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16. Abstract Conventional hot mix asphalt (HMA) is produced by heating the aggregate and the asphalt binder to elevated temperatures that are typically in the range of 150C to 160C. These temperatures ensure that the viscosity of the asphalt binder is low enough to effectively coat the aggregate particles. During the past decade, warm mix asphalt (WMA) has been introduced to reduce the mixing temperatures by approximately 30C compared to HMA. Workability at these reduced temperatures is typically achieved by the use of chemical additives in the asphalt binder or by foaming the asphalt binder using small percentages of water. The use of WMA is associated with advantages such as reduced emissions during mixture production, extended paving season and reduced aging in the asphalt binder. In case of the WMA and the HMA, one of the important physical properties that dictates the quality of coating is the surface tension of the asphalt binder at mixing temperatures. In this study, the surface tension of different liquid asphalt binders was measured at typical mixing temperatures. The effect of binder type, temperature, and chemical additives used to produce WMA on the surface tension of the binder was evaluated. Three different binders with and without three different chemical additives were used in this study. The dynamic surface tension was measured using four different rates of surface formation and at several different temperatures within the range of 140C and 170C. Results show that the surface tension of asphalt binder depends on the rate of surface formation, temperature and source of the asphalt binder. Dynamic surface tension of asphalt binders suggests that asphalt binders behave similar to surfactants. The addition of chemical warm mix additives did not significantly reduce the surface tension of the binder compared to the control.					
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**WETTING CHARACTERISTICS OF ASPHALT BINDERS AT
MIXING TEMPERATURES**

by

Patricia Hennig Osmari
Zelalem Arega
Amit Bhasin, Ph.D.

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Workability of Asphalt Binders at Mixing Temperatures for Hot and Warm Mix Asphalt

Southwest Region University Transportation Center
Center for Transportation Research
The University of Texas at Austin
Austin, Texas 78712

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ABSTRACT

Conventional hot mix asphalt (HMA) is produced by heating the aggregate and the asphalt binder to elevated temperatures that are typically in the range of 150°C to 160°C. These temperatures ensure that the viscosity of the asphalt binder is low enough to effectively coat the aggregate particles. During the past decade, warm mix asphalt (WMA) has been introduced to reduce the mixing temperatures by approximately 30°C compared to HMA. Workability at these reduced temperatures is typically achieved by the use of chemical additives in the asphalt binder or by foaming the asphalt binder using small percentages of water. The use of WMA is associated with advantages such as reduced emissions during mixture production, extended paving season and reduced aging in the asphalt binder. In case of the WMA and the HMA, one of the important physical properties that dictates the quality of coating is the surface tension of the asphalt binder at mixing temperatures. In this study, the surface tension of different liquid asphalt binders was measured at typical mixing temperatures. The effect of binder type, temperature, and chemical additives used to produce WMA on the surface tension of the binder was evaluated. Three different binders with and without three different chemical additives were used in this study. The dynamic surface tension was measured using four different rates of surface formation and at several different temperatures within the range of 140°C and 170°C. Results show that the surface tension of asphalt binder depends on the rate of surface formation, temperature and source of the asphalt binder. Dynamic surface tension of asphalt binders suggests that asphalt binders behave similar to surfactants. The addition of chemical warm mix additives did not significantly reduce the surface tension of the binder compared to the control.

EXECUTIVE SUMMARY

The ability of an asphalt binder to intimately coat the surface of an aggregate particle is essential to ensure the production of a durable mix. Viscosity and surface tension dictate the ability of a fluid to coat the surface of a solid. While viscosity quantifies the resistance of a liquid to flow, surface tension is the driving force that promotes wetting. In general, lower surface tension promotes wetting and intimate coating of rough surfaces (as in the case of aggregate particles). In the context of asphalt mixtures, viscosity of liquid asphalt binders at typical mixing and compaction temperatures is measured on a routine basis whereas to the best of the authors' knowledge, surface tension of asphalt binders at these temperatures has not been measured. Knowledge of surface tension at mixing temperatures is important to understand the mechanisms by which foaming or use of chemical additives facilitate coating of aggregates to produce warm mix asphalt (WMA). For example, in the context of foaming, the extent to which different asphalt binders can be foamed and concomitant mixing and coating efficiency achieved is related to the surface tension of the binder. In the context of chemical additives, one of mechanisms proposed to facilitate coating at warm mix temperatures is the ability of the additives to act as surfactants. In other words the chemical additives are expected to reduce the surface tension of the binder to enhance coating.

The objective of this study was to measure the dynamic surface tension of typical asphalt binders with and without chemical additives at several different temperatures typically associated with the production of hot and warm mix asphalt. The motivation of this study was that this information can be used in future studies to better understand the mechanisms of aggregate coating and the influence of additives to promote mixing.

Three different binders were used in this study. Surface tensions of these binders were measured at several different temperatures in the range of 140°C to 170°C using the maximum differential bubble pressure method. Surface tensions were also measured by varying the rate of formation of the bubble surface from 0.1 bubbles per second to 1.0 bubbles per second as well as by incorporating three different types of chemical additives.

Results from this study indicate that asphalt binders have a surface tension that varies from 35 to 64 dynes/cm depending on the rate of surface formation, temperature and type of binder. The surface tension of the binders reduces linearly with an increase in temperature. This is consistent with the behavior of several other liquids. At any given temperature, surface tension of asphalt binders is dependent on the source and type of the asphalt binder.

Results also indicate that asphalt binders tend to have a significant "surfactant like"

behavior even without any post production modifier or additive. In other words, surface tension of the binders was shown to be strongly dependent on the rate of formation of the surface. This finding also indirectly lends more credence to the colloidal theory of asphalt binder. Finally, the three warm mix chemical additives used in this study did not result in any significant surfactant like behavior beyond what was already observed with unmodified asphalt binders.

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CHAPTER 1. INTRODUCTION

1.1 INTRODUCTION AND OBJECTIVES

Inadequate or improper coating of aggregate particles by the asphalt binder has a direct bearing on the durability of the asphalt mixture. For example inadequate coating of aggregate particles can greatly amplify distresses such as moisture induced damage. In this context, inadequate coating also refers to lack of intimate wetting of the aggregate surface (that can have varying degrees of roughness at a micrometer length scale) by the liquid binder. With the relatively recent introduction of Warm Mix Asphalt (WMA) technology, there has been a renewed interest to evaluate the ability of asphalt binders to coat aggregate particles. This is because WMA technologies allow asphalt mixtures to be produced and compacted at 20 to 40°C lower than conventional hot mix asphalt. Although there are more than 20 different technologies to produce WMA, these technologies can be broadly classified into two categories: (1) chemical additive based technologies and (2) foaming based methods. Chemical additives used to produce WMA allow the asphalt binder to coat aggregate particles and maintain a workable asphalt mixture at relatively reduced temperatures compared to conventional hot mix. The mechanism by which chemical additives facilitate coating of aggregate particles at reduced temperatures is ascribed to one or a combination of the ability of the additive to:

- reduce the viscosity of the asphalt binder at a given temperature,
- reduce interfacial friction between coated particles and promote compaction, and
- act as a surfactant that improves wetting of the aggregate particles at reduced temperatures.

Based on the evaluation of selected asphalt binders and chemical WMA additives, Hanz et al. (2010) proposed that a likely mechanism by which WMA additives promote workability was by improving the lubricity of the asphalt binders. They demonstrated that the viscosity of asphalt binders at any given temperature did not change significantly with the addition of WMA additive. They proposed a method to measure the lubricity of asphalt binders using a dynamic shear rheometer (DSR). Using this method, they demonstrated that addition of the WMA additive improved lubricity of the asphalt binder, which corresponded well with the reduced compaction effort associated with the WMA mixtures. However, Hanz et al.

(2010) also reported that aggregate coating reduced with a decrease in mixing temperature and that in many cases this reduction was not significantly improved by the presence of the chemical additive. In another study, Bennert et al. (2010) measured the influence of different WMA additives on the lubricity of asphalt binders using a DSR. Similar to the previous study, Bennert et al. (2010) also demonstrated a good correlation between the compactibility of asphalt mixtures to the lubricity related parameters of the binders with and without WMA additives. However, Bennert et al. (2010) did not evaluate the coating of aggregate particles at reduced mixing temperature.

The two most important properties of an asphalt binder that dictate its ability to coat aggregate particles are its viscosity and surface tension. Perhaps a simplified albeit clear explanation of the interplay between these two properties on wetting and coating is given by Wulf et al. (2000): *“Without going into details surface tension can be regarded as the driving force and viscosity as the resistance of wetting”*. In the asphalt industry, viscosity of the asphalt binder is routinely used as a measure of its workability during asphalt mixture production and placement. The effect of WMA additives on the viscosity of the asphalt binder is also well documented in the literature. However, there are very few studies that have evaluated the effect of temperature and WMA additives on the surface tension of the asphalt binder at typical mixing temperatures. Surface tension and viscosity of asphalt binders are also critical to understand the characteristics of foamed asphalt binder (e.g. expansion ratio and half life), which is also used to produce WMA (Kim and Little, 1990).

The objective of this study was to measure the surface tension of the asphalt binder at typical mixing temperatures as well as the influence of WMA additives on surface tension. While the effect of temperature and additives on binder viscosity are well documented in the literature, to the best of the authors' knowledge surface tension of asphalt binders at typical mixing temperatures is not documented. This report presents a method to measure the surface tension of asphalt binders at typical mixing temperatures as well as the effect of temperature and additives on the surface tension of binder. The findings from this study are important to explain and understand the impact of temperature and WMA additives on the coating of aggregate particles during mixture production. Surface tension of binders is also a critical material property that dictates the ability of the asphalt binder to expand and foam when foamed asphalt binders are used to produce WMA.

