles reach the maximum packing state at the stage of particle contact, then they are deformed and coalesced. If bitumen particles can be closely packed, the water loss of emulsion in the first drying stage is more, thus bitumen emulsion require more drying time to be demulsified. Meanwhile, the residual water content of emulsion at the beginning of the second drying stage is low, thus short drying time is required in the second drying stage so that bitumen emulsion can hardens more quickly. Besides, few pores are formed during the second drying stage due to the low residual water content so that good film properties can be obtained for emulsion. Therefore, the maximum packing fraction of bitumen particles, which can affect the chemical stability, drying process and film properties of emulsion, can be used as a reasonable index to judge the quality of emulsion.

Actually, it is a general consensus in the latex field that particles packing can greatly affect the properties of latex film [26–28]. Plenty of efforts have focused on how to improve the particles packing in latex and suspension [28–33]. In the field of bitumen emulsion, based on the drying curve of bitumen emulsion, an experimental method was proposed to calculate the maximum packing fraction of bitumen particles in our previous study [34]. Results showed that the maximum packing fraction of bitumen particles for a given bitumen emulsion differed little with the initial bitumen concentration and drying temperature, thus it can be as a constant parameter for a given bitumen emulsion. Meanwhile, a high value of the maximum packing fraction of bitumen particles indicates long drying time before demulsification but short drying time after demulsification. Therefore, it was proved as a reasonable index to judge the quality of bitumen emulsion from the drying and demulsifying aspects [34, 35].

3 Research objective

This work is mainly to study the quality of bitumen emulsions with the similar grade of chemical stability but different bitumen particles size distribution. As mentioned previously, a higher value of the maximum packing fraction of bitumen particles indicates a better quality bitumen emulsion. To obtain a better quality bitumen emulsion, the mechanism influencing the maximum packing fraction of bitumen particles is studied. Meanwhile, the maximum packing fraction of bitumen particles is essentially related to bitumen particle size distribution and bitumen particles

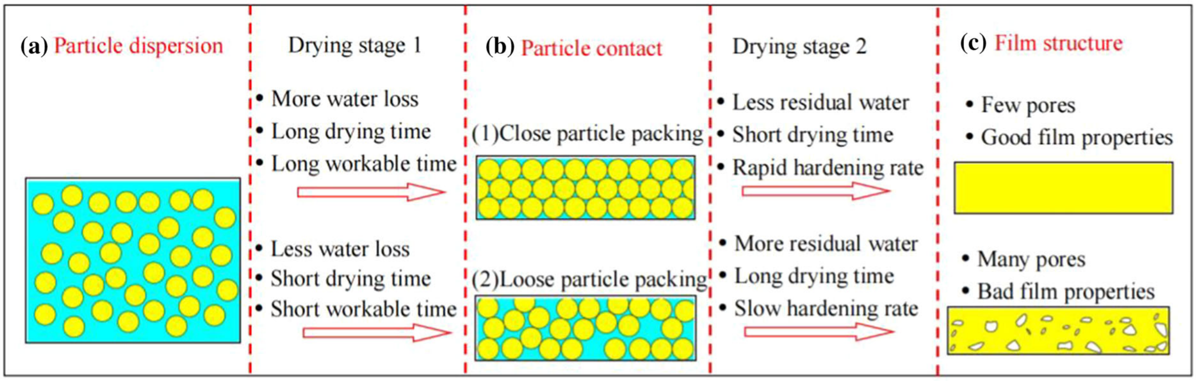

Fig. 1 Illustration about effect of particle packing on the chemical stability, drying process and film properties of emulsion

interaction. Considering these, the objectives of this study are as follows:

- To study the maximum packing fraction of bitumen particles for bitumen emulsions with the similar grade of chemical stability but different bitumen particles size distribution by drying method;
- To analyze the mechanism influencing the maximum packing fraction of bitumen particles;
- To establish an empirical relation of the maximum packing fraction of bitumen particles with the essential properties of bitumen emulsion (bitumen particle size and emulsion viscosity) for quickly judging the quality of bitumen emulsion.

4 Materials and experimental methods

4.1 Materials

Emulsions with the similar grade of chemical stability but different bitumen particles size distribution were firstly prepared. Twelve slow setting cationic asphalt emulsions were produced by cationic emulsifier, water, and paving grade base bitumen 60/80 in the laboratory. The general properties of the base bitumen as well as its chemical components are given in Table 1. The first nine emulsions were produced by an emulsifier (coded as LF) from Shanghai Focusen Pavement Engineering Co., Ltd. in Shanghai, China. The other three emulsions were produced by an emulsifier (coded as KZW) from Tianjin Kangzewei Co., Ltd. in Tianjin, China. The twelve emulsions have the basic formula during production in which emulsifier, water and bitumen contents are 4%, 36% and 60%, respectively. Besides, the pH value of emulsifier solutions are also adjusted between 2 and 3 by hydrochloric acid. Through adding small doses of different stabilizers and adjusting production temperatures, bitumen emulsions with different particle size distributions are obtained as shown in Fig. 2. The bitumen particle size distribution was measured by a laser particle size analyzer (Mastersize 2000, Malvern Instruments Ltd., UK). Since stabilizers and production temperatures mainly affect the emulsifying ability of emulsifier and the viscosity of aqueous solution, the main differences of different emulsions produced by LF are the particles size distribution and viscosity. Similarly, the emulsions with KZW have the same differences as the emulsions with LF.

Except for the above self-made emulsions, three commercial cationic emulsions are also used in this study, including a slow-setting emulsion (SS), a medium-setting emulsion (MS) and a rapid-setting emulsion (RM). In these fifteen emulsions of Fig. 12, samples 4 and 13 are bimodal emulsions, whose secondary peak of the bitumen particle size distribution is right and left, respectively.

