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Effect of emulsifier content on the rheological properties of asphalt emulsion residues

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ABSTRACT: Rheological measurement was employed to study the effect of emulsifier content on the properties of asphalt emulsion. Three kinds of emulsifiers are employed, and both temperature and frequency sweep were carried out in this study. Through the analysis of the viscoelastic parameters, the emulsifier content has an obvious influence in the properties of asphalt emulsions. As the content is higher, both the viscosity and modulus increase at a given temperature and/or frequency. The rut factor also increases with the emulsifier content, which indicates an enhanced resistance of emulsified asphalt mixtures to deformation. Rheological results can guide the selection of optimal emulsifier concentration for a given method of preparation. Results of softening point, penetration, ductility and storage stability also show good agreement with the rheological measurements. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41806.

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INTRODUCTION

Asphalt emulsions are obtained by dispersing asphalt globules in water with an emulsifying agent. They have been used for various surface treatments such as the traditional chip seals to construction of new pavements for low volume roads.[1] To improve their performance, different additives were added into the emulsions, such as polymer latex. They have different performances during the application process. The complexity of this system is highly elevated and it is difficult to understand physical behavior of emulsified asphalts. Therefore, understanding and predicting the behavior and performance characteristics of emulsified asphalts is becoming an important topic for researchers.

It was reported that emulsified asphalt characteristics, such as stability and workability, is associated with its rheological properties, interfacial viscosity, elasticity and the electro-kinetic properties of the emulsion.[2] Mercado *et al.* measured the viscosity to investigate the heteroflocculation of a cationic oil-in-water emulsion via rheometer.[3] It is assumed that the emulsion heteroflocculation is the result of direct oil droplets adhesion on the sand surface, followed by their coalescence around the sand particles. Nuñez *et al.* studied the effect of concentration, mean drop diameter and distribution on rheological behavior. It was found that bimodal emulsions are of great importance in the processes of transporting, handling and commercializing extremely viscous hydrocarbons.[4] Dynamic modulus could also be used to determine the stiffness of asphalt emulsion mixtures.[5] Given the same moisture content, CIR-foam specimens exhibited higher dynamic modulus and larger flow numbers than CIR-emulsion specimens. Marasteanu and Clyne characterize asphalt emulsions via rheological measurement of residues. Different species of emulsions and cured methods were investigated. Their disadvantage and advantage were easy to obtain in this method.[6] It showed that the polymer-modified emulsion residues have a reduced temperature susceptibility compared to the unmodified ones, similar to the effect seen in polymer-modified asphalt binders. Herein, rheological measurement is employed to investigate the performance of emulsions used in cold-recycled asphalt mixtures at different emulsifier contents. Based on these results, the optimal condition of asphalt emulsion formulas was obtained. This research could offer some empirical basis to guide formulation of emulsified asphalts. Rheological measurement is proved to be a favorable way to optimize preparation conditions of emulsified asphalt.

EXPERIMENTAL

Materials

Three kinds of cationic slow-set emulsifiers named INDULIN SBT, W-5, MQ3 were employed to prepare asphalt emulsions, which were purchased from MeadWestvaco in China and used as

Additional Supporting Information may be found in the online version of this article.