1.2 REPORT STRUCTURE

Chapter 2 of this report presents a background on the different methods that can be used to measure the surface tension of asphalt binders in its liquid state as well as a detailed description of the method that was adopted for this study. Chapter 3 presents the experiment design, materials used for this study as well as the detailed test procedure that was followed to measure the surface tension of asphalt binders. Chapter 4 presents the results from this study including a statistical analysis identifying the most significant factors that influence the surface tension of the binders. Finally, Chapter 5 presents a summary of results from this study and the conclusions drawn from these results.

CHAPTER 2. BACKGROUND

2.1 ROLE OF SURFACE TENSION IN WETTING OF SOLID SURFACES AND FOAMING OF LIQUIDS

The importance of a liquid's surface tension on its ability to effectively wet and coat the surface of solids is well documented in areas of study other than asphalt binders and mixtures. Hashim et al. (2001) discussed the significance of lowering the surface tension of metals in the production of metallic composites of silicon carbide particles with aluminum as a matrix. Wulf et al. (2000) evaluated the impact of surface tension of polymer melts in powder coatings. Surface tension is continually controlled and adjusted for powder coating formulations. Schwartz and Weidner (1995) and Chow (1998) evaluated the influence of irregular forms and surface roughness on wetting and coating. The work by Chow (1998) is more relevant to binder-aggregate wetting and is discussed in more detail in the following paragraphs.

Myers (1996; 1998) presents analytical models to describe flow in thin films as well as lubrication driven by surface tension. The solutions presented are for several different applications such as coating of irregular surfaces and drying of paint on a rough surface. Intuitively it is expected that the rate with which a liquid wets a solid surface is related to the liquid surface tension as well as the liquid viscosity. Blake and De Coninck (2002) mathematically modeled the influence of these two factors on the velocity with which a liquid wets a solid surface. They report that the driving force for a liquid to wet the surface of a solid is given as $F_w = \gamma_{LV} (\cos \theta^0 - \cos \theta)$ where, γ_{LV} is the surface tension of the liquid-vapor interface (where vapor is typically atmospheric air), θ^0 is the equilibrium contact angle achieved by the liquid on the solid surface and θ is the contact angle at any time prior to reaching equilibrium. It must be noted in this equation that γ_{LV} is a property of the liquid whereas θ is determined by the properties of the liquid and the solid surface that is being wetted by the liquid. The equation clearly demonstrates that the driving force for the liquid to achieve equilibrium contact (angle) with the solid surface is directly proportional to its surface tension. In addition to the driving force due to surface interactions, Blake and De Coninck (2002) also incorporated the effect of liquid viscosity on the rate of wetting. They demonstrated that the rate of wetting was inversely proportional to the liquid viscosity. In their analysis, Blake and De Coninck (2002) also include the effect of specific solid-liquid interactions, denoted by a parameter κ_s^0 , on the rate of wetting. Specifically, strong

solid-liquid interactions that increase the driving force F_w and rate of wetting, also to some extent reduce the rate of wetting through the parameter κ_s^0 . A direct consequence of these counteracting interactions is that the rate of wetting decreases as the contact angle decreases from approximately 120° to 0° , where the latter is the case for typical binder-aggregate systems. In summary, the findings from Blake and De Coninck (2002) suggest that in the context of asphalt binder wetting the surface of the aggregate, the rate of wetting is likely to be slow on account of the strong solid-liquid interactions. In addition, this rate would increase with an increase in the surface tension of the liquid and decrease with an increase in the viscosity of the liquid.

Coating of smooth ideal surfaces can be used as the basis to understand and model the physics of wetting and coating. However, aggregate surfaces are rough and highly textured and far from ideal. In addition, the surface texture of the aggregates is significantly different for aggregates for different sources. For example, different types of commonly used aggregates for mixture production can have specific surface areas that vary by two orders of magnitude (Robl et al., 1991; Bhasin and Little, 2006). Chow (1998) presents a detailed analysis on the effect of surface roughness on the wetting of solid surfaces by a liquid. He characterized surface roughness using a roughness parameter (also referred to as Wenzel roughness) that varied from 1 for a smooth surface to values greater than 1 for rough surfaces. The roughness parameter basically is the ratio of the non-planar to planar-surface area. Chow (1998) was able to account for the change in the contact angle at a solid-liquid interface that was due to the roughness of the solid surface. Through a series of mathematical manipulations he was able to demonstrate that rougher surfaces reduce the contact angle of the liquid and promote wetting. This is best exemplified in Figure 2.1, also referred to as the Zisman plot. Figure 2.1 is a schematic that illustrates the relationship between the contact angle at a solid-liquid interface to the surface tension of the liquid. In this plot, critical surface tension is defined as the surface tension of the liquid at or below which the liquid will completely wet the surface of the solid. A liquid with a surface tension that is less than the critical surface tension will not completely wet the surface of the solid and result in a contact angle at the solid-liquid interface that is greater than 0 . The schematic in Figure 2.1 illustrates that the critical surface tension for a solid surface decreases with an increase in roughness. In the context of bitumen wetting an aggregate surface, the findings from Chow (1998) as illustrated in this schematic can also be interpreted as follows. Consider aggregates with similar mineralogy and surface free energy. In this case a binder with lower surface tension is desirable for aggregates with lower surface texture to ensure

complete wetting of the aggregate surface. It must also be noted that such results are not only relevant to compare aggregates from different sources but are also important in the context of complete coating of individual aggregate particles from any given source. This is because individual aggregate particles demonstrate a distribution of surface roughness at smaller length scales. Therefore smooth areas localized on the surface of aggregate particles will not be coated (or intimately wetted) when mixed with binders that have a surface tension higher than the critical surface tension.

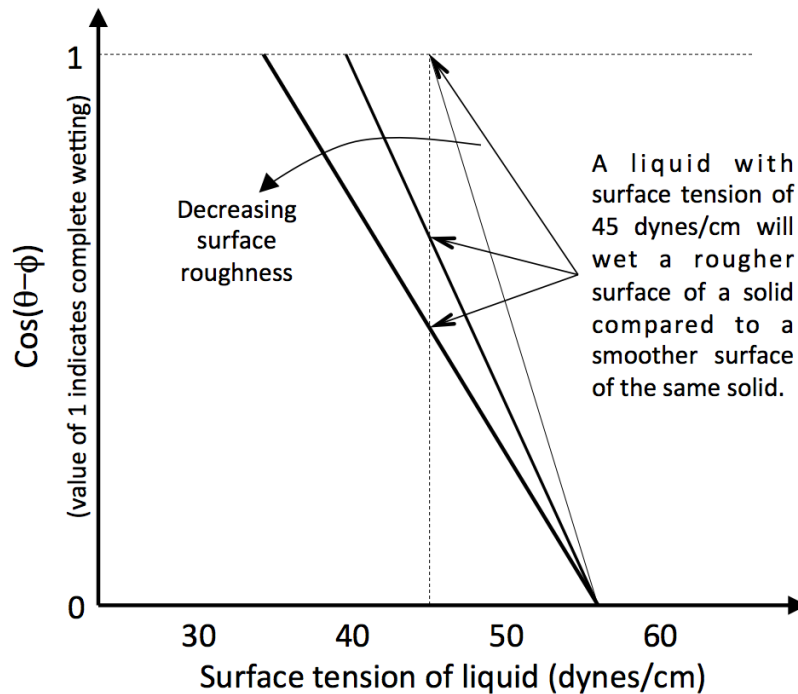


Figure 2.1. Schematic of the influence of surface roughness on critical surface tension

(Adapted based on data from Chow, 1998)

2.2 METHODS TO MEASURE SURFACE TENSION OF BINDERS AT ELEVATED TEMPERATURES

There are several techniques that can be used to accurately measure the total surface tension of liquids. One of the oldest and most reliable technique is the capillary rise method. Consider a very small section of an arbitrarily curved surface with radii of curvature R_1 and R_2 . If the pressure difference in the convex and concave side of the surface is ΔP , and the surface tension of the surface is γ , then it can be shown by considering a small radial

extension of the surface that,

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2.1)$$

This fundamental equation of capillarity is due to Young and Laplace, and is referred to as the Young-Laplace equation. Figure 2.2 illustrates the capillary rise of a liquid in a capillary tube.

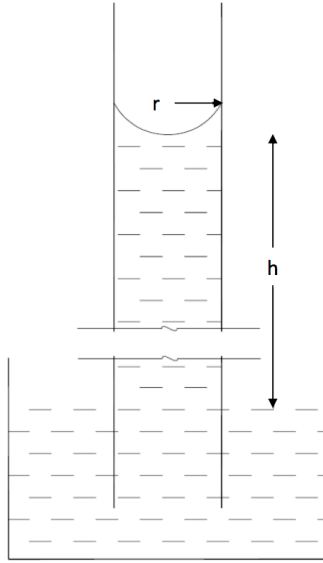


Figure 2.2. Capillary rise of a liquid

When a liquid meets the surface of a solid, the meniscus of the liquid forms an angle θ with the surface of the solid. This angle is referred to as the contact angle. If the diameter of the capillary tube is sufficiently small the two radii of curvature can be approximated as $r/\cos\theta$, where r is the radius of the capillary tube. Using the Young-Laplace equation it can be shown that:

$$\Delta\rho gh = \frac{2\gamma\cos\theta}{r} \quad (2.2)$$

where, $\Delta\rho$ is the difference in density of liquid and the gas phase above it, g is the acceleration due to gravity, h is the height of the capillary column, and γ is the surface energy of the liquid. If the contact angle is greater than 90° , $\cos\theta$ is negative and from equation 2.2 the capillary rise h , is negative. In other words, if the contact angle is greater than 90° , the liquid inside the capillary tube falls below the level of the liquid outside. In the case of a

clean glass capillary column, the contact angle of water and most organic liquids is nearly zero and therefore $\cos \theta$ in equation 2.2 can be set to 1. If the diameter of the capillary column is not small, then various other numerical solutions can be used to determine the true shape of the meniscus (Bashforth and Adams, 1883). While the use of a capillary column is apparently a straightforward technique to measure the surface tension of a liquid, this method poses several practical constraints when used with asphalt binder at elevated temperatures. For example, it is difficult to maintain the capillary column at constant elevated temperatures while making measurements. High viscosity of the binder also adds a dimension of time for the binder to come to equilibrium and finally the dark color of the asphalt binder makes it difficult to accurately record the height of the meniscus.