Table 1 Properties of the base bitumen

Property	Value
General properties	
Penetration at 25 °C (0.1 mm)	72
Softening point R&B (°C)	47.0
Ductility at 15 °C (cm)	> 100
Kinetic viscosity at 60 °C (Pa s)	227
Flash point (°C)	276
SARA composition	
Saturates (mass fraction, %)	13.9
Aromatics (mass fraction, %)	41.5
Resins (mass fraction, %)	32.4
Asphaltenes (mass fraction, %)	12.4

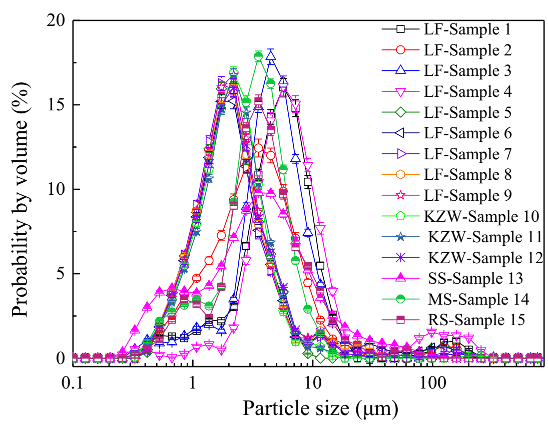

Fig. 2 The particle size distribution of bitumen emulsion

4.2 Drying test of emulsions

The drying test of emulsions is performed to calculate the maximum packing fraction of bitumen particles according to our previous studies [34, 35]. Cylindrical plastics culture dish with the diameter of 52 mm and the height of 15 mm was used in the drying test of bitumen emulsion, which was shown in Fig. 3. In our previous study [34], the condition of bitumen emulsion specimen was studied to obtain an ideal typical drying curve of non-skin emulsion drying. Drying specimens with the thickness of 3 mm and the initial bitumen content of 40% were recommended [34], which were also used in this study. Therefore, the tested bitumen emulsions were firstly diluted by water to bitumen emulsion with concentration of 40%. The drying test was performed in a temperature-controlled environmental chamber at 25 °C. Meanwhile, the air flow speed and relative humidity around the place of test specimens were around 0.4 m/s and 38%. The water loss of specimens was measured in the regularly time intervals ranging from 0.5 to 1 h. The drying test was performed thrice for each specimen.

To normalize the drying process, all gravimetric parameters were expressed by mass per unit area (expressed in g/m^2), and the evaporation rate was expressed by the mass of evaporated water per unit area and unit time (expressed in g/m^2/h). Based on the gravimetric measurement, the volume fraction of bitumen particles (ϕ) during drying can be calculated by the following equation:

$$\phi = \frac{m_{P,unit}/\rho_P}{m_{P,unit}/\rho_P + (m_{W,unit} - m_{loss,unit})/\rho_W} \quad (1)$$

where $m_{\mathrm{P,unit}}$, $m_{\mathrm{W,unit}}$, and $m_{\mathrm{loss,unit}}$ are the mass of the bitumen particles, initial water and water loss by unit area, respectively; ρ_{P} and ρ_{W} are the density of bitumen and water, respectively.

Fig. 3 Drying test of asphalt emulsion

4.3 Viscosity test

The viscosity of bitumen emulsion is an index of the interaction among bitumen particles according to the rheology theory of suspension [36]. Since the bitumen contents in bitumen emulsion change significantly during drying, the viscosity of bitumen emulsions with different concentrations (approximately ranging from 63% to diluted content at 40%) was studied for the following analysis of bitumen particles packing. It should be stated here that the real bitumen contents of bitumen emulsions are about 63%, which are slightly higher than the value in the basic formula before production. A coaxial-cylinder rheometer with a controlled temperature of (23 ± 0.1)°C was used to determine the viscosity of bitumen emulsions. The emulsion specimens were sheared with a linearly increasing shear rate from 0 to 100 s^{-1} in 1 min. The apparent viscosity of all specimens can reach equilibrium when shear rate is above approximately 80 s^{-1}. The average value of the viscosity measured above this arbitrary selected threshold was used in the analysis as the reference high shear Newtonian plateau viscosity.

4.4 Observation test of bitumen particles packing

The packing process of bitumen particles was directly observed by three-dimensional digital microscope during drying. The employed three-dimensional digital microscope is an optical microscope with high-magnification at 5000 × . It can directly obtain the digital image of specimens without any treatment. The employed magnification was 700 × in this study. To investigate the evolution of bitumen particles packing during drying, a very thin film of diluted bitumen emulsion was directly observed by the three-dimensional digital microscope. A video of the bitumen particles evolution during drying was recorded.

5 Methods for data analysis

5.1 Determination of maximum packing fraction of bitumen particles from drying

5.1.1 Physical description of the emulsion drying

A typical drying process of bitumen emulsion is shown in Fig. 4. It can be seen from Fig. 4 that the drying process of bitumen emulsion can be roughly divided into three stages. According to the basic mechanisms of the drying and film formation process of emulsion [22–25], the drying process of emulsion is mainly related to the particles evolution in emulsion during drying. The successive particles evolution as well as the corresponding drying stages can be described as followed:

(1) The first stage corresponds to the particles in the semi-diluted regime when the particles concentration is far from the maximum particle packing fraction in Fig. 5(a). The bitumen emulsion has a free evaporation surface, thus its evaporation rate can be equal to that of pure water or dilute emulsifier solution. This regime ranges from the initial state, ϕ_0, to the critical volume fraction of particles, $\phi_{crit,}$ at which bitumen particles approach and the irreversible coalescence of bitumen particles may begin as Fig. 5(b).

(2) The second stage corresponds to the compact regime when the increase in the bitumen volume fraction beyond ϕ_{crit} takes place with the further packing, deformation and irreversible coalescence of bitumen particles with the further drying. The evaporation rate sharply decreases in this stage because the area of evaporation surface is getting smaller. This process is determined by the flow out of water from the gap among the compact particles until they are coalesced to a roughly continuous film as Fig. 5(d). In this stage, there is a moment like Fig. 5(c) when bitumen particles reach the maximum particle packing state.

(3) The final stage corresponds to the diffused regime when the bitumen molecules are inter-diffused among particles, thus becoming the continuous bitumen phase with the inclusions of aqueous phase in Fig. 5(d). The residual water in the film escapes either by diffusion through the capillary channels between the coalescing particles or extrusion due to the reconfiguration of the bitumen phase. In this stage, the evaporation rate is much smaller and tends to zero.