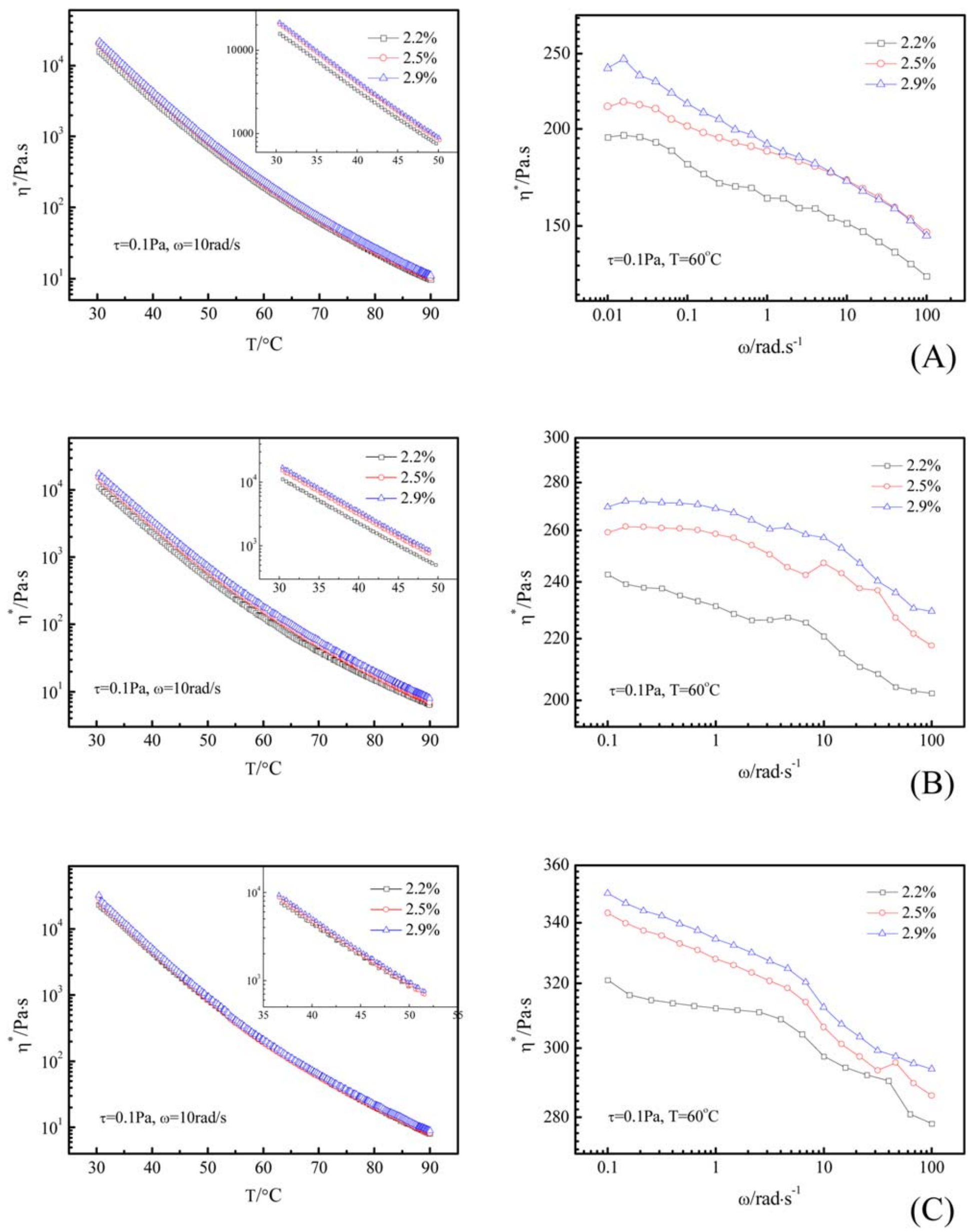

Figure 1. Variation of complex viscosity at different amounts of (A) SBT, (B) W-5, and (C) MQ3 as a function of temperature (T) and frequency (ω). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

received. INDULIN SBT is a complex reaction product specifically formulated for CSS emulsions. INDULIN W-5 can be used to produce either a cationic or anionic slow-setting asphalt emulsion. They are designed to perform in a wide variety of applications including slow set slurry surfacing, tack coat, fog seal, and solventless cold mix applications such as recycling and base stabilization. INDULIN MQ3 is an emulsifier for cationic quick-set and micro-surfacing emulsions. It is specially designed to give improved control of mixing and curing properties with a wide range of aggregates and processing conditions. AH-90 paving asphalt was purchased from Shell Corporation, China. Its physical properties, softening point, penetration and ductility are 44.6°C, 81.2 dmm (25°C) and more than 100 centimeters (25°C) respectively, measured according to ASTM D36, D5, and D113.

An aqueous phase was prepared by dispersing the emulsifier in distilled water (the water was heated to 55°C). Asphalt emulsion was prepared by homogenizing 65 wt % asphalt (the asphalt temperature was 140°C) with 35 wt % aqueous phase in a high-speed colloid mill.

Measurements of Physical Properties

Softening point, penetration and low temperature ductility of asphalt emulsion residues were measured according to ASTM D36, D5 and Chinese specification GB/T 4508, respectively.