Another common method to measure the surface tension of liquids is the pendant drop method. In this method, surface free energy of the liquid is measured from the shape of the liquid drop when it is dispensed from a thin capillary tube or needle just before it detaches itself from the tip. Mathematical models based on the Laplace equation 2.1 and extended by Bashforth and Adams (1883) are used to analyze the shape of the drop which is captured in the form of an image. Figure 2.3 shows a schematic of the pendant drop.

$$\frac{1}{R_1} + \frac{\sin \phi}{x} = -\frac{zg\Delta\rho}{\gamma} + \frac{2}{a} \quad (2.3)$$

where, $\Delta\rho$ is the difference in densities of the liquid and the gas, z , x , and ϕ are the coordinates of a point related to the shape of the drop, a is the radius of curvature at the apex of the drop and R_1 is the radius of curvature at the point (x,y) . Simplified forms of this equation were also developed to facilitate computation of the shape of the drop. With the advent of fast computers the analysis of the pendant drop is done by fitting a theoretical curve to the entire drop profile and using it to estimate the surface energy of the liquid. The limitations of using the pendant drop method to measure the surface tension of asphalt binders at elevated temperatures are similar to those associated with the use of the capillary rise method.

The third method to measure the surface tension of a liquid is the maximum bubble pressure method. A brief description of the bubble pressure method is provided here. A more detailed description can be found in the literature (Adam, 1940; Mysels, 1959; Adamson and Gast, 1997). A schematic set up for the maximum bubble pressure method is shown in Figure 2.4. In this method an inert gas is injected through one end of a capillary tube while the other end is immersed in the bulk of the liquid. As a gas is injected into the tube

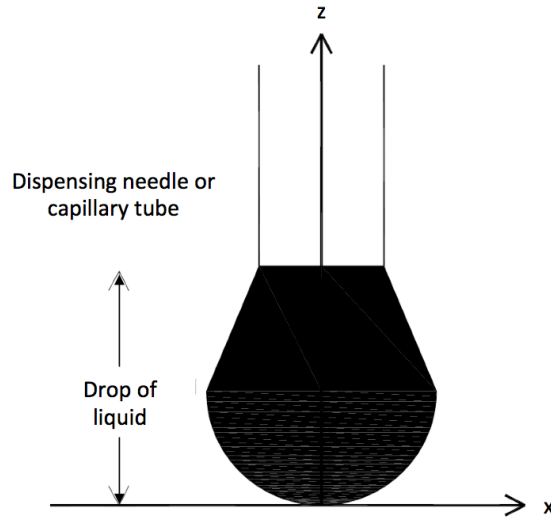


Figure 2.3. Schematic representation for the pendant drop method

a bubble is formed creating a pressure difference across the surface of the bubble. This pressure difference, ΔP , is given by $P_{inside} - P_d$, where P_{inside} is the pressure in the tube and P_d is the pressure corresponding to the hydrostatic head. The growth of the bubble is in the form of a section of a sphere. When the bubble just begins to form, the radius of curvature of the bubble is at its maximum and the internal pressure is at its lowest. As the injected gas forms a bubble at the end of the tube, the radius of curvature gradually decreases to a minimum. The minimum radius of curvature occurs when the radius of the drop is equal to the outer radius of the tube (if the liquid does not wet the surface of the tube). If the liquid wets the surface of the tube, then the minimum radius of curvature will be equal to the inner radius of the tube. The pressure at this stage is the maximum pressure. After this stage, the bubble size grows rapidly and the bubble breaks from the end of the tube and escapes. Following the Young-Laplace equation, the surface tension of the liquid can then be back calculated by experimentally measuring the maximum pressure, P_{max} , in the tube as follows:

$$\gamma = \frac{r}{2} (P_{max} - (\rho_l - \rho_g)gd) \quad (2.4)$$

where, γ is the total surface tension of the liquid, ρ_l and ρ_g are the densities of the liquid and gas respectively, r is the radius of the capillary tube (inner or outer depending on whether the liquid wets or does not wet the tube), and d is the depth to which the capillary tube is immersed into the liquid. Figure 2.5 illustrates a schematic of the various stages of

the bubble formation and the corresponding pressure measured in the tube.

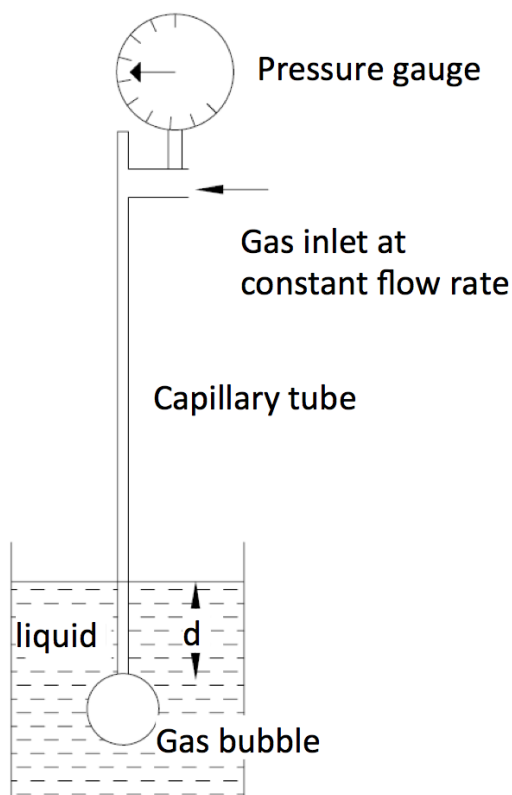


Figure 2.4. Schematic representation for the maximum bubble pressure method

Since the bubble pressure method relies on the use of the gas being injected into a large mass of the liquid, the temperature of the liquid can be more accurately controlled. Also, the parameter that is measured in this case is the air pressure inside the capillary tube and therefore this technique is very appropriate for use with dark opaque liquids such as asphalt binders. One other advantage of the bubble pressure method is that it can be used to measure the dynamic surface tension of a liquid. In the case of liquids with impurities the surface tension of the liquid can change with time. For example, consider a liquid containing a surfactant that is initially homogeneously distributed within the liquid. The surface properties of this liquid will change with time as the surfactants move to the surface of the liquid (or interface of the liquid with another solid). Mobility of the surfactant molecules will dictate the rate with which the surface tension of the liquid changes. Methods such as the Wilhelmy Plate device measure the surface tension of a liquid or solid after the surface has reached a state of equilibrium. In contrast, the bubble pressure method can be used to

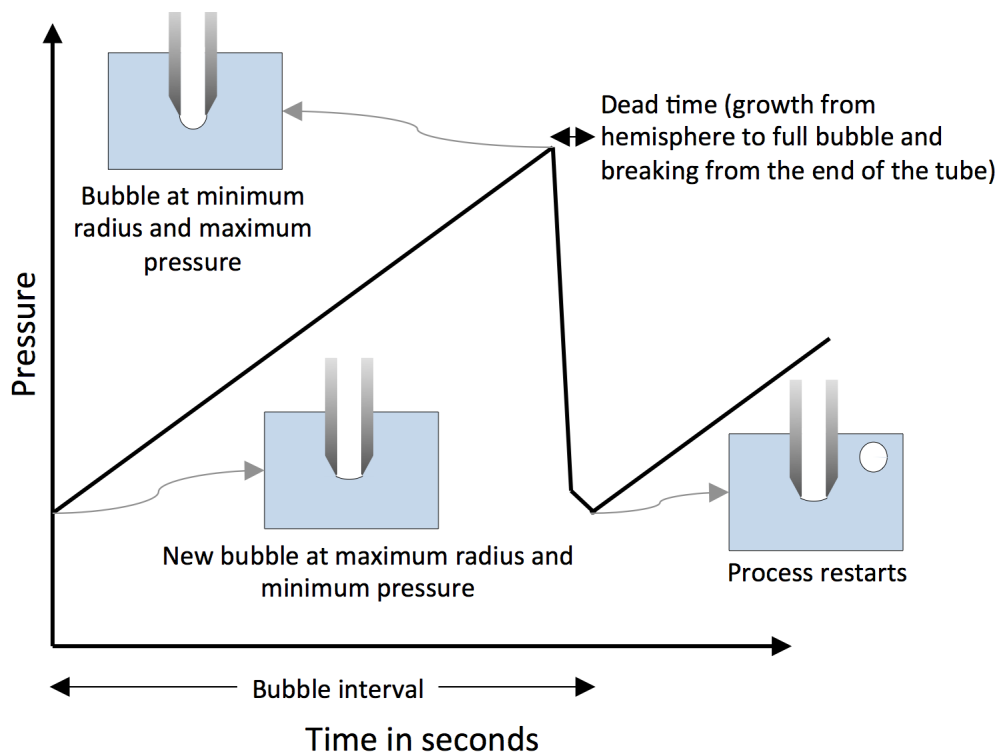


Figure 2.5. Schematic representation of the various stages of bubble formation and corresponding pressure recorded

measure the dynamic surface tension of the liquid by varying the bubble interval (Figure 2.5). At higher bubble intervals, a new surface of the liquid is rapidly formed. Such a surface would have a lower concentration of surfactant (or similar molecules with preferred interfacial affinity) and consequently represent a different surface tension. On the other hand, at lower bubble intervals, a new surface of the liquid is formed more slowly. This allows different molecular species to arrive at the surface and come to an equilibrium. In other words, as the bubble interval increases, the surface tension of the liquid approaches the equilibrium value.