5.1.2 Quantitative analysis of maximum packing fraction of bitumen particles

According to the above physical model of the relation between the particles evolution and drying rate, bitumen particles can reach the maximum particle packing state (ϕ_m) in a moment at the second stage. If the moment can be found, the maximum packing fraction of bitumen particles can be obtained. Theoretically, there is no obvious particles deformation and coalescence about bitumen particles before the drying time of ϕ_m, but a significant particles deformation and

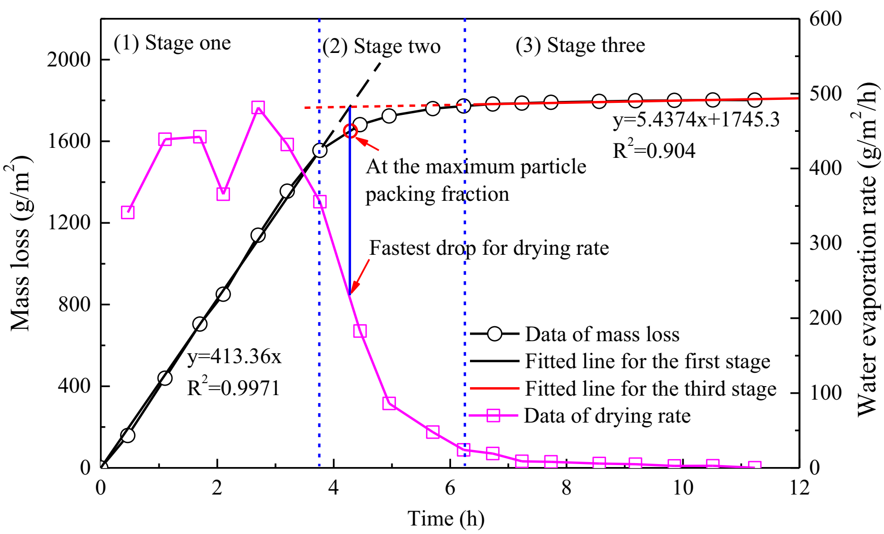

Fig. 4 Drying process of bitumen emulsion

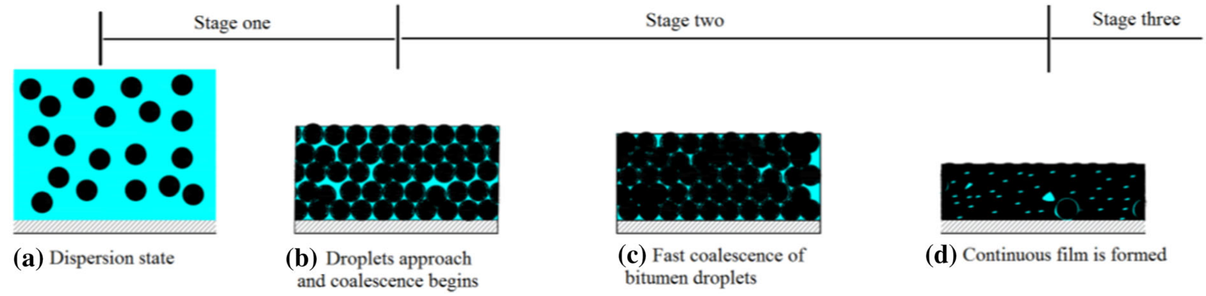

Fig. 5 Schematic representation of the three-stage drying process

coalescence are occurred after this moment [21, 26]. Therefore, the area of evaporation surface and the connection channels of water in emulsion are significantly changed in the drying time of ϕ_m. In other words, the change of the evaporation rate at the point of ϕ_m should be maximum in the drying curve. Since the data of water loss is recorded in the regularly time intervals ranging from 0.5 to 1 h, the accurate curve of the drying rate is unknown. Therefore, as shown in Fig. 4, the cross point of the fitted lines of the first and third stage is used to estimate the drying time of ϕ_m according to our previous studies [34, 35]. Then, the corresponding water loss can be accurately estimated from the curve of mass loss versus drying time. After knowing the water loss, the maximum packing fraction of bitumen particles can be calculated according to Eq. (1).

According to the determination method of the maximum packing fraction of bitumen particles in the above paragraph, the boundaries among different stages should be firstly identified. Our previous work indicated that the boundaries could be identified by studying the water evaporation rate [34]. As shown in Fig. 4, the water evaporation rate firstly undulates and then decreases sharply with the drying time, and finally slowly tends to zero. The first boundary, which the later evaporation rate decreases sharply compared to the average evaporation rate before this point, can be observed. Similarly, the second boundary, which the later evaporation rate decreases very slowly, can be found.

According to the above method of the maximum packing fraction of bitumen particles, an example is given to determine the two boundaries of the three stages and the maximum packing fraction of bitumen particles in Fig. 4.

5.2 Viscosity prediction of bitumen emulsion under different concentrations

The viscosities of bitumen emulsions with different concentrations were studied for the following analysis of bitumen particles packing. The viscosity of a suspension under different particle volume fractions is predicted by the well-known Krieger and Dougherty model of Eq. (2) [37].

$$\eta_r = \frac{\eta}{\eta_0} = \left(1 - \frac{\phi}{\phi_m}\right)^{-K} \quad (2)$$

where η_r is the relative viscosity defined as a ratio of the emulsion viscosity (η) to the viscosity of suspending medium (η_0, its value is 0.000936 Pa·s for water at 23 °C); K is a fitting parameter, commonly ranging from 2 to 3, determined from experiments; ϕ_m is the maximum particle packing fraction under highly-ordered state. The curve of η_r and ϕ is directly fitted by the software Matlab. As an example, a typical fitting results of a bitumen emulsion are shown in Fig. 6. It