Rheological Measurements

The rheological measurements were carried out on a DHR-1 Rheometer (produced by TA Instruments, America) with parallel plate geometry (25 mm in diameter). The scatter in the experimental

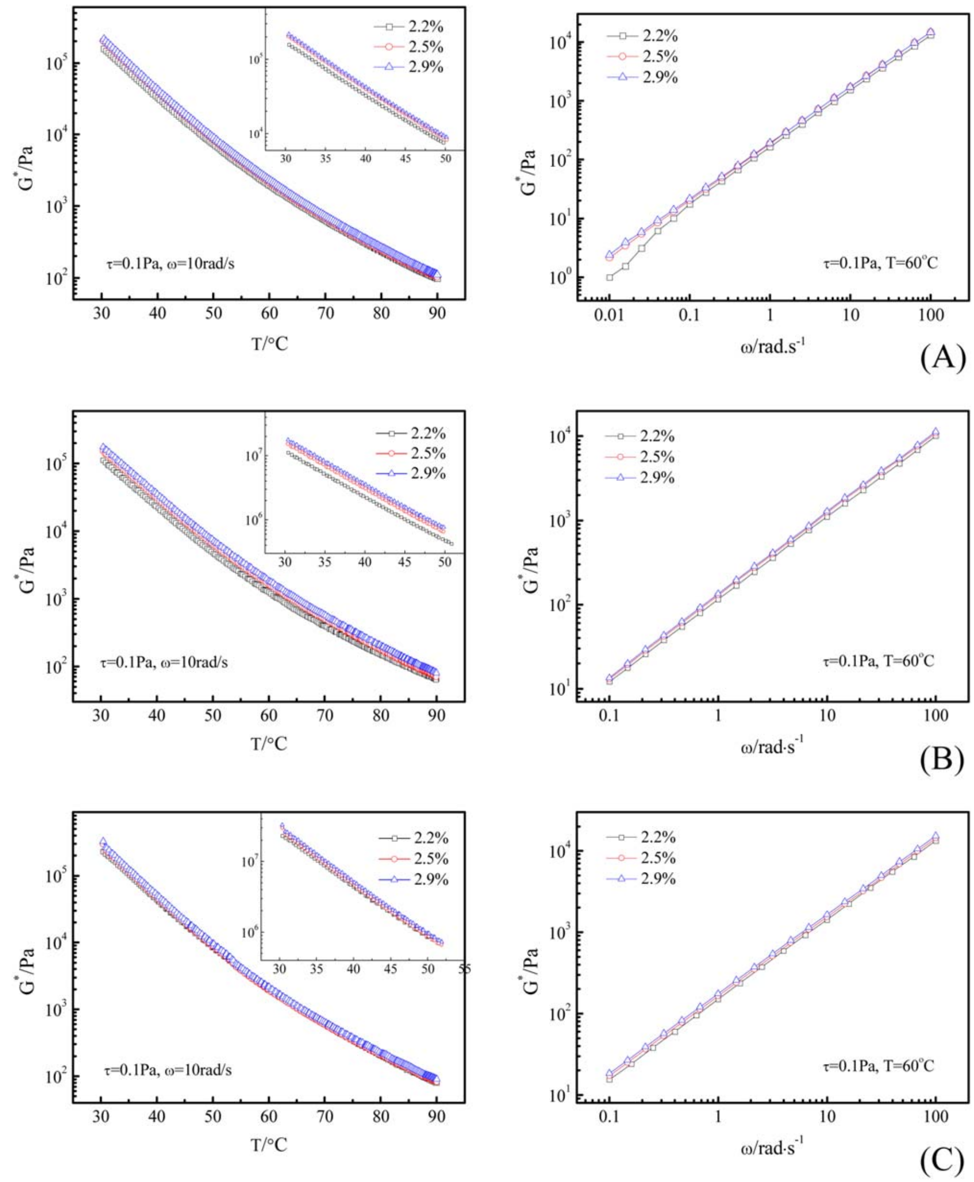

Figure 2. Variation of complex modulus at different amounts of (A) SBT, (B) W-5, and (C) MQ3 as a function of temperature (T) and frequency (ω). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

