Using Rheological Properties to Evaluate Storage Stability and Setting Behaviors of Emulsified asphalts

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Abstract

Rheological properties for different emulsion families (slow, medium, and rapid sets; anionic and cationic) were studied to follow their breaking behaviors and to evaluate storage stability and overall workability. Different tests were designed to simulate the applications of emulsified asphalts in the field. To evaluate the storage and stability of emulsions a temperature sweep was used to compare their stability. A high shear rate test was used to simulate spraying while a recovery test was used to simulate setting and curing. The preliminary results indicated that rheological property can be a useful tool to predict the stability of emulsified asphalts. By simulating application conditions, the rheological tests can generate useful information to understand the breaking behavior of different emulsified asphalts.

Introduction

As a versatile and economical product, emulsified asphalts have been used for various surface treatments such as the traditional chip seals to construction of new pavements for low volume roads [1]. The introduction of polymer modified emulsified asphalt has improved the performance of emulsions significantly. Polymer additives have added further complexities to the understanding, description, and physical behavior of emulsified asphalts [2]. The complexity of an emulsified asphalt microstructure results in different performances during the application process. Understanding and predicting the behavior and performance characteristics of emulsified asphalts is becoming an important topic for researchers. Emulsified asphalt characteristic, such as stability and workability, are associated with its rheological properties. Current tests and specifications for emulsified asphalts do not offer any clear relationship on the behavior of emulsified asphalts during storage, transportation or their field applications [3-6]. Alternatively, a description of their rheological properties may offer insight not only to their workability but also to their performance. Only limited researches have been conducted to understand the rheological properties of emulsified emulsions with their characteristic behavior in the field[7-9].

In a previous study, a Dynamic Shear Rheometer (DSR) was used to evaluate the rheological properties of several types of emulsified asphalts [10]. Rheological properties were obtained by testing emulsified asphalts with test protocols developed for asphalt

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testing, such as stress sweep, frequency sweep, creep and recovery. The results demonstrated that rheological measurements can be used to predict the field applications of emulsified asphalts. In this study, several new tests were developed to simulate application conditions of emulsified asphalts. Emulsified asphalts were studied at various temperatures and time. The differences in rheological properties between emulsion types were correlated to various emulsion processes. Temperature sweep test was conducted to compare with the storage stability. A three-step (low shear rate – high shear rate- low shear rate) test was developed to simulate spraying and setting characteristics for different emulsions

Experimental Design

Materials
Eight types of emulsions were studied and included slow, medium, and rapid sets. The emulsions were: CSS-1, CMS-2, CMS-2S, CRS-2, CRS-2P, HFRS-2, HFRS-2P, and CHFRS-2P. CSS-1, CMS-2, CMS-2S, CRS-2, CRS-2P, and CHFRS-2P are cationic emulsions, while HFRS-2 and HFRS-2P are anionic emulsions. Both CMS-2 and CMS-2S contained fuel. CHFRS-2P, HFRS-2 and HFRS-2P are high float emulsions. CRS-2P, CHFRS-2P and HFRS-2P are rapid sets and polymer modified. All emulsions typically had an average residue of 65% except for one CRS-2P (1) with a residue of 72%.

Equipment
Rheological measurements were conducted using a controlled stress Bohlin CVO Dynamic Shear Rheometer (DSR). Stress sweeps, time sweep and temperature sweep tests were all conducted on this DSR. A Bohlin Peltier system equipped with a cup-and-bob geometry (C25) was used. C25 is the coaxial geometry with a 25mm diameter bob.

Test Protocol

Amplitude Sweep Test
A stress sweep was first conducted to determine the flow behavior for different emulsions. Measurements were performed at 30°C with a shear stress range from 0.01 to 10 Pa and at one Hz. The complex shear modulus G* versus stress/strain plot was used to determine the linear viscoelastic region.

Temperature Sweep Test
Emulsified asphalts were heated from 25°C to 85°C at a rate of 3°C per minute. Oscillation tests were performed at one Hz and at 1% shear strain at predetermined temperature intervals. The 1% shear strain was determined based on the linear viscoelastic region as determined by stress sweep measurements. The temperature at which the storage modulus G' equals the loss modulus G'' (G'= G'' or tanδ = 1) was considered as the gel or set point temperature for the emulsion [11].