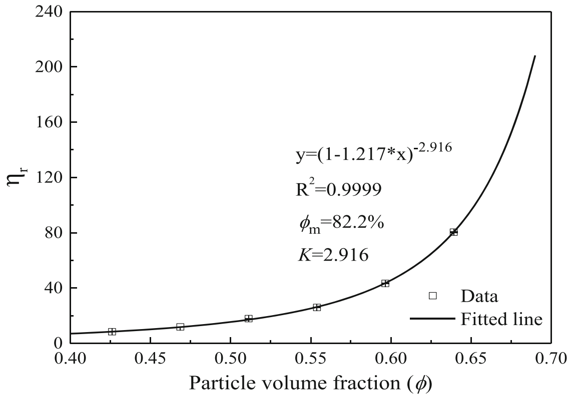

Fig. 6 Viscosity prediction of bitumen emulsion by the Krieger and Dougherty model

can be seen that the determination coefficient R^2 is nearly equal to 1, thus the viscosity of emulsion can be accurately predicted by the Krieger and Dougherty model. After knowing the parameters ϕ_m and K, the viscosity of bitumen emulsion at different particle volume fractions can be predicted.

6 Results

As shown in Fig. 7, the maximum particle packing fractions of different bitumen emulsions are calculated by drying curve and viscosity predication methods, respectively. It can be seen from Fig. 7 that the maximum particle packing fraction calculated by drying curve method differs greatly from that calculated by viscosity predication method for most of bitumen emulsions. This phenomenon is probably due to the following reasons: (1) the value of ϕ_m fitted by the Krieger and Dougherty model is not a constant because it also highly depends on the other parameter K; (2) it is assumed that the viscosity of suspending medium in Eq. (2) is equal to that of water, which ignores the effect of emulsifier and different stabilizers on the viscosity of water; (3) the particle packing state under shear condition may also differs greatly from that under free drying state. Essentially, the ϕ_m calculated by viscosity predication method, which is just a fitted value, cannot be used to accurately evaluate the particle packing state during drying. Therefore, the following analysis is based on the values of ϕ_m calculated by the drying curve method.

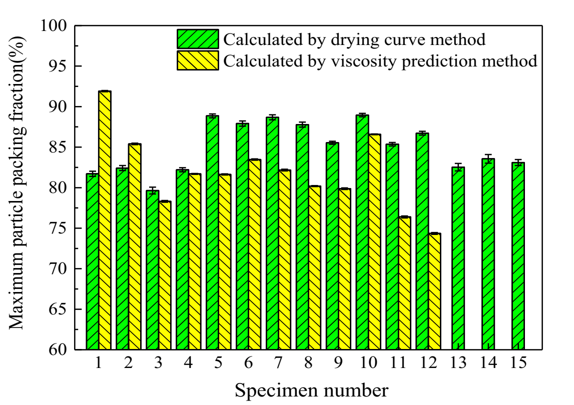

Fig. 7 Maximum particle packing fraction of different bitumen emulsions

It can be noted that the ϕ_m value calculated by drying curve method differs greatly for different bitumen emulsions although the same emulsifier type and dosage are used during the emulsion production. As mentioned previously, the ϕ_m can affect the drying process and film properties of bitumen emulsion. Therefore, the properties of bitumen emulsions with the same emulsifier can be significantly different if their particle size distribution is different.

7 Discussion on ϕ_m

7.1 Direct observation of bitumen particles packing

Video 1 shows the evolution process of bitumen particles packing. It can be clearly seen from Video 1 that the motion of small bitumen particles is very active, but large bitumen particles are almost motionless. As a result, small bitumen particles can fill gaps due to their active motion so that they are densely packed. However, large bitumen particles are acted as obstacles during the packing process of small bitumen particles. Because of this obstacle effect, as shown in Fig. 8, pores are normally formed around large bitumen particles in the end of particles packing process. Overall, the motion ability of bitumen particles in emulsion, which is highly related to bitumen particle size, can greatly affect the packing state of bitumen particles. Based on this observation, the mechanism influencing the maximum packing

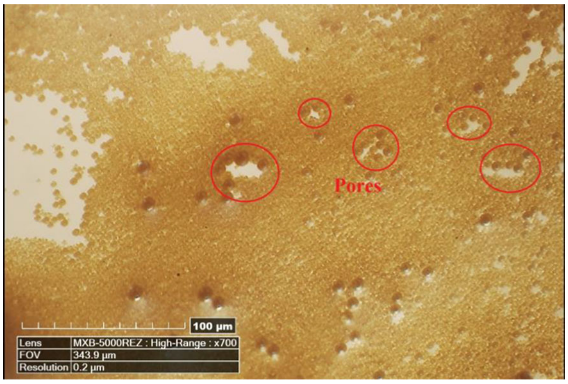

Fig. 8 Bitumen particles packing state

fraction of bitumen particles during drying is discussed in the following.

7.2 Prediction of ϕ_m

7.2.1 *Theoretical model of ϕ_m*

Essentially, the motion ability of particle in a dilute suspension is due to particle Brownian motion. It can be evaluated by the particle diffusion coefficient (D) according to Stokes–Einstein relation [26] in Eq. (3).

$$D = \frac{kT}{3\pi\eta R} \tag{3}$$

where kT is the thermal energy; R is the particle diameter; η is the medium viscosity. Because bitumen emulsion is a highly-concentrated emulsion, the diffusion of a bitumen particle can be strongly affected by other bitumen particles. Thus, the diffusion speed of bitumen particle should be related to the viscosity of bitumen emulsion, not the viscosity of water. Therefore, the motion ability of bitumen particle in emulsion should be related to the bitumen particle size and the viscosity of emulsion.

As mentioned previously, the direct observation of bitumen particles packing indicates that the motion ability of bitumen particles in emulsion greatly dominates the packing state of bitumen particles. Therefore, an empirical relation about ϕ_m and D can be given in Eq. (4).

$$\phi_m \propto D \tag{4}$$

Combined with Eqs. (3) and (4), it can be inferred that the ϕ_m may have a positive correlation with $1/R$ and $1/\eta$, which can be expressed as Eq. (5).

$$\phi_m = \frac{a}{R} + \frac{b}{\eta} + c \tag{5}$$

where η is the emulsion viscosity; a and b are the positive coefficients related to the effect of the particle size and the viscosity on ϕ_m, respectively; c is a fitting parameter. To confirm the validity of this relation of ϕ_m with R and η, effect of bitumen particle size and emulsion viscosity on ϕ_m is studied through Eq. (5) in the following sections.