data is $<\pm 5\%$. Replicate measurements of each sample studied in this article have been carried out, which shows the same variation trend. Before carrying out oscillatory measurements, a stress sweep test has been made to determine the parameters of applied stress and strain that define the linear viscoelastic regime so that appropriate parameters can be selected for the rheological measurements.[7,8] After a proper stress was selected, the oscillatory rheological measurements of the dynamic shear moduli were carried out. Temperature swept between 30 and 90°C was applied at a fixed frequency of 10 rad s^{-1}, and frequency swept was set up between 0.01 and 100 rad s^{-1} at 60°C. The rheological parameters were measured for calculating viscoelastic parameters such as complex modulus (G^*), storage modulus (G'), loss modulus (G'') and phase angle (δ). G^* is defined as the ratio of maximum (shear) stress to maximum strain and provides a measure of the total resistance to deformation when the asphalt is subjected to shear loading.[9] It contains elastic and viscous components, which are designated as the (shear) storage modulus (G') and shear loss modulus (G''). The phase angle, defined above as the phase difference between stress and strain in an oscillatory test, is a measure of the viscoelastic balance of the material behavior. Phase angle for purely elastic and purely viscous materials is equal to 0° and 90°, respectively.[10]

RESULTS AND DISCUSSION

Rheological Properties

The complex viscosity of pure asphalt is shown in Figure S1 of the Supporting Information. It is a little higher than that of emulsified asphalts in both temperature sweep and frequency sweep. As the temperature or frequency increases, the complex viscosities of the three emulsified asphalts prepared by SBT, W-5, and MQ3 decrease as shown in Figure 1. The complex