Owing to the advantages of the bubble pressure method discussed above, this technique was used to measure surface tensions of different asphalt binders with and without additives for this study. More specifically, a variation of this technique referred to as the differential maximum bubble pressure method was used. The following section presents a description of this technique along with a discussion on the significance of bubble intervals on measuring dynamic surface tension.

2.3 DIFFERENTIAL MAXIMUM BUBBLE PRESSURE METHOD

From equation 2.4 it is evident that in order to use the maximum bubble pressure method to measure the surface tension of a liquid, the density of the gas and the liquid as well as the depth of immersion of the capillary probe must be known. Also, inaccuracies in the measurement of these values can result in errors in the measured surface tension of the liquid. A variation of the bubble pressure method, referred to as the maximum differential bubble pressure method is used to overcome these limitations. For example, equation 2.4 can be rewritten in terms of the maximum pressure in the capillary tube as:

$$P_{max} = \frac{2\gamma}{r} + \Delta\rho g d \quad (2.5)$$

Now consider that there are two capillary tubes immersed in the liquid with different radii, r_1 and r_2 , such that the orifices are at depths d_1 and d_2 . The maximum differential pressure between the two capillaries can be written as:

$$\Delta P_{max} = 2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \gamma + \Delta\rho g (d_1 - d_2) \quad (2.6)$$

For a given set up when the density difference $\Delta\rho$ is similar for different liquids being evaluated, equation 2.6 is a straight line relationship between the maximum pressure difference ΔP_{max} and surface tension γ . Therefore, by using two liquids with different and known surface tension values, it is possible to calibrate the differential maximum bubble pressure setup for use with any other liquid as long as the difference in density is not significant amongst the calibration and test liquids. The influence of density difference on the measured surface tension values can further be minimized by adjusting the relative depths of the two capillary tubes ($d_1 - d_2$) as a function of their radii ($r_1 - r_2$). These adjustments were incorporated in the instrument employed for this study. A more detailed mathematical description of these adjustments can be found in the literature Schramm and Green (1992). In summary, the use of maximum differential bubble pressure method is a more robust technique to estimate surface tension of liquids because of it does not require precise measurement of the liquid densities being measured or the depth of immersion of the probe in the liquid being measured.

CHAPTER 3. MATERIALS AND TEST METHOD

3.1 SELECTION OF MATERIALS

The three main objectives of this study were to evaluate whether:

1. asphalt binders from different sources have significantly different surface tensions at typical mixing and compaction temperatures,
2. addition of chemical additives have a significant affect on the surface tension of asphalt binders, and
3. rate of surface formation has a significant affect on the surface tension of the asphalt binders (dynamic surface tension).

In order to achieve the aforementioned objectives, three different asphalt binders and three different chemical WMA additives were used for this study. With the maximum differential bubble pressure method, the rate of surface formation is controlled by adjusting the rate at which bubbles are formed in the liquid. Table 3.1 lists all the material and bubble rate combinations used in this study. The three different additives used in this study are commercially available for the production of WMA and are therefore reported anonymously for this research. Note that the surface tension measurements were carried out at several different temperatures from 140°C to 170°C for each of the combinations listed in Table 3.1.

Table 3.1. Materials and bubble rates used for surface tension measurement

Binder	Additives	Bubble Rate (bubbles per second)
PG 64-22	Control	0.1
PG 70-22	Additive A	0.2
PG 76-22	Additive B	0.5
	Additive C	1

In order to prepare samples of binder with the additives, the additives were blended in with the asphalt binder using a RW 20 Digital Overhead Mixer equipped with a four-blade propeller. Binders were heated in the oven in quart-gallon cans at their respective storage

temperature for 30 minutes. Subsequently, the cans were inserted into a thermoelectric temperature controlled enclosure and maintained at the mixing temperature of the asphalt binder. The suppliers of all additives recommend the use of conventional (hot mix) mixing temperatures to blend the additives with the asphalt binder. Before adding the additives, the binder was stirred for 2 minutes in order to obtain a uniform temperature distribution; the addition was performed manually and slowly to attain a homogenous distribution of the additive. Based on the recommendations of the additive producer, the binder was stirred in the overhead mixer at a constant speed for 20 minutes to allow complete homogenization of the additive. Henceforth, the term “modified binders” will be used to identify binders modified using the WMA additives for brevity. In order to ensure consistency, the control binders were subjected to the same blending procedure for 20 minutes without any additive. Since the blending was carried out in bulk in a quart size can using a shear mixer, it was expected that the difference in aging due to blending would not be significant. This was verified by comparing the complex shear modulus for one of the control asphalt binders before and after blending for 20 minutes.

3.2 TEST PROCEDURE

This section describes the procedure used to measure the surface tension of the asphalt binders using the maximum differential bubble pressure (MDBP) method. The instrument used for this study was manufactured by Sensadyne (model QC3000). Argon was used as the inert gas to create the bubbles through two tubes immersed in the test liquid. The Argon gas was delivered to the tubes or probes via a metering valve. The two probes are made of stainless steel with 4.0 mm and 0.5 mm diameters, referred to as the large and small orifice, respectively (Figure 3.1). A temperature sensor is also attached adjacent to the two tubes such that temperature of the liquid is recorded at the same depth as the bubbles in the liquid.

Prior to any testing the temperature sensor was calibrated using ice cold and hot water (in a heating mantle) and an externally calibrated thermocouple. After completing the temperature calibration, distilled water and iso-propyl alcohol were used to calibrate the surface tension values at a given bubble rate. The following steps were followed for calibration with a liquid. A beaker containing the liquid was placed on an adjustable height stage; the stage was raised until the tube assembly along with the temperature sensor was immersed in the liquid by at least 10 mm. The metering valves for the instrument were adjusted to achieve the desired bubble rate in both the small orifice as well as the large

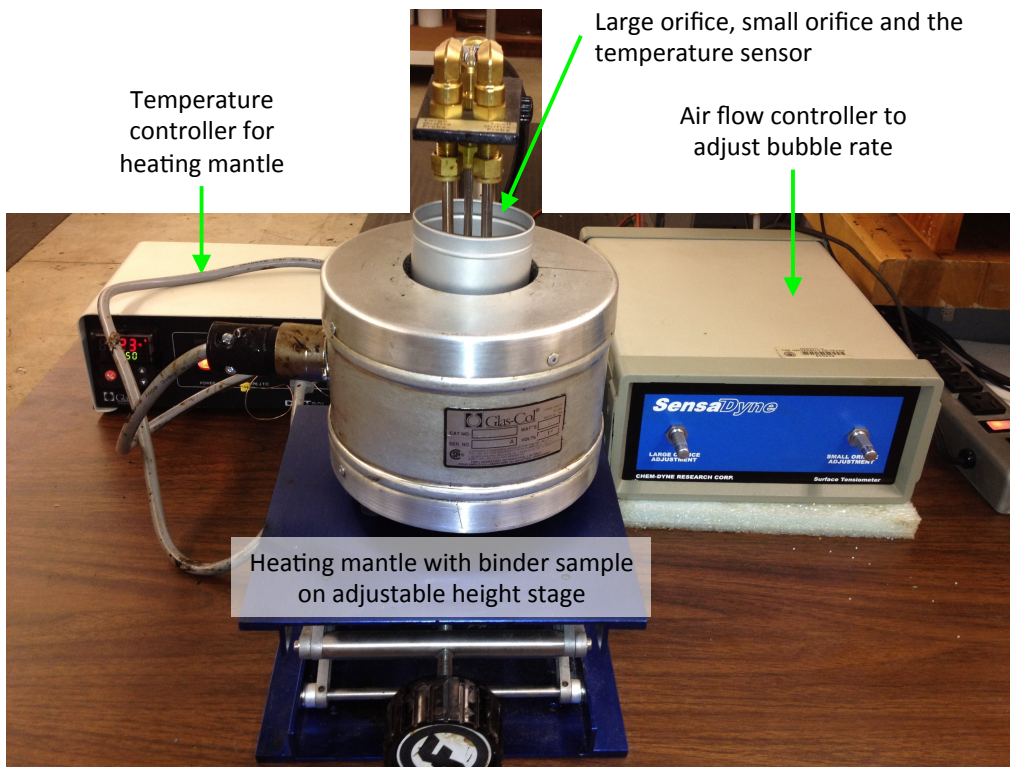


Figure 3.1. Metering valves used to adjust the bubble rate in the large and small orifice

orifice (Figure 3.2). Once the desired bubble rate was achieved, data were collected for the temperature of the liquid and differential bubble pressures (measured by the sensor in volts) over time. The process was repeated for the second calibration liquid. The known surface tension values for the two liquids at the measurement temperature were used to calibrate the instrument (Figure 3.3). Figure 3.4 shows a typical screen shot for the data collected while calibrating with water. The increase in bubble pressure to a maximum value as shown in the earlier schematic (Figure 2.4) is clearly seen in this figure. Note that the bubble rate changed slightly from one liquid to another or when the asphalt binder was used, however this change was small compared to the range of values being measured.