Time Sweep Test (3-step test)
Continuous shear experiments were performed at 30°C. Tests were conducted in three steps. At first, the sample was submitted to a shear rate of 0.1 s^{-1} for 180 seconds. The

shear rate was then increased to 100 s^{-1} for 180 seconds. Immediately after the high shear phase, the shear rate was decreased to 0.1 s^{-1}. The viscosity versus time plot was generated to monitor the change in rheological properties. This test was used to simulate the application process of emulsified asphalt in the field. Step one represents the storage of the emulsified asphalt in the tank (low shear). Step two simulates the spraying and/or pumping of the emulsified asphalt. The final step represents an emulsified asphalt viscosity recovery after spraying on the pavement surface. The test can also be used to evaluate the "run off" of emulsified asphalts after spraying, for example in a chip seal operation.

Results and Discussions

Linear Viscoelastic Region

Figures 1 and 2 are examples of test results for the amplitude sweep tests.
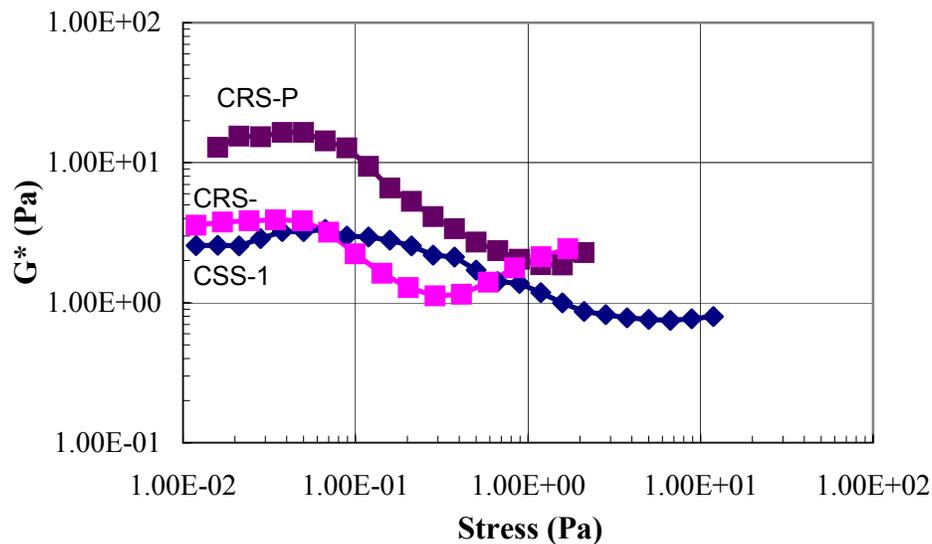
Figure 1. Amplitude Sweep Test (Stress)
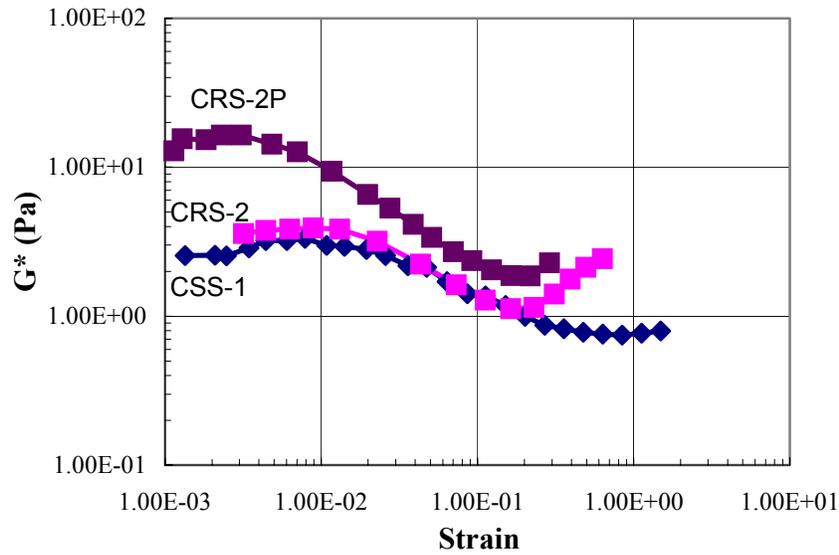
Figure 2. Amplitude Sweep Test (Strain)

The linear viscoelastic range (LVR) is illustrated by the relationship between the complex shear modulus G* versus shear stress and shear strain. The linear viscoelastic region was defined as the level where G* drops to 90% of the original G* value [10]. From the data, the emulsified asphalts have a limited linear viscoelastic region. For shear stress, the LVR is below 0.1 Pa. For the strain sweep, CRS-2P had the lowest strain (~1%), while the LVR of CSS-1 was close to 10% strain. To ensure the test was conducted in the LVR, a target strain of 1% was selected for all experiments.