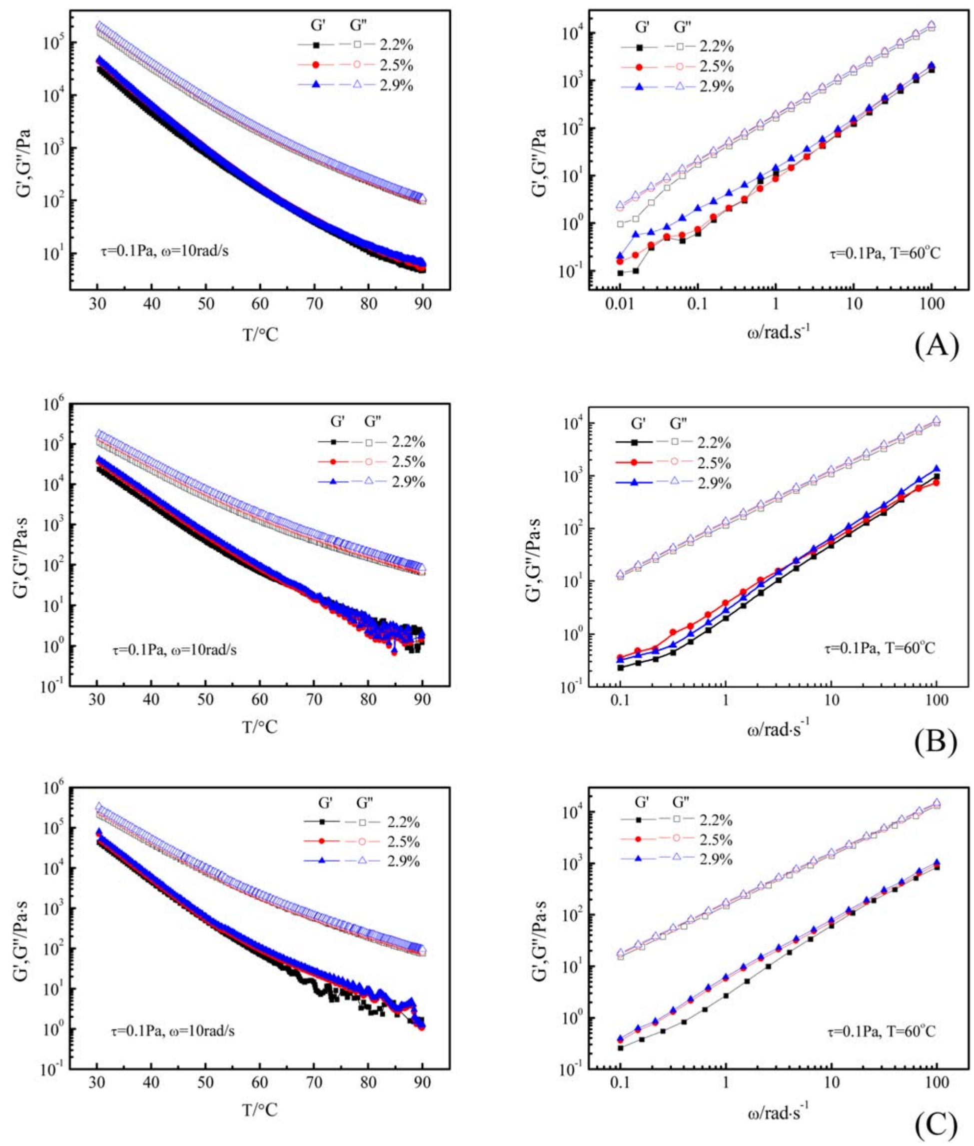

Figure 3. Variation of storage modulus (■, ●, ▲) and loss modulus (□, ○, △) at different amounts of (A) SBT, (B) W-5, and (C) MQ3 as a function of temperature (*T*) and frequency (*ω*). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

viscosity is affected by the temperature remarkably. It is well known that the increasing of the temperature can give rise to crimple of polymer molecules, and results in dehydrating and destruction of the associational structure. As a consequence, the viscosities of the three systems are much lower. The change of frequency could affect the internal structure of emulsified asphalts, and network structures may be destroyed in some extent. This result also brings the descent of viscosity. As shown in Figure 1, viscosities decrease with the increase of frequency, and the difference among the complex viscosities of samples with different contents at low temperatures is greater than the difference at high temperatures. As the emulsifier has a hydrophilic and hydrophobic moiety, it could perform as a bridge to combine water and asphalt. As a result, the complex viscosity increases with the addition of emulsifier. However, the increasing of the temperature can give rise to crimple of the complex, and dehydrating and destruction of the associational structure take place. The sheer force with high frequency also could destruct the associational structure. Thus, the difference in rheological properties becomes much smaller at high frequencies.

It is clear to observe that the complex viscosity is also relevant to the content of emulsifier. As the content is higher in each system, the viscosity increases at a given temperature or frequency. The curves of 2.5 and 2.9% are above that of 2.2% in the whole range of measured temperature or frequency for each system. Among the three systems, the effect of emulsifier content is relatively strong in the system with W-5 and weak in the system with MQ3. It indicates that this effect is also affected by the kinds of emulsifiers, while the tendency of decrease in complex viscosity will not change.

Complex modulus (G^*) provides a measure of the total resistance to deformation.[9] The ability of asphalt mixtures to resist deformation is highly affected by temperature and frequency.