7.2.2 *Effect of bitumen particle size on ϕ_m*

Equation (5) is used to establish the relation of ϕ_m with bitumen particle size and emulsion viscosity. However, bitumen particles in emulsion have a wide particle size distribution, and the emulsion viscosity is also changed during drying due to the increasing particle concentration. Thus, a representative particle size and emulsion viscosity should be used to establish the relation of ϕ_m with bitumen particle size and emulsion viscosity. Since the emulsion viscosity is mainly dependent on the volume fraction of bitumen particle, it is hypothesized that the viscosity of different emulsions differs little at the same particle volume fraction. In this hypothesis, the effect of viscosity on the ϕ_m can be ignored for different emulsions. Thus, the Eq. (5) can be simplified as:

$$\phi_m = \frac{a}{R} + c \tag{6}$$

Particle sizes ranging from 10 to 90th cumulative volume percentile are used as representative particle sizes to study the effect of bitumen particle size on ϕ_m. As an example, particle size R_{50} (particle diameter for the 50th cumulative volume percentile) is used to study the ϕ_m of bitumen emulsions with LF emulsifier in Fig. 9. It can be seen from Fig. 9 that the ϕ_m indeed has a positive correlation with $1/R$. Meanwhile, the fitting results of the relation of ϕ_m and different representative particle sizes are shown in Table 2. It can be seen from Table 2 that the determination coefficient for all selected representative particle sizes

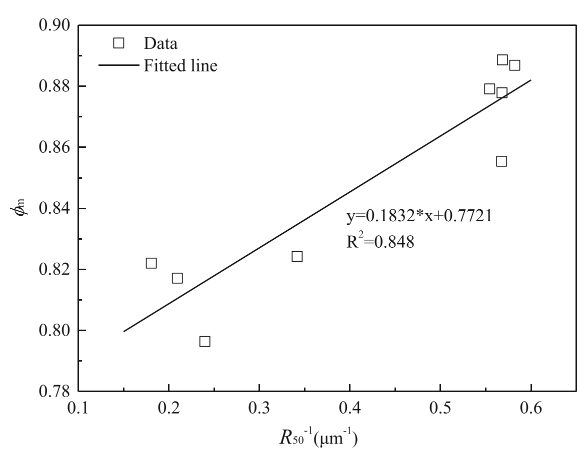

Fig. 9 Relation of the ϕ_m and R_{50} for bitumen emulsions with LF emulsifier

Table 2 Regression parameters of the relation of ϕ_m and representative particle size

Representative particle size	Fitting parameter		Determination coefficient, R^2
	a	*c*	
R_{10}	0.081	0.7682	0.7006
R_{20}	0.1078	0.7719	0.7982
R_{30}	0.1344	0.7713	0.8314
R_{40}	0.1591	0.7715	0.8437
R_{50}	0.1832	0.7721	0.8480
R_{60}	0.2129	0.7726	0.8461
R_{70}	0.2530	0.7728	0.8329
R_{80}	0.3158	0.7731	0.7990
R_{90}	0.4359	0.7757	0.7000

can be higher than 0.7. Especially when particle size is from R_{30} to R_{70}, the determination coefficient can be higher than 0.8. Therefore, Eq. (6) is suitable for describing the relation of ϕ_m with bitumen particle size. Besides, the determination coefficient firstly increases and then decreases with the increasing representative particle size. R_{50} has the highest determination coefficient with ϕ_m.

7.2.3 *Effect of emulsion viscosity on* ϕ_m

Equation (5) is used to study the effect of emulsion viscosity on ϕ_m. Similarly to study the effect of bitumen particle size on ϕ_m, a representative emulsion viscosity should be also given in here. It should be stated here that the bitumen particle size distributions of different emulsions differ greatly, thus the effect of the difference in bitumen particle size on the ϕ_m cannot be ignored when studying the effect of emulsion viscosity on ϕ_m. Since R_{50} has the highest determination coefficient with ϕ_m, the original model of Eq. (5) can be rewritten as Eq. (7) to study the effect of emulsion viscosity on ϕ_m.

$$\phi_m = \frac{a}{R_{50}} + \frac{b}{\eta} + c \quad (7)$$

The predicted emulsion viscosities at particle volume fractions ranging from 40 to 70% are used to study their relation with ϕ_m. The emulsion viscosities are predicted by Eq. (2) based on the relation of viscosity and ϕ. As an example, the emulsion viscosity with particle volume fraction at 60% (η_{60}) is employed to study the ϕ_m of bitumen emulsions with LF emulsifier according to Eq. (7). The fitting results are shown in Fig. 10. It can be seen from Fig. 10 that

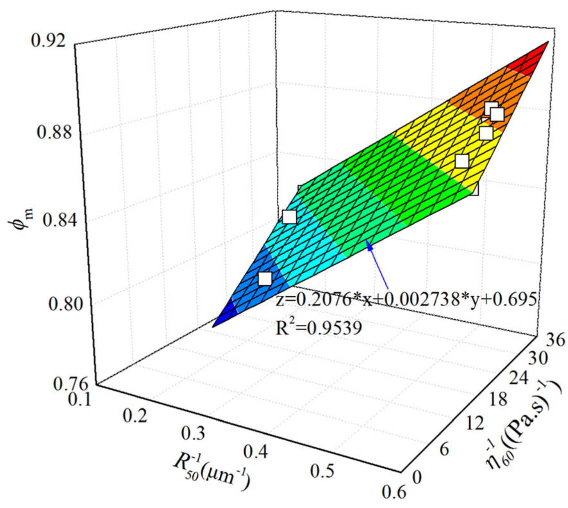

Fig. 10 Relation of the ϕ_m with R_{50} and η_{60} for bitumen emulsions with LF emulsifier

the determination coefficient using Eq. (7) can be much higher than that using Eq. (6). Meanwhile, the fitting results of the relation of ϕ_m with R_{50} and different representative emulsion viscosities are shown in Table 3. It can be seen from Table 3 that the determination coefficient of all fitting results are very high except for the fitting result by η_{70}. Since the particle volume fraction of the tested emulsions is far from 70%, the predicted η_{70} for some emulsions may significantly differ from the real η_{70}, which can be responsible for this low determination coefficient of η_{70}. Overall, Eq. (7) is suitable for describing the relation of ϕ_m with emulsion viscosity.