Gel Point - Storage Stability and Break

Figure 3 shows the temperature sweep test result for CRS-2P. As the temperature increases, G* decreases reaching a minimum and then increases with temperature. There is a crossover point (G'=G" or tanδ =1 or δ = 45°) where the viscoelastic behavior changes from a dominant viscous, liquid-like (G">G') to a dominant elastic solid-like behavior (G'>G"). This cross over point is also called the gel point [11] or the characteristics modulus [12], and has been used in emulsion rheology to correspond to the change of behavior from a more liquid-like to a solid-like.
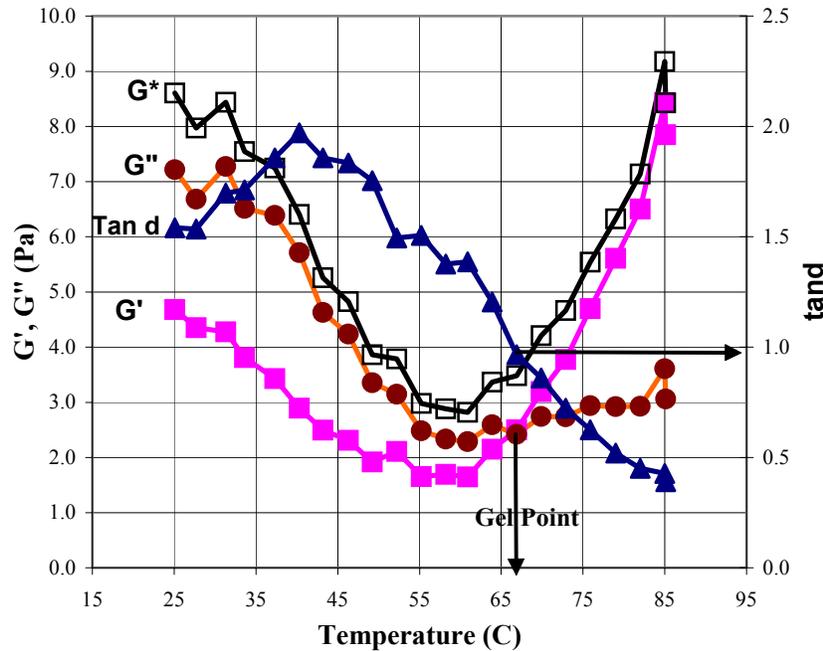
Figure 3: Temperature Sweep Test (CRS-2P)

Not all emulsified asphalts tested show this crossover behavior. Figure 4 shows the temperature sweep test results for CRS-2. Unlike CRS-2P, the G* and G" of CRS-2 decreases continuously as temperature increases, while G' maintains a relative constant level. The value of tanδ decreases as temperature changes but remains above one through the temperature range. There is no crossover point for G' and G", and G" is higher than G' throughout the temperature range. This means the emulsion behavior is predominantly viscous and remains in the liquid state. This could indicate that the crossover point may be related to the interaction between particles. For CRS-2, the emulsifier imparts a purely electrostatic interaction between asphalt droplets. Since the same asphalt and emulsifier were used to make both emulsions, the early setting point for CRS-2P is attributed to the presence of polymer latex. This imparts a steric (polymeric) stabilization to the CRS-2P. In essence, particle interaction is different for both emulsions. For CRS-2P, in addition to interaction between asphalt droplets, there are two more interaction types: latex-to-latex particles and latex particles to asphalt droplets [2]. The last two interactions may be more temperature sensitive than the interaction between asphalt droplets. The coalescence between these particles may start accelerating as temperature increases. A gel structure may start to form in the emulsion, interpreted as a change from liquid (G">G') to a solid-like behavior (G'>G"). This could also imply that CRS-2P is less stable than CRS-2 during storage.
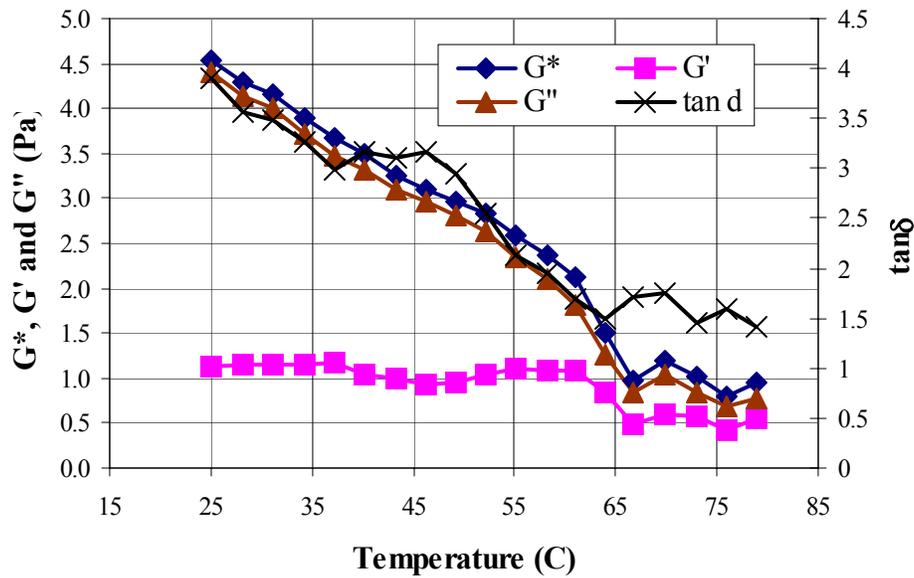
Figure 4: Temperature Sweep Test (CRS-2)