Surface tension of a binder sample was measured after completing the temperature and surface tension calibrations. The binder sample was poured in a 50 cc capacity metal container placed inside a heating mantle with automatic temperature control. The heating mantle was placed on a stage with adjustable height (Figure 3.1). The sample was heated until it reached the lowest test temperature and allowed to come to thermal equilibrium for



Figure 3.2. Metering valves used to adjust the bubble rate in the large and small orifice



Figure 3.3. Two different liquids are used to calibrate the device to measure surface tension

approximately five minutes. The sample stage was then raised so that the tube assembly along with the temperature sensor were completely immersed in the binder with the orifices being at least 10 mm below the surface of the binder. Argon was bubbled through the sample for approximately five minutes to allow for the bubble rate to stabilize. The Sensadyne

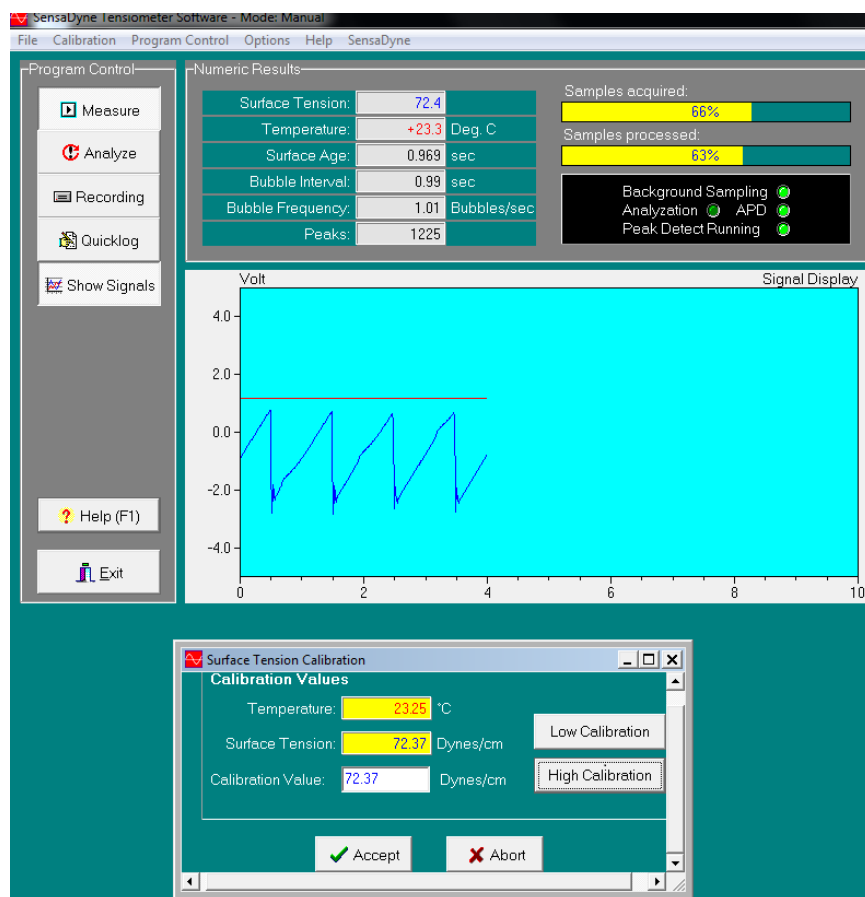


Figure 3.4. Two different liquids are used to calibrate the device to measure surface tension

software was used to record the maximum differential bubble pressure between the two orifices along with the temperature of the binder in real time. Data collected over any window of time can be selected to analyze and determine the surface tension. Typically data from 10 to 15 bubbles were used to determine the surface tension. Once the testing was completed, the process was repeated by increasing the temperature of the heating mantle by 3 to 5°C until the highest desired temperature was reached.

Once a test with a binder sample was complete (over a range of temperatures), the tubes were cleaned by immersing them in a container with mineral spirit and allowing the Argon gas to bubble through the probes for at least 30 minutes. The process was repeated by immersing the tubes in acetone for another 30 minutes. Care was taken to examine and ensure that the probes were clean prior to being used for another set of measurements (Figure 3.5).

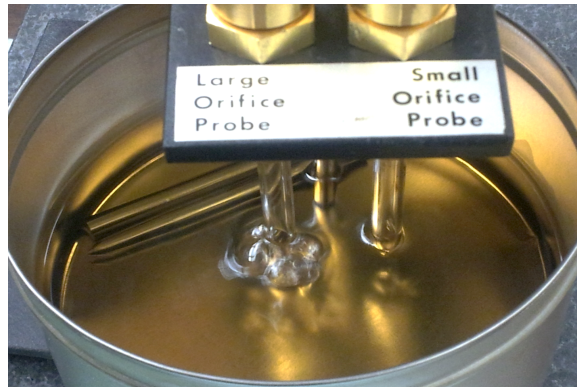


Figure 3.5. The tubes are immersed in mineral spirit and Argon is bubbled through the tubes to clean the orifice

CHAPTER 4. RESULTS AND DISCUSSION

4.1 OVERVIEW

The surface tension of the binders were measured over a range of temperatures. At least three replicate tests were conducted in a randomized order for each combination of binder and additive at each bubble rate. Figure 4.1 illustrates the typical results from three replicate test samples of the same binder measured at several different temperatures. Results from these tests indicate that, within the temperature range used for testing, the surface tension of the binder decreased linearly with an increase in temperature of the binder. The behavior is typical of most liquids Adamson and Gast (1997).

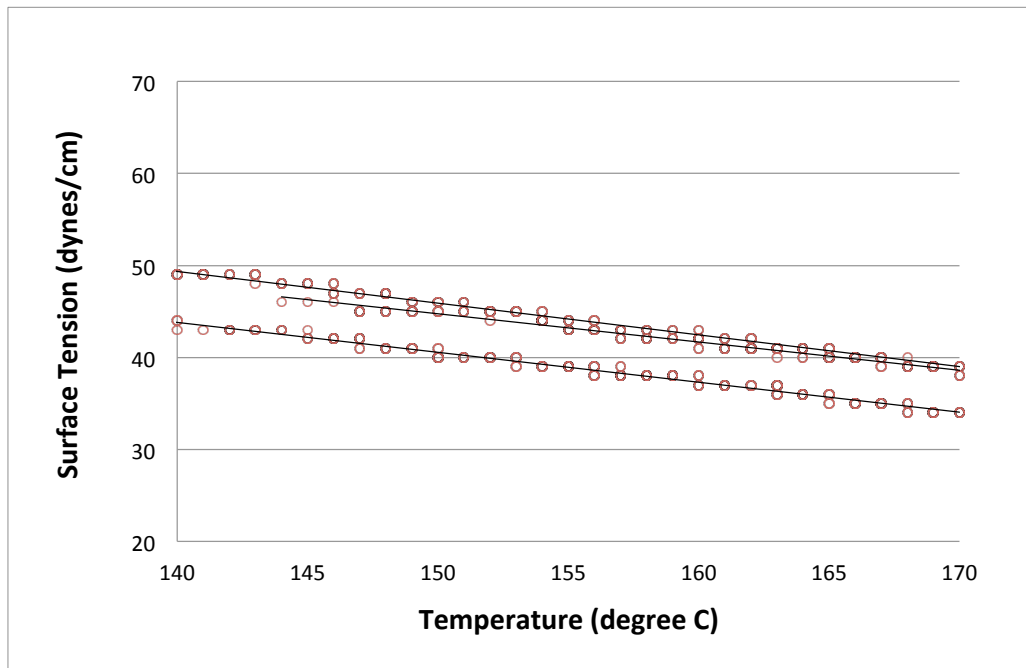


Figure 4.1. Typical results for the PG76-22 binder without additive at 0.5 bubbles per second

Based on the results, the slope and intercept were computed using the surface tension versus temperature relationship for each test. These two metrics were then used to evaluate the influence of binder type, additive and bubble rate on the surface tension of the asphalt binders. A relative comparison of the slopes can be used to evaluate the effect of various factors on the temperature sensitivity of surface tension. Similarly, the intercept can be

used to evaluate the effect of various factors on the relative values of surface tension. It must be noted that the intercept is being used as a metric to compare the relative values of the surface tension. The values of the intercept must not be interpreted as the surface tension of the binder at 0°C. This is because the binder will undergo structural changes as it cools and it is possible for the surface tension - temperature relationship to become nonlinear.

4.2 RESULTS

The surface tensions of all control and modified binders were measured using at least three replicate samples at several different temperatures within the range of 140°C to 170°C. Surface tension was found to be inversely proportional to the test temperature for all samples tested at all bubble rates. This section evaluates the influence of binder type, bubble rate, and additive on the measured surface tension of the binder.

Figures 4.2 and 4.3 compare the surface tensions of the three binders at two different bubble rates. Results from this figure clearly illustrate that at any given bubble rate, the surface tension of the binder depends on the source (type) of binder. The differences were more exaggerated at higher bubble rates. Figure 4.4 illustrates the influence of bubble life on the surface tension of the three binders at 140°C. This figure clearly illustrates that the life of the bubble has a strong influence on the surface tension of the asphalt binder. For a given binder, the surface tension measured using a lower bubble rate (longer times of formation) was lower than the surface tension measured using a higher bubble rate (shorter times of formation). Such rate dependency is characteristic of liquids with a surfactant. A longer time of formation allows the surfactant to migrate to the new surface being formed, which in this case is the surface of the bubble, and reduce its surface tension. As the rate of bubble formation is lowered (allowing for longer bubble surface formation time), the surface tension values reach an asymptotic value referred to as its equilibrium surface tension.

In the case of the unmodified binders shown in Figure 4.4, the change in surface tension with the rate of bubble formation reflects the chemically heterogeneous nature of asphalt binders and potential “surfactant like” behavior of certain molecular species. The differences in surface tension with the life of the bubble surface or bubble rate are most likely related to the mobility of molecular species that act similar to surfactants by moving towards the surface and reducing its surface tension. Figure 4.5 illustrates that this effect, as expected, reduces with an increase in temperature.