Table 3 Regression parameters of the relation of ϕ_m and representative particle size

Representative emulsion viscosity	Fitting parameter			Determination coefficient, R^2
	a	*b*	*c*	
η_{40}	0.1795	0.001206	0.5891	0.9309
η_{45}	0.1856	0.001434	0.6786	0.9404
η_{50}	0.1926	0.001729	0.6468	0.9478
η_{55}	0.2001	0.002132	0.6726	0.9524
η_{60}	0.2076	0.002738	0.6950	0.9539
η_{65}	0.2153	0.003782	0.7132	0.9527
η_{70}	0.1903	0.004266	0.7513	0.8819

7.2.4 Final prediction model of ϕ_m

According to the analysis of the Sects. 7.2.3 and 7.2.4, it is proved that the Eq. (5) is suitable to establish the relation of ϕ_m with bitumen particle size and emulsion viscosity. To accurately predict the ϕ_m of bitumen emulsion by Eq. (5), the most representative bitumen particle size and emulsion viscosity are analyzed. Particle sizes ranging from 10 to 90th cumulative volume percentile and emulsion viscosities at particle volume fractions ranging from 40 to 70% are used to establish their relation with ϕ_m by Eq. (5), and the determination coefficients are shown in Fig. 11. As shown in Fig. 11, the determination coefficients of fitting results can be very high when bitumen particle size is selected from R_{40} to R_{70} and emulsion viscosity is selected from η_{55} to η_{65}. R_{50} and η_{60} have the highest determination coefficient with ϕ_m, thus they are the best representative bitumen particle size and emulsion viscosity. Therefore, an empirical prediction model of ϕ_m is proposed in Eq. (8).

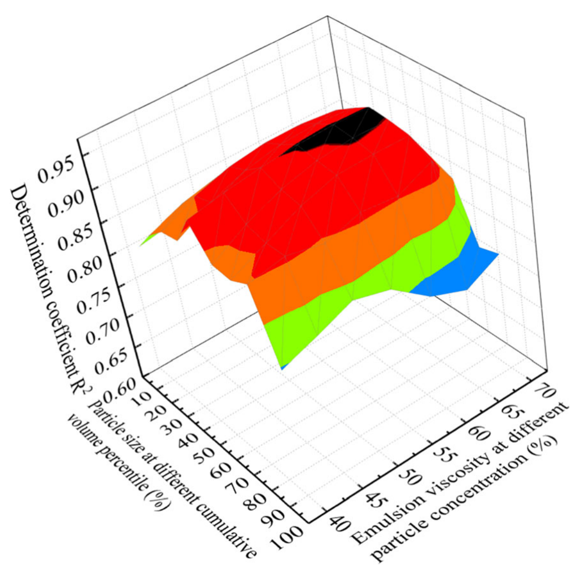

Fig. 11 Determination coefficients of the relation of ϕ_m with different bitumen particle sizes and emulsion viscosities

$$\phi_m = \frac{0.2076}{R_{50}} + \frac{0.002738}{\eta_{60}} + 0.695 \quad (8)$$

7.2.5 Accuracy and validation of the prediction model

Based on this prediction model of Eq. (8), the prediction results and their accuracy of ϕ_m for the nine emulsions with LF emulsifier are shown in Table 4. It can be seen from Table 4 that the maximum absolute deviation of ϕ_m is only about 0.01, thus the prediction accuracy of ϕ_m can be very high and acceptable. Meanwhile, the ϕ_m of three emulsions with KZW emulsifier and three commercial emulsions are also studied to verify the usability of the model in Eq. (8) for other emulsions. The prediction results and accuracy are also shown in Table 4. Although the model of Eq. (8) is deduced according to the ϕ_m results of bitumen emulsions with LF emulsifier, the low prediction deviations of ϕ_m for bitumen emulsions with KZW emulsifier and three commercial bitumen emulsions indicate that the model of Eq. (8) is also suitable for other bitumen emulsions. Meanwhile, the employed commercial medium-setting (MS) and rapid-setting (RS) emulsions can also have very low prediction deviations for ϕ_m. Thus, this prediction model of ϕ_m can be suitable for bitumen emulsions with different breaking grades. Besides, the prediction model can give high prediction accuracy for bimodal emulsions (i. e. LF-4 and SS). Overall, the proposed model can give an accurate prediction result about ϕ_m

Table 4 Prediction results and accuracy of ϕ_m for different emulsions

Specimen	R_{50} (μm)	η_{60} (Pa•s)	Predicted ϕ_m	Tested ϕ_m	Deviation of ϕ_m
LF-1	4.775	0.03787	0.8106	0.8171	− 0.0065
LF-2	2.926	0.03964	0.8344	0.8242	0.0102
LF-3	4.170	0.05696	0.7941	0.7964	− 0.0023
LF-4	5.537	0.02990	0.8228	0.8221	0.0007
LF-5	1.759	0.04132	0.8776	0.8886	− 0.0110
LF-6	1.804	0.03823	0.8797	0.8791	0.0006
LF-7	1.718	0.04269	0.8783	0.8868	− 0.0085
LF-8	1.761	0.04323	0.8748	0.8778	− 0.0030
LF-9	1.762	0.05037	0.8663	0.8554	0.0109
KZW-1	1.836	0.03100	0.8933	0.8896	0.0037
KZW-2	1.874	0.04738	0.8626	0.8536	0.0090
KZW-3	1.816	0.04990	0.8633	0.8672	− 0.0039
SS	3.842	0.03051	0.8388	0.8310	0.0078
MS	3.004	0.04289	0.8279	0.8356	− 0.0077
RS	3.245	0.04594	0.8186	0.8253	− 0.0067

for different bitumen emulsions if knowing R_{50} and η_{60}.