Figure 5 and 6 show results for the temperature sweep test for a series of emulsion types. This test can be used to predict the storage stability for different emulsions. For CSS-1, the changes in G* is minimal and the phase angle remains high. This indicates CSS-1 will have a stable shelf life as observed. CRS-2P is much more sensitive to temperature change, which indicates a shorter shelf life than that for CSS-1.
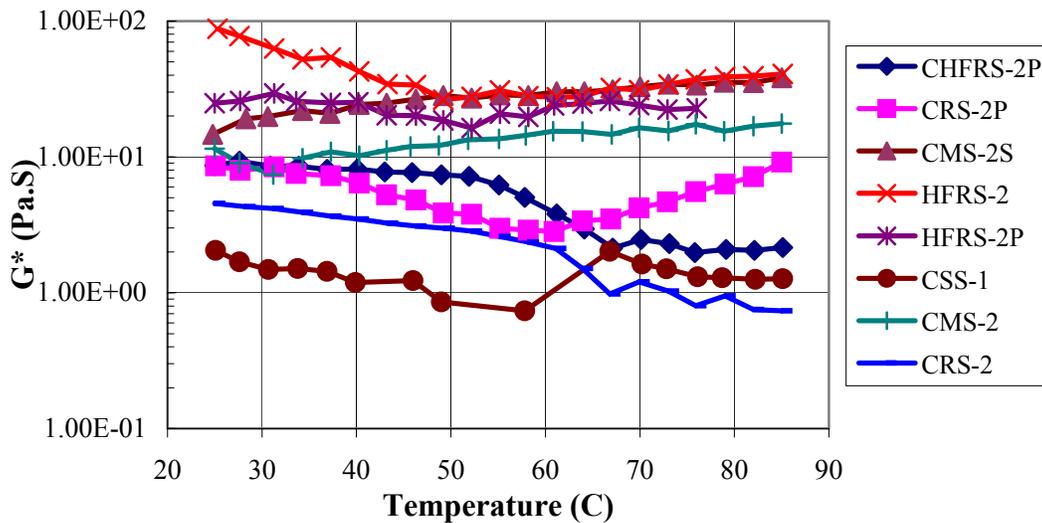
Figure 5: Temperature Sweep Test (G*)
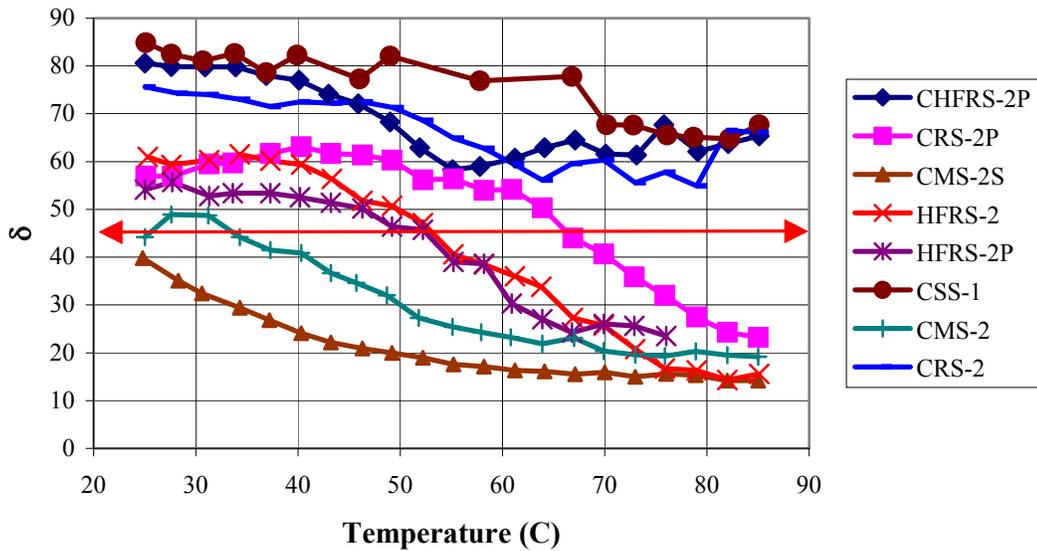
Figure 6: Temperature Sweep Test (δ)