While the chemical heterogeneity of asphalt binders is certainly not a new finding, these results illustrate that (i) the equilibrium surface tension of the binder can be as low as approximately 75% of its surface tension measured at higher bubble rates or shorter surface life and (ii) the surface of the binder approaches the equilibrium surface tension when the surface life is approximately 5 to 10 seconds. Depending on the context, this information can have different implications. For example, in the context of the stability of foamed asphalt binders used in warm mix applications, the foam bubbles are produced rapidly and the life of these bubbles can be in the order of a few seconds. The solubility of water in the binder to produce foam and the size of the bubbles produced are related to the surface tension of the binder. In the context of overall wetting and coating of asphalt binders, these results suggest that for all practical purposes the equilibrium surface tension of the binder will dictate the coating and wetting of the binder with the aggregate surface since the binder will be expected to remain in contact with the aggregate surface at the mixing temperatures for well over a few seconds.

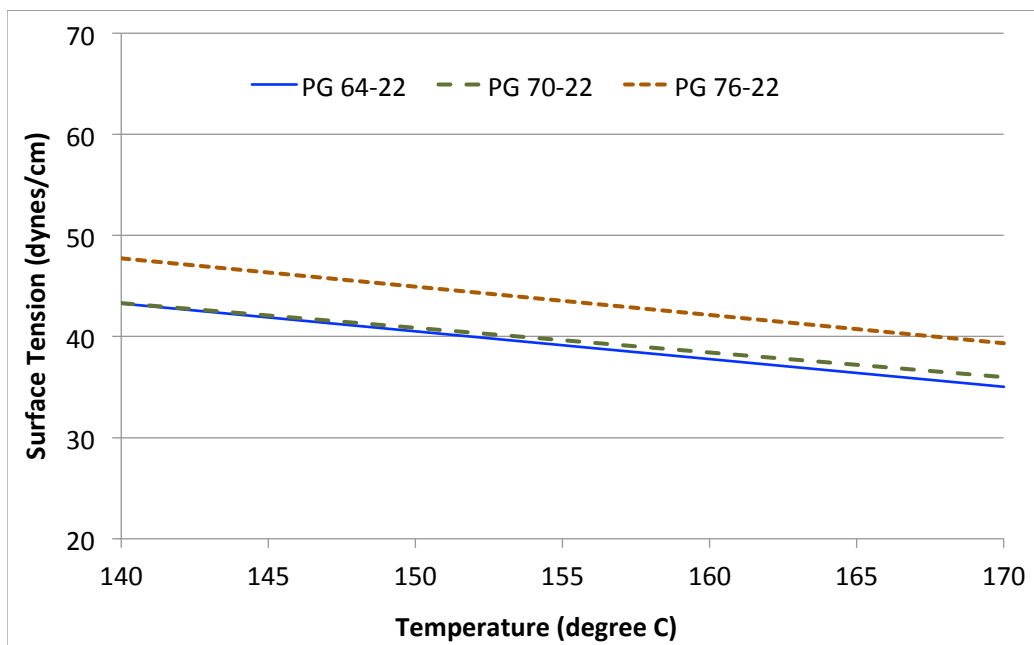


Figure 4.2. Surface tension for the three binders without any additive at 0.1 bubbles per second

One of the objectives of this study was also to evaluate whether or not some of the chemical warm mix additives act as a surfactant to reduce the surface tension of the binder and promote wetting and coating of the asphalt binder at reduced temperatures. To this end,

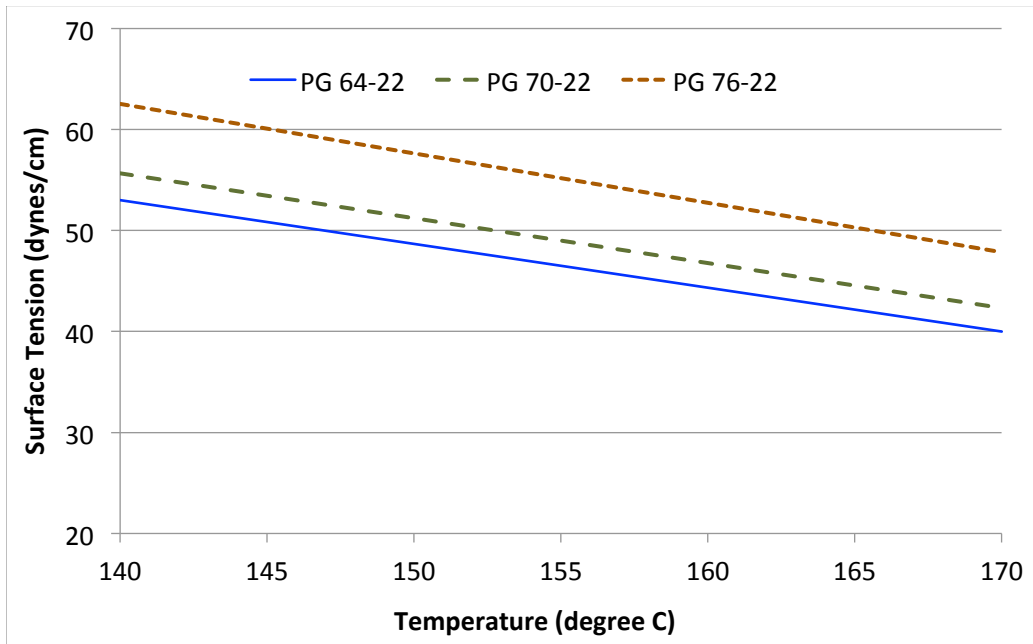


Figure 4.3. Surface tension for the three binders without any additive at 1.0 bubbles per second

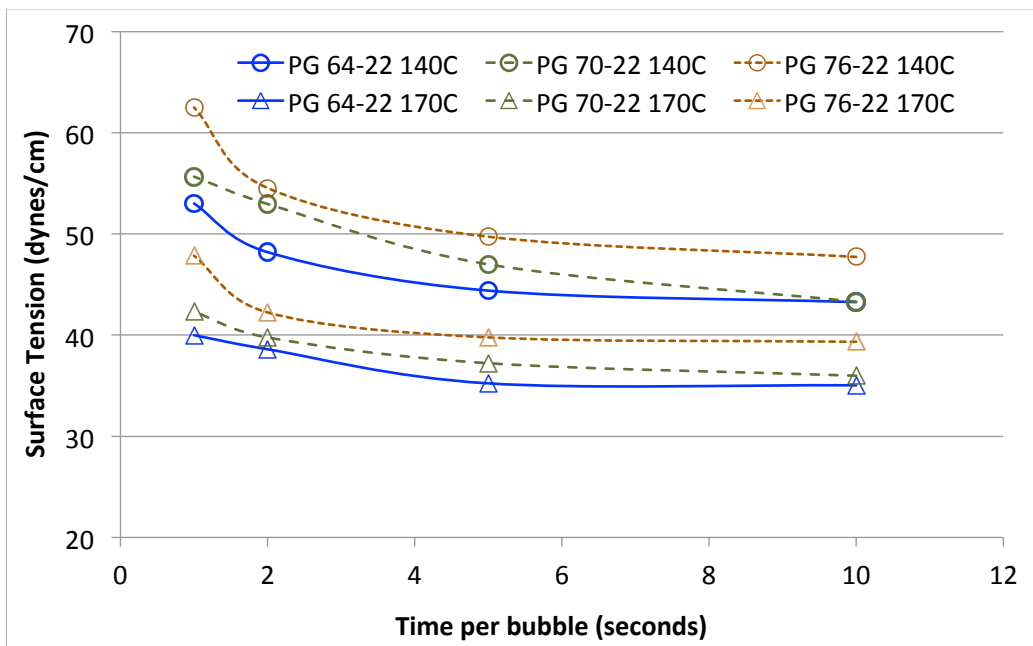


Figure 4.4. Surface tension for the three binders without any additive at 140 and 170°C as a function of bubble life

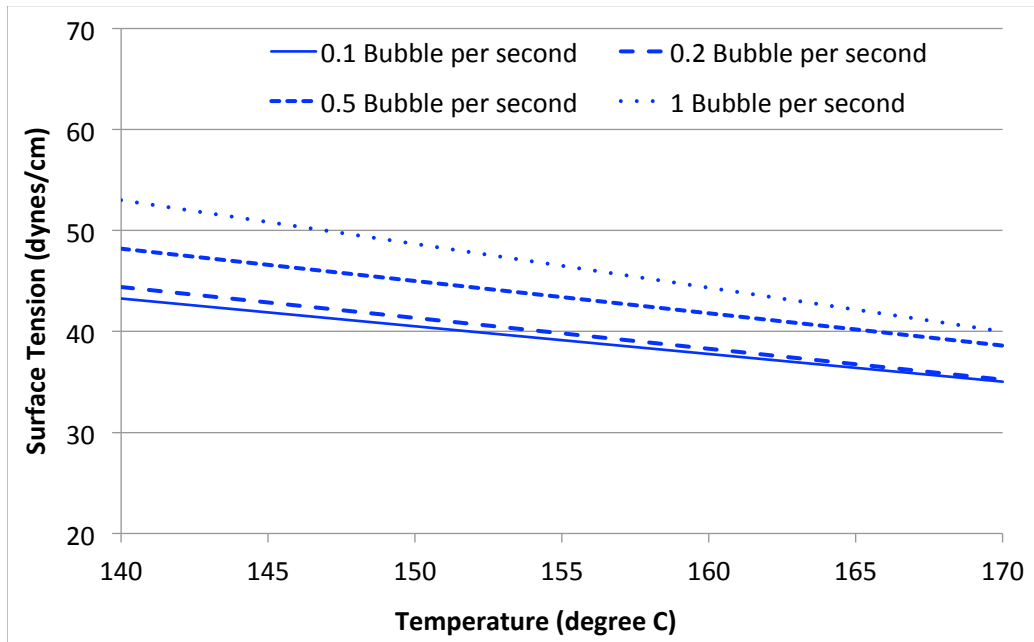


Figure 4.5. Surface tension for the PG 64-22 binder at all four rates of bubble formation

the surface tensions of each of the three binders were also measured after combining them with three different chemical additives. Figures 4.6 through 4.9 illustrate the influence of additives on the surface tension of PG 64-22 and PG 76-22 binders at two different bubble rates (highest and lowest) at different temperatures. Results for the PG 70-22 binder were similar to results from PG 64-22. Results show that the role of additives as a surfactant to lower the surface tension of the binder was not very significant at any given bubble rate and temperature. For the PG 64-22 binder one of the additives slightly increased its surface tension while the other two additives slightly decreased its surface tension. This effect was more pronounced for lower bubble rates than for higher bubble rates; the former provides more time for the surfactant to mobilize and get to the surface of the binder. For the PG 76-22 binder all three additives slightly reduced the surface tension of the binder. As with PG 64-22 binder, this effect was more prominent at the lower bubble rates and also at lower temperatures. Figure 4.10 more clearly illustrates the effect of bubble rate and additive type on the surface tension of the binder at 140°C. However, in all cases the influence of additives was small and statistically insignificant as will be shown later.