It should be stated here that although the prediction model is established through slow-setting bitumen emulsions, results indicate that it can be also suitable for medium-setting and rapid-setting emulsions. This is because water evaporation is the only driving factor for the demulsification of bitumen emulsion. In this situation, emulsifier can provide enough repulsive force among bitumen particles, thus the coalescence of bitumen particles can be only occurred when particles reach their maximum packing state. Therefore, this prediction model can be suitable for pure bitumen emulsions with different breaking grade.

7.2.6 *Scientific contribution of the prediction model of ϕ_m*

According to the prediction model of Eq. (8), the ϕ_m is mainly dependent on the two essential properties of bitumen emulsion, i.e. bitumen particle size and the emulsion viscosity. The two essential properties of bitumen emulsion are highly related to the production parameters of emulsion, i.e. emulsifier type and dosage, pH value, stabilizer, and production process. However, the production parameters of bitumen emulsion are difficult to be understood by pavement engineers and scholars because there are a wide variety of emulsifiers and stabilizers in the market. Meanwhile, the components of different commercial emulsifiers differ greatly. In most cases, pavement engineers and scholars only care about the emulsifying effect of bitumen emulsion. Bitumen particle size distribution is a direct index of the emulsifying effect of bitumen emulsion. It can be known according to Eq. (8) that the better emulsifying effect of bitumen emulsion indicates the better quality of bitumen emulsion. Therefore, to judge the quality of bitumen emulsion, pavement engineers and scholars do not need to understand the effect of the production parameters (e.g. emulsifier) but care about the emulsifying effect of bitumen emulsion if they know the relation of ϕ_m and bitumen particle size. This empirical prediction model can give a good quantitative relation of ϕ_m with the essential properties of bitumen emulsion (R_{50} and η_{60}). Thus, this model can quickly evaluate the quality of bitumen emulsion based on its essential properties, and helps to quantitatively understand the effect of bitumen particle size and emulsion viscosity on the quality of bitumen emulsion.

8 Conclusions

The maximum packing fraction of bitumen particles (ϕ_m) for different bitumen emulsions is studied by the drying curve method. The mechanism influencing the ϕ_m of different emulsions is analyzed, and an empirical relation of ϕ_m with the essential properties of bitumen emulsion (bitumen particle size and emulsion viscosity) is established. Based on this work, the following conclusions can be drawn:

(1) Although bitumen emulsions are produced by the same emulsifier type and dosage, the ϕ_m of different bitumen emulsions can differ greatly if their particle size distribution is different. Therefore, the drying and film properties of bitumen emulsions with the same emulsifier still can be significantly different due to the different ϕ_m.

(2) The packing state of bitumen particles depends on the motion ability of bitumen particles in emulsion due to particle Brownian motion. It is mainly dominated by the bitumen particle size and emulsion viscosity. The smaller bitumen particle size and emulsion viscosity can lead to a higher ϕ_m.

(3) An original ϕ_m prediction model is proposed to relate the ϕ_m of bitumen emulsion to the bitumen particle size (R) and emulsion viscosity (η). The ϕ_m prediction equation is $\phi_m = 0.2076/R_{50} + 0.002738/\eta_{60} + 0.695$, where R_{50} is the particle diameter for the 50th cumulative volume percentile and η_{60} is the emulsion viscosity with particle volume fraction at 60%. This empirical model can give a good quantitative relation of ϕ_m with the essential properties of bitumen emulsion (R_{50} and η_{60}). The model can be used to quickly evaluate the quality of bitumen emulsion and help to quantitatively understand the effect of bitumen particle size and emulsion viscosity on the quality of bitumen emulsion.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Asphalt Institute. A basic asphalt emulsion manual: Manual series no. 19 (MS-19). 4th ed. Lexington, KY: Asphalt Emulsion Manufactures Association, 2008
2. Robati M, Carter A, Perraton D (2015) New conceptual model for filler stiffening effect on asphalt mastic of microsurfacing. J Mater Civil Eng 27(11):04015033. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001264
3. Ouyang J, Yang W, Chen J, Han B (2020) Effect of superplasticizer and wetting agent on the pavement properties of cold recycled mixture with bitumen emulsion and cement. J Mater Civil Eng 32(6):04020136. https://doi.org/10.1061/(ASCE)MT.1943-5533.0003194
4. Grilli A, Graziani A, Bocci E, Bocci M (2016) Volumetric properties and influence of water content on the compactability of cold recycled mixtures. Mater Struct 49(10):4349–4362. https://doi.org/10.1617/s11527-016-0792-x
5. Adams J, Ilias M, Castorena C, Kim YR (2018) Performance-graded specifications for asphalt emulsions used in Chip seal preservation treatments. Transport Res Rec 2672(12):20–31. https://doi.org/10.1177/0361198118770169
6. Walubita L, Epps-Martin A, Glover CJ (2005) A surface performance graded (SPG) Specification for surface treatment binders: development and Initial Validation. (No. FHWA-TX-05/1710–2). Texas Transportation Institute, Texas A & M University System
7. Kim YR, Adams J, Castorena C et al (2017) NCHRP report 837: performance-related specifications for Asphalt binders used in preservation surface treatments. National Research Council, Washington, D.C
8. American society for testing and materials, standard test methods and practices for emulsified Asphalts, ASTM D244–09, West Conshohocken, PA, 2017
9. American society for testing and materials, standard practice for recovering residue from emulsified Asphalt using low temperature evaporative technique, ASTM D7497–09, West Conshohocken, PA, 2016
10. American association of state highway and transportation officials. standard practice for recovering residue from emulsified Asphalt using low-temperature evaporative techniques. AASHTO PP 72, Washington, D.C., 2013
11. Ouyang J, Pan B, Xu W, Hu L (2019) Effect of water content on volumetric and mechanical properties of cement bitumen emulsion mixture. J Mater Civil Eng 31(6):04019085. https://doi.org/10.1061/(ASCE)MT.1943-5533.0002736
12. Ouyang J, Hu L, Li H, Han B (2018) Effect of cement on the demulsifying behavior of over-stabilized asphalt emulsion during mixing. Constr Build Mater 177:252–260. https://doi.org/10.1016/j.conbuildmat.2018.05.141
13. Ziyani L, Gaudefroy V, Ferber V et al (2014) Chemical reactivity of mineral aggregates in aqueous solution: relationship with bitumen emulsion breaking. J Mater Sci 49(6):2465–2476. https://doi.org/10.1007/s10853-013-7938-9
14. Wang F, Liu Y, Hu S (2013) Effect of early cement hydration on the chemical stability of asphalt emulsion. Constr Build Mater 42:146–151. https://doi.org/10.1016/j.conbuildmat.2013.01.009
15. Acevedo S, Gutierrez X, Rivas H (2001) Bitumen-in-water emulsions stabilized with natural surfactants. J Colloid Interf Sci 242(1):230–238. https://doi.org/10.1006/jcis.2001.7728
16. Fang X, Winnefeld F, Lura P (2016) Precipitation of anionic emulsifier with ordinary Portland cement. J Colloid Interf Sci 479(1):98–105. https://doi.org/10.1016/j.jcis.2016.06.042