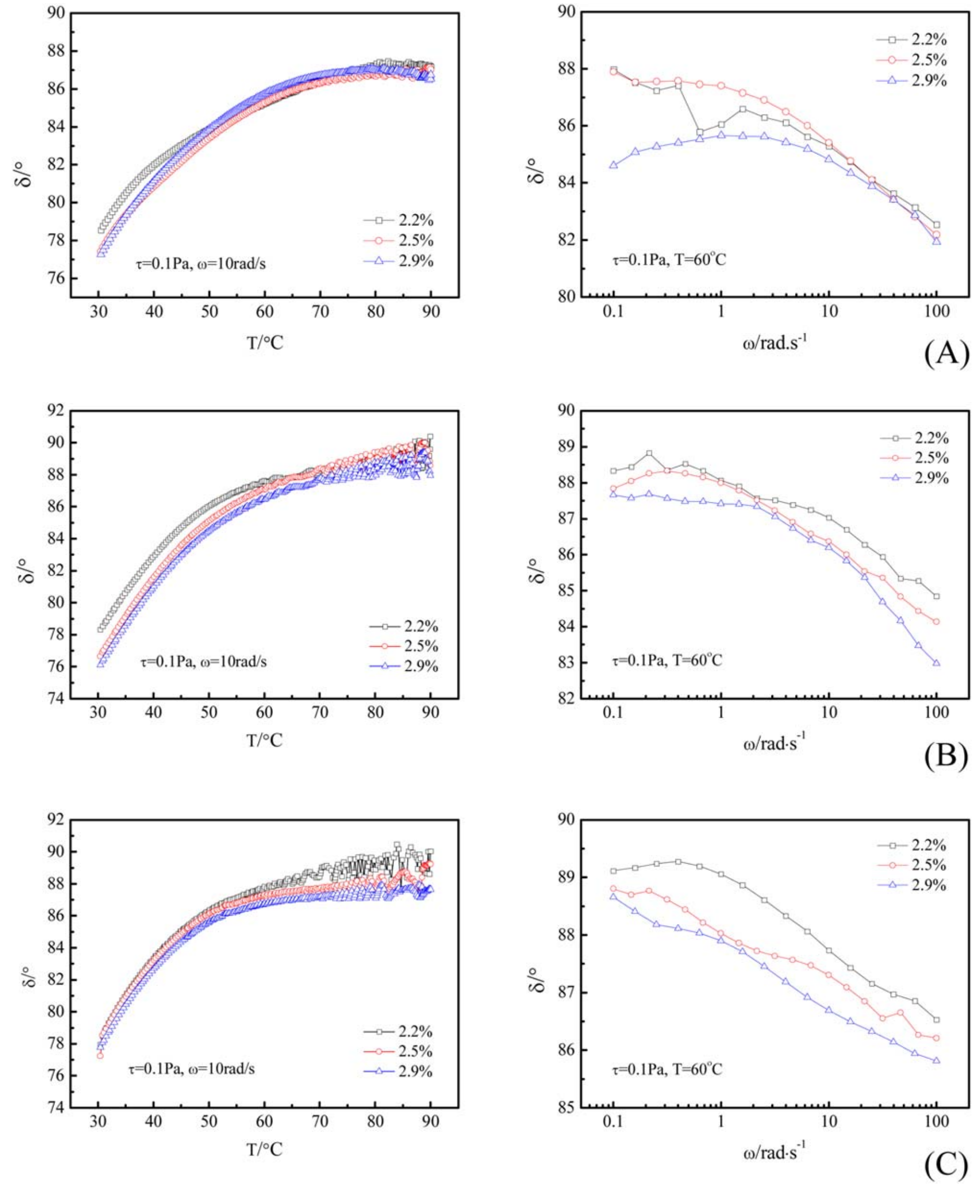

Figure 4. Variation of phase angle at different amounts of (A) SBT, (B) W-5, and (C) MQ3 as a function of temperature (T) and frequency (ω). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Both impacts were investigated in this study, and results were shown in Figure 2. The effect of temperature and emulsifier content on complex modulus is similar to that on the complex viscosity. In Figure 2, complex modulus decreases quickly with the increase of temperature and increases with frequency. The complex modulus is larger as the content of emulsifier increases, while the curves of 2.5 and 2.9% almost overlap. The difference among the curves of 2.2, 2.5, and 2.9% is relatively large in the system with W-5 and small in that with MQ3. In the SBT, W-5 and MQ3 systems, there are 11.6, 30.3, and 8.4% difference in complex modulus at 60°C when emulsifier content is increased from 2.2 to 2.9%.

As shown in Figure 3, storage and loss moduli decrease sharply with the increase of temperature and increase with frequency. Loss modulus is larger than storage modulus in each system. Larger loss modulus means a liquid-like behavior with $G'' > G'$, thus the systems are more viscous than elastic. The difference between them is obvious at elevated temperatures, and it becomes large with the increase of temperature. However, the difference between $G'$and G'' has a little change with the frequency. The curves of G' and G'' in frequency sweep measurement are almost parallel with each other. Only in the system with W-5, it is smaller at higher frequency. The effect of emulsifier content on storage and loss moduli is similar to that of complex modulus. They are larger as the content increases in systems of SBT and MQ3. In the W-5 system, the sample of 2.5% shows the highest value of G' at low frequencies while that same system shows the lowest value of G' at high frequencies. It seems that this phenomenon does not take place if the content exceeds a certain value. The storage and loss moduli of

2.5% are close to those of 2.9%. In practical application, the stability of emulsified asphalt does not increase any more as the content of emulsifier exceeds a certain value. In the emulsions, droplets of asphalt are dispersed in water with the aid of emulsifier. As all the droplets of asphalt were stabilized to form a homogeneous emulsion, there is no need to add more emulsifier. As a result, the properties will not be greatly affected with redundant emulsifier. The content of 2.9% should be higher than the amount that the emulsion actually needs to stabilize asphalt droplets. Therefore, the results of systems with 2.5 and 2.9% emulsifier are similar to each other.