The results above clearly indicate that the binder type, bubble rate, and to a lesser extent the additive type influence the surface tension of the asphalt binders. A statistical analysis

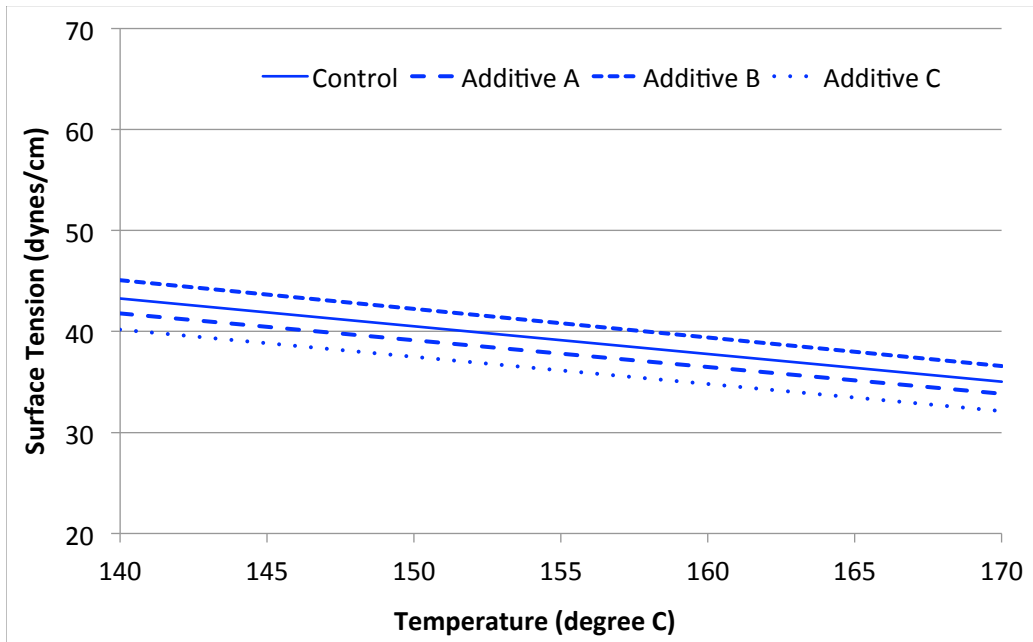


Figure 4.6. Influence of additives on the surface tension of the PG 64-22 binder at a bubble rate of 0.1 bubbles per second

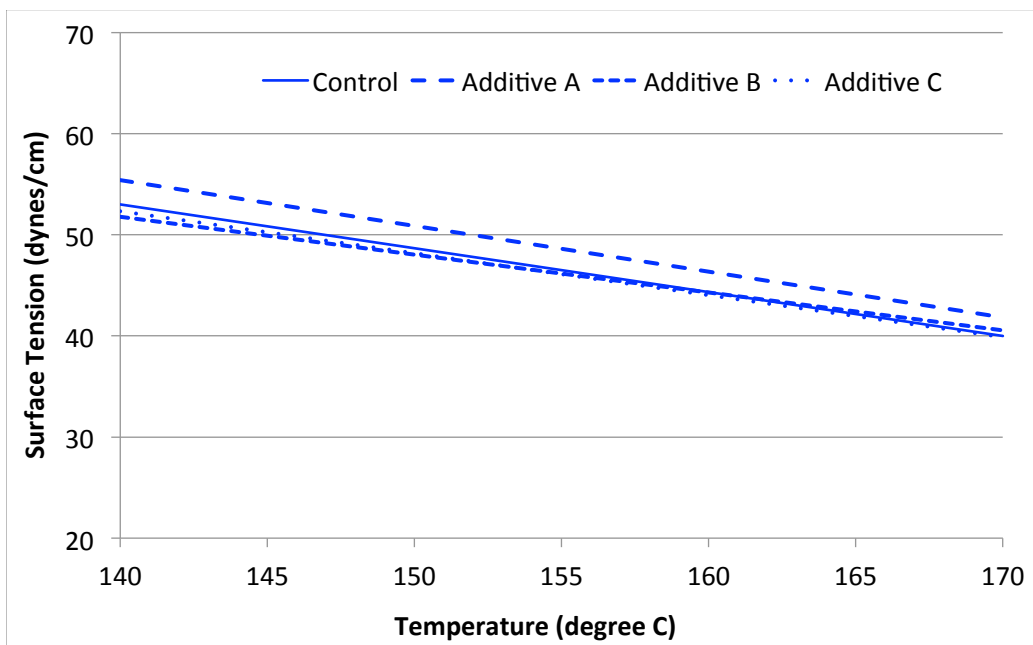


Figure 4.7. Influence of additives on the surface tension of the PG 64-22 binder at a bubble rate of 1.0 bubbles per second

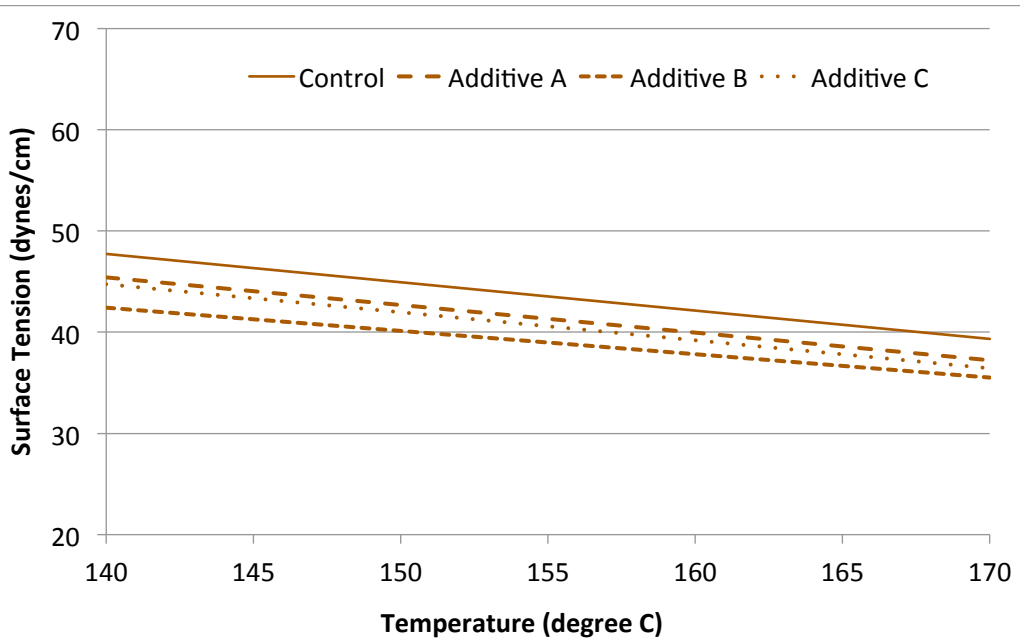


Figure 4.8. Influence of additives on the surface tension of the PG 70-22 binder at a bubble rate of 0.1 bubbles per second

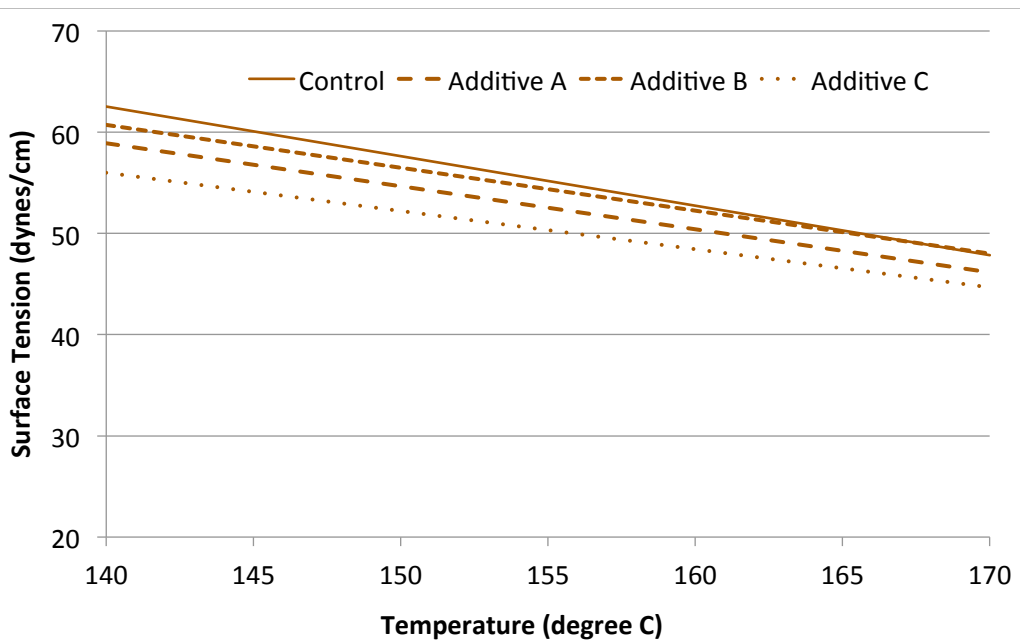


Figure 4.9. Influence of additives on the surface tension of the PG 70-22 binder at a bubble rate of 1.0 bubbles per second