17. Hu SG, Wang T, Wang FZ, Liu ZC (2009) Adsorption behaviour between cement and asphalt emulsion in cement–asphalt mortar. Adv Cem Res 21(1):11–14. https://doi.org/10.1680/adcr.2007.00034
18. Ouyang J, Tan Y, Corr DJ, Shah SP (2016) Investigation on the mixing stability of asphalt emulsion with cement through viscosity. J Mater Civil Eng 28(12):04016149. https://doi.org/10.1061/(ASCE)MT.1943-5533.0001657
19. Ouyang J, Tan Y, Li Y, Zhao J (2015) Demulsification process of asphalt emulsion in fresh cement-asphalt emulsion paste. Mater Struct 48(12):3875–3883. https://doi.org/10.1617/s11527-014-0446-9
20. Swiertz D, Johannes P, Tashman L, Bahia H (2012) Evaluation of laboratory coating and compaction procedures for cold mix asphalt. J Assoc Asphalt Paving Technol 81:81–107
21. Toussaint A, Wilde MD (1997) A comprehensive model of sintering and coalescence of unpigmented latexes. Prog Org Coat 30(3):113–126. https://doi.org/10.1016/S0300-9440(96)00679-0
22. van Tent A, te Nijenhuis K (2000) The film formation of polymer particles in drying thin films of aqueous acrylic latices: II. Coalescence, studied with transmission spectrophotometry. J Colloid Interf Sci 232(2): 350–363. https://doi.org/10.1006/jcis.2000.7189
23. Du Chesne A, Bojkova A, Gapinski J, Seip D, Fischer P (2000) Film formation and redispersion of waterborne latex coatings. J Colloid Interf Sci 224(1):91–98. https://doi.org/10.1006/jcis.1999.6645
24. Croll SG (1986) Drying of latex paint. J Coat Technol 58(734):41–49
25. Vanderhoff JW, Bradford EB, Carrington WK (1973) The transport of water through latex films. Journal of Polymer Science, part C: Polymer Symposium 41:155–174. https://doi.org/10.1002/polc.5070410116
26. Keddie J, Routh AF (2010) Fundamentals of latex film formation: processes and properties. Springer Science & Business Media, Berlin
27. Chevalier Y, Pichot C, Graillat C et al (1992) Film formation with latex particles. Colloid Polym Sci 270(8):806–821. https://doi.org/10.1007/BF00776153
28. Roulstone BJ, Wilkinson MC, Hearn J (1992) Studies on polymer latex films: II. Effect of surfactants on the water vapour permeability of polymer latex films. Polym Int 27(1):43–50. https://doi.org/10.1002/pi.4990270107
29. Talapin DV, Shevchenko EV, Bodnarchuk MI, Ye XC, Chen J, Murray CB (2009) Quasicrystalline order in self-assembled binary nanoparticle superlattices. Nature 461:964–967. https://doi.org/10.1038/nature08439
30. Rabani E, Reichman DR, Geissler PL, Brus LE (2003) Drying mediated self-assembly of nanoparticles. Nature 426:271–274. https://doi.org/10.1038/nature02087
31. Wozniak M, Derkachov G, Kolwas K, Archer J et al (2015) Formation of highly ordered spherical aggregates from drying microdroplets of colloidal suspension. Langmuir 31(28):7860–7868. https://doi.org/10.1021/acs.langmuir.5b01621
32. Lee SY, Gradon L, Janeczko S, Iskandar F, Okuyama K (2010) Formation of highly ordered nanostructures by drying micrometer colloidal droplets. ACS Nano 4(8):4717–4724. https://doi.org/10.1021/nn101297c
33. Tzitzinou A, Keddie JL, Geurts JM et al (2000) Film formation of latex blends with bimodal particle size distributions: consideration of particle deformability and continuity of the dispersed phase. Macromolecules 33(7):2695–2708. https://doi.org/10.1021/ma991372z
34. Ouyang J, Meng Y, Tang T, Miljković M, Tan Y (2021) Characterization of the drying behaviour of asphalt emulsion. Constr Build Mater 274:122090. https://doi.org/10.1016/j.conbuildmat.2020.122090
35. Ouyang J, Cao P, Meng Y, Tang T (2021) Investigation on the drying and demulsification process of filler-bitumen emulsion paste. Mater Struct 54(1):1–12. https://doi.org/10.1617/s11527-020-01600-x
36. Barnes HA (2000) A Handbook of Elementary Rheology. University of Wales Institute of Non-Newtonian Fluid Mechanics, Aberystwyth
37. Krieger IM, Dougherty TJ (1959) A mechanism for non-Newtonian flow in suspensions of rigid spheres. J Rheol 3(1):137–152. https://doi.org/10.1122/1.548848

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