The phase angle is generally considered to be more sensitive to the chemical and physical structure than complex modulus for the modification of asphalts.[11] It increases with the temperature and decreases with the frequency as shown in Figure 4. A plateau is discovered at high temperatures. As the emulsifier content is higher, phase angle decreases remarkably in the systems of W-5 and MQ3. Only in the SBT system, the phase angle for the 2.2% emulsion is lower than the others at 60–70°C. Higher content does not relate to smaller phase angle. The phase angle of 2.9% is similar to that of 2.5%, especially in the system with SBT. Emulsifier content has a great effect on the angle at a given frequency. The difference among the three samples of 2.2, 2.5, and 2.9% is larger in frequency sweep measurement than that in temperature sweep measurement. For example, the largest difference in phase angle is 1.3 and 3.4% in the temperature and frequency sweep measurement of system SBT as the emulsifier content increases from 2.2 to 2.9%. With the content of 2.9%, the phase angle is lower than that of 2.2% and the corresponding curve is below the other two in the whole range of frequency.

In strategic highway research program (SHRP) specifications, the rut factor ($G^*/\sin\delta$) was selected to express the contribution of the asphalt binder to permanent deformation.[12,13] This value reflects the total resistance of a binder to deformation under repeated loading (G^*) and the relative amount of energy dissipated into non-recoverable deformation ($\sin\delta$) during a loading cycle. The $G^*/\sin\delta$ value should be larger than 1000 Pa at 10 rad s^{-1} for the binder at a maximum pavement design temperature. With a higher value of the parameter rate, there is higher resistance to permanent deformation. As shown in Figure 5, the rut factor declines with the increase of temperature. It is also affected by the content of emulsifier. The rut factor becomes larger as the content is higher. The curve of 2.2% is below the other two curves and the difference between the curves of 2.5 and 2.9% is small in each system. The rut factor is likely to change little as the emulsifier content further increases. The temperatures, at which $G^*/\sin\delta$ is equal to 1000 Pa, for the three samples of SBT are 65.6, 66.5, and 67.0°C, for W-5 are 61.7, 63.6, and 65.0°C, for MQ3 are 64.7, 65.3, and 66.0°C. Therefore, the increase of emulsifier content could enhance the resistance of emulsified asphalt mixtures to deformation in some extent.