It can be seen from figure 5, that G* for CMS-2 and CMS-2s increases as temperature increases. This may be caused by the evaporation of the fuel during the test. Both emulsion also have a lower phase angle than the other emulsions and G' is higher than G" for almost all temperatures. This is interpreted to mean that the addition of fuel changes the interaction between particles. Fuel particles may attenuate the electrostatic interaction therefore enabling asphalt droplets to approach each other to form a gel-like structure causing an early setting of the emulsion. At higher temperatures (60 to 85°C), the δ of both emulsions remains at a constant level. This indicates the gel-structures formed in CMS-2 and CMS-2S is more temperature stable than the structure in CRS-2P. Figure 6 also shows that HFRS-2 and HFRS-2P have similar gel point temperatures and is lower than that observed for CRS-2P. By adding certain chemicals, these anionic high float emulsions achieve a gel-like structure [1]. This gel-like structure is probably due to the very different microstructure that the chemical additives impart to these anionic emulsions. Further work is needed to further explain the crossover point (G'=G") differences between cationic and anionic emulsions.

Differences in gel points may be used to explain the relative rate of breaking. The gel point is the change from liquid to solid-like behavior. The lower the gel point, the shorter the breaking time may be needed under the same conditions. For the same family of emulsions, the temperature sweep test can be used to rank the time of breaking between different samples and can be used as a consistency test. Figure 7 shows an example of using the gel point to evaluate the breaking time of two CRS-2P emulsions having different asphalt residues. The gel point for the higher asphalt residue CRS-2P (1) is at 60°C, compared to that for the lower asphalt residue CRS-2P (2) at 67°C. From the gel point, CRS-2P (1) should break faster than CRS-2P (2). The higher asphalt residue for the CRS-2P (1) is likely responsible for the observed lowering of the gel point. The

temperature sweep test can be used as a predictive tool for an emulsion breaking and setting characteristics.
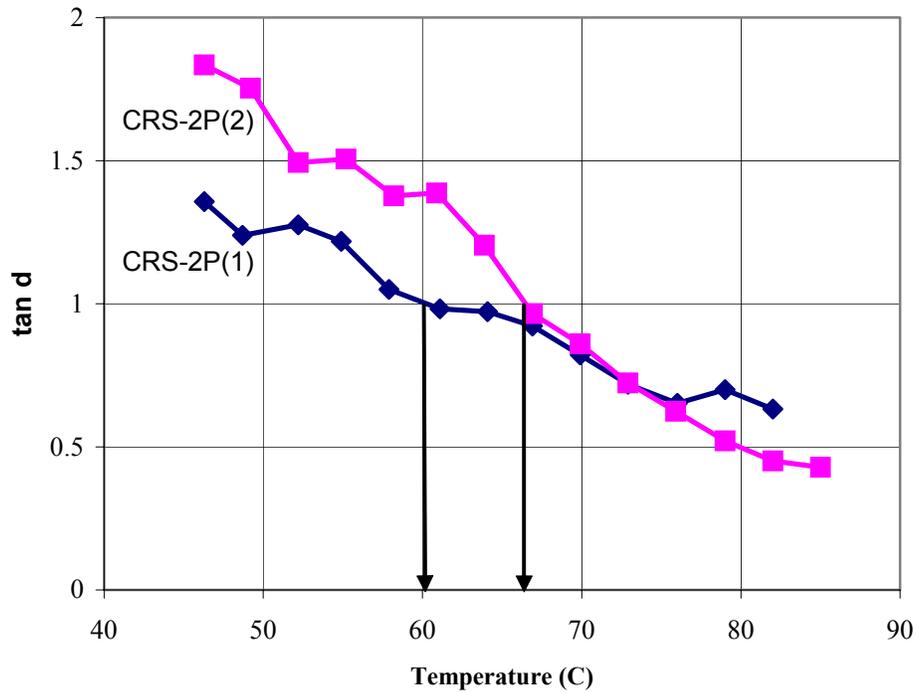
Figure 7: Gel Points for two CRS-2P