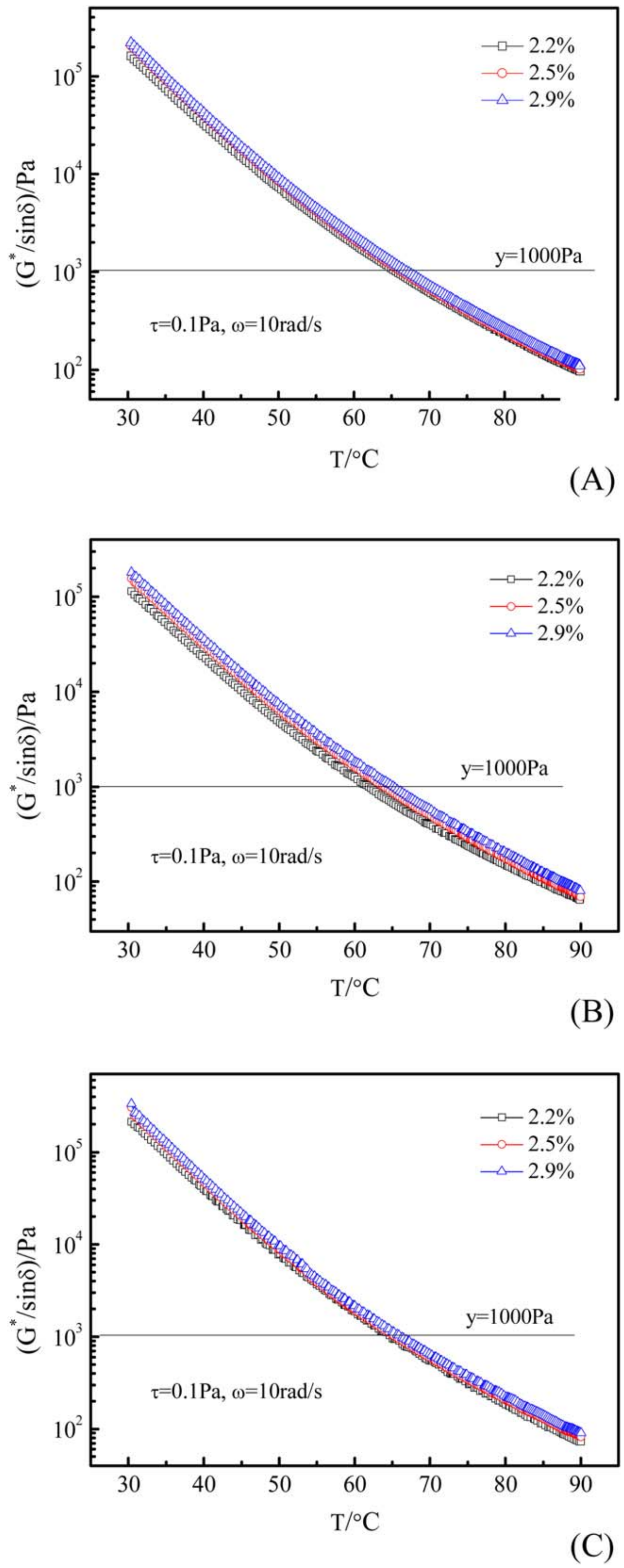

Figure 5. Variation of rut factor ($G^*/\sin\delta$) at different amounts of the emulsifier as a function of temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Physical Properties

Table I shows the softening point, penetration, low temperature ductility and storage stability of asphalt emulsions. It is clear to

Table I. Properties of Emulsified Asphalts at Different Amounts of Asphalt Emulsions

	SBT			W-5			MQ3		
System property	2.2%	2.5%	2.9%	2.2%	2.5%	2.9%	2.2%	2.5%	2.9%
Softening point (°C)	43.0	44.7	45.1	42.5	43.8	44.3	44.2	44.9	45.5
Penetration (dmm)	85.6	92.6	101.1	87.3	94.7	101.5	83.2	89.6	98.3
Ductility (5°C) (cm)	40.1	33.9	20.6	38.6	30.4	20.7	42.3	35.2	22.5
Storage stability (5 day) (%)	6.1	4.2	3.5	7.0	4.9	4.0	5.6	3.9	3.5

observe that the penetration increases remarkably with the content of emulsifier and the ductility at low temperature is much lower at higher content of emulsifier. The softening point has little relevant to the content and increases slightly. For example, there are 4.6, 15.3, and 48.6% difference in softening point, penetration and ductility when emulsifier content is increased from 2.2 to 2.9% in the SBT system. This result is in good agreement with that of viscosity as a function of temperature. Stability of asphalt emulsions stored after 5 day is not good as the content is 2.2%, while the other two samples show favorable storage stability.

The content of asphalt in the emulsion is 65 wt %. As the content of emulsifier is <2.2%, we cannot obtain an emulsion with 65 wt % asphalt. If the content of emulsifier is much higher, it is not economical and the demulsifying of emulsified asphalt mixture may be affected. The results show that the rheological properties of 2.5% are higher than those of 2.2%, but close to 2.9%. Furthermore, the storage stability of the system with 2.5% emulsifier is lower than 5% in Table I. The softening point and penetration of 2.5% are higher than 2.2%, and ductility is still larger than 30 cm. Based on above results, the optimal content of the emulsifier could be 2.5%, which is also proved in above rheological study.

CONCLUSIONS

The effect of emulsifier content on the rheological properties of asphalt emulsion residues was investigated in this study. Three kinds of emulsifiers were employed to reveal this effect. At a given temperature or frequency, viscosity and modulus increase with the content, but the difference between the samples with contents of 2.5 and 2.9% is very small. For all the target samples, loss modulus is much higher than storage modulus and close to complex modulus. It indicates that the asphalt emulsions are more viscous than elastic in the region of measured temperature and frequency, corresponding to a liquid-like behavior. Phase angle of 2.9% is the lowest under temperature sweep or frequency sweep. The rut factor has a slight increase as the content is higher than 2.5%. It is safe to say the optimal content for this system could be 2.5%. This conclusion is further confirmed by the results of physical properties of all the target samples. The one with the addition of 2.5% emulsifier has relatively pronounced increase in softening point and penetration, but slight decrease in ductility at low temperature. It also shows favorable storage stability. Therefore, rheological study can be a favorable way to optimize preparation conditions of emulsified asphalt and used in the applications of the development of cold-recycled asphalt emulsion formulas.

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