Flow Behavior - Spray

When emulsified asphalts are sprayed on the pavement, the emulsions first flow through the spray nozzle at high speed (high shear rate). To keep a smooth flow through the nozzle low viscosity is desirable. When the emulsion is placed on the pavement surface a higher viscosity is preferred to avoid emulsion run off. Due to the shear rate dependency of the emulsified asphalt, the emulsion viscosity will drop when it is under a high shear rate [10]. To avoid run off, the viscosity needs to recover to the original level in a short period of time after it reaches the pavement surface. To evaluate the change of viscosity at these conditions, a three-step time sweep test was developed. Figure 8 shows results for this test. The viscosity ratio is the ratio between viscosity values at different times and viscosity values at the end of step one.
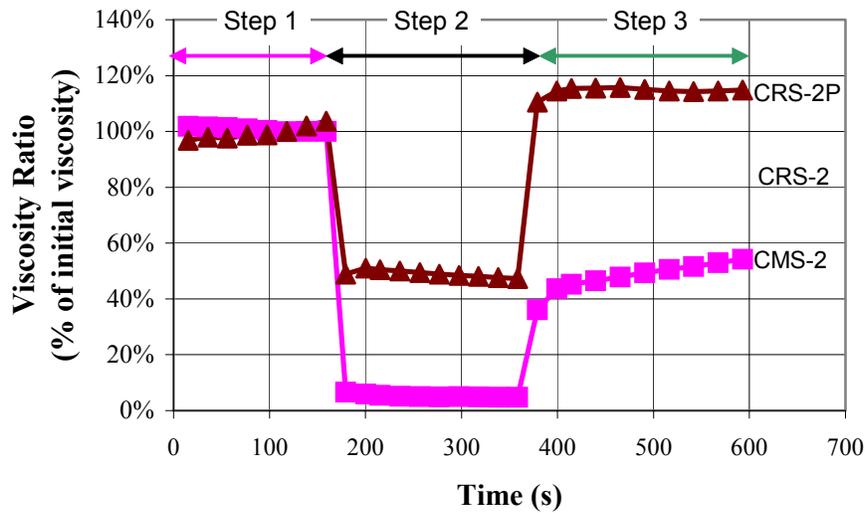
Figure 8: 3-step Time Sweep Test

From figure 8, the emulsion viscosities decrease at high shear rates. The viscosities for CRS-2P and CMS-2 decrease to a constant value immediately after application of high shear while the viscosity for CRS-2 changes gradually in Step two. The CMS-2 viscosity decreases to less than 10% of the original value. The viscosity for CRS-2P is about 50% of the original viscosity while the CRS-2 retains 70% of its viscosity.

When the high shear is stopped, CRS-2P recovers its original viscosity immediately. CMS-2 recovers gradually to 50% and CRS-2 regains 80% of its original viscosity. The results show CRS-2P has favorable workability when it is sprayed and the tendency for run off after the application is relatively small. The addition of fuel on CMS-2 increases its workability.

Conclusions

1. Rheological measurements can be used to predict the field applications of emulsified asphalts. The difference in rheological properties can be related to the different type of interactions in the emulsified asphalts: electrostatic, steric, cationic, and anionic.
2. Gel point determined by temperature sweep test can be used to study storage stability and setting time for different emulsions. The gel point may be related to the interaction of particles in emulsified asphalt.
3. Spraying of an emulsion can be simulated using a high shear rate test. The flow curve determined using this test can be used to understand the behavior of emulsified asphalt during the application on the pavement surface.

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