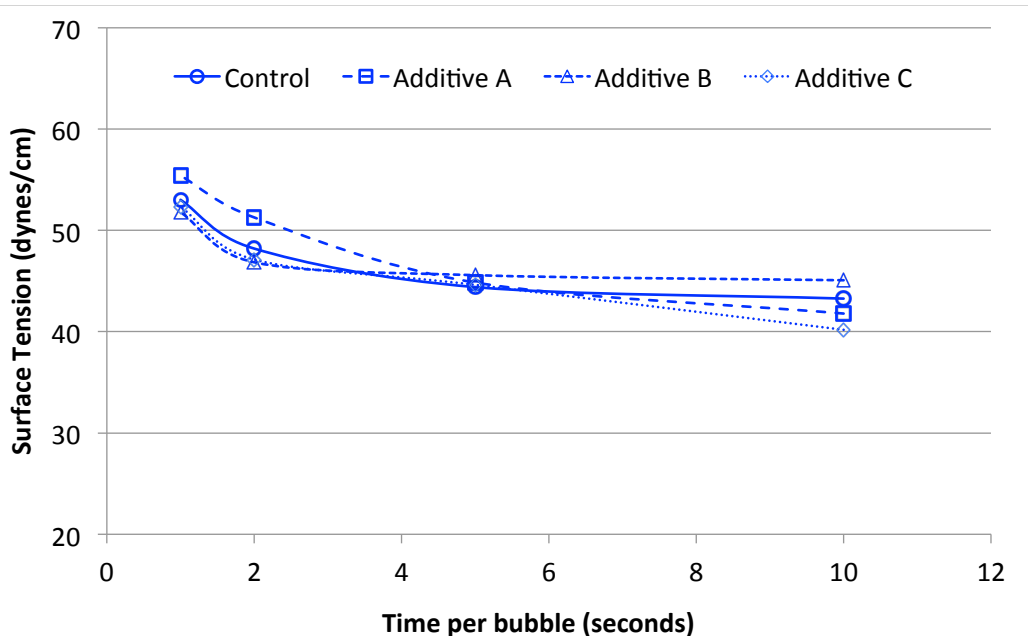


Figure 4.10. Influence of additives and bubble rate on the surface tension of the PG 64-22 binder at 140°C

was conducted using the slope and intercept information obtained from each of the replicate samples for all the binders tested with and without additives at different bubble rates. The results were analyzed for the main effect treating the slope and intercept of the measured surface tension versus temperature relationship as two different dependent variables and binder type, additive type and bubble rate as three independent variables. Figures 4.11 and 4.12 illustrate the results from this analysis. An analysis of variance was also conducted to identify whether or not the independent variable or a combination of these variables were significant. Tables 4.1 and 4.2 present the results from the ANOVA. Based on these results it is clear that the binder type and bubble rate influence the surface tension of the asphalt binders as well as its temperature sensitivity. The type of additive did not significantly influence the surface tension of the binder.

Table 4.1. Results from ANOVA for slope of temperature versus surface tension

Factor	p-value
Binder Type	0.034
Additive Type	0.412
Bubble Rate	0.000
Binder Type * Additive Type	0.675
Binder Type * Bubble Rate	0.046
Additive Type * Bubble Rate	0.765
Binder Type * Additive Type * Bubble Rate	0.413

Table 4.2. Results from ANOVA for slope of temperature versus surface tension

Factor	p-value
Binder Type	0.003
Additive Type	0.487
Bubble Rate	0.000
Binder Type * Additive Type	0.652
Binder Type * Bubble Rate	0.198
Additive Type * Bubble Rate	0.800
Binder Type * Additive Type * Bubble Rate	0.602

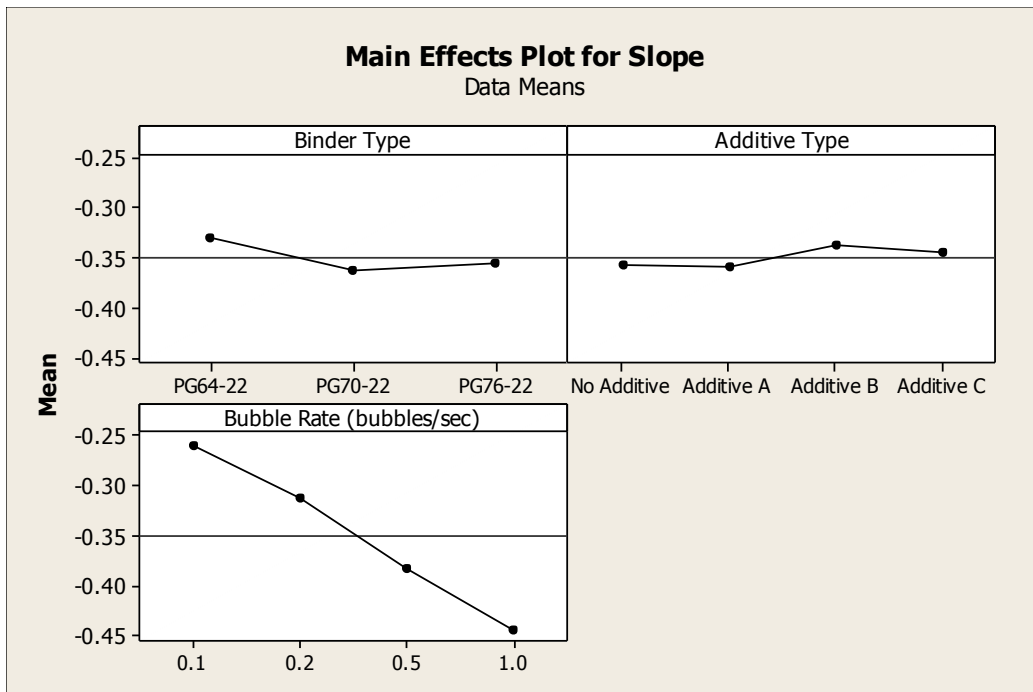


Figure 4.11. Analysis of the main effects based on the slope of the surface tension versus temperature relationship for different binders, modifiers and bubble rates

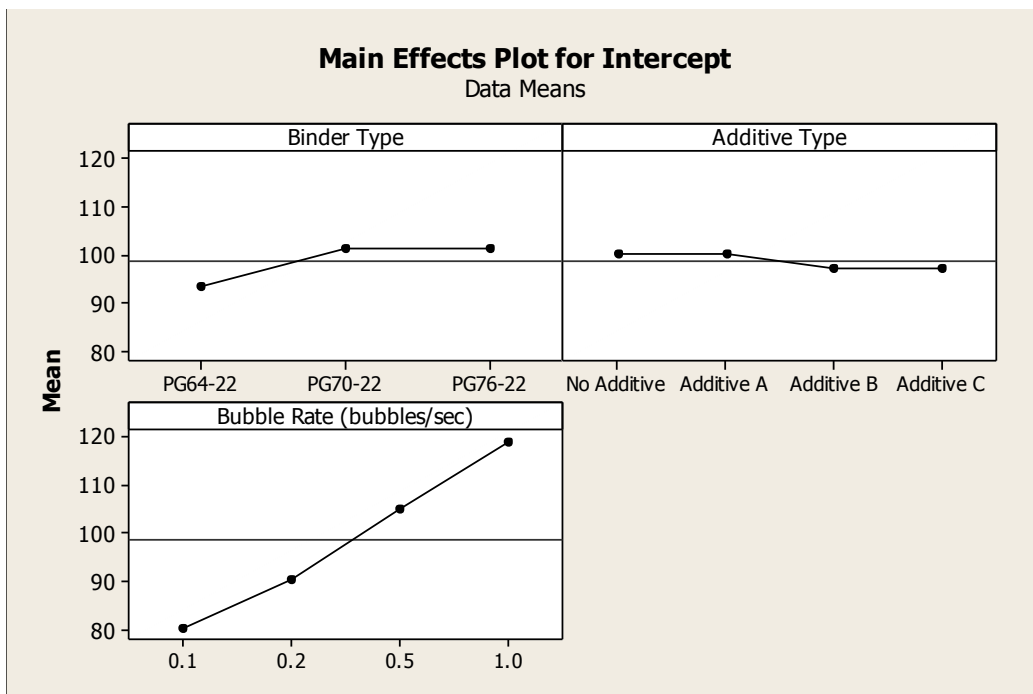


Figure 4.12. Analysis of the main effects based on the intercept of the surface tension versus temperature relationship for different binders, modifiers and bubble rates

CHAPTER 5. DISCUSSION AND CONCLUSION

The ability of an asphalt binder to intimately coat the surface of an aggregate particle is essential to ensure the production of a durable mix. Viscosity and surface tension dictate the ability of a fluid to coat the surface of a solid. Both of these properties are extensively used in industries such as polymer coating and printing. While viscosity quantifies the resistance of a liquid to flow, surface tension is the driving force that promotes wetting. In general lower surface tension promotes wetting and intimate coating of rough surfaces (as in the case of aggregate particles). In the context of asphalt mixtures, viscosity of liquid asphalt binders at typical mixing and compaction temperatures is measured on a routine basis whereas to the best of the authors' knowledge, surface tension of asphalt binders at these temperatures has not been measured. This is particularly interesting in the context of warm mix asphalt (WMA) that is produced using water foaming or chemical additives. With regards to foaming, the extent to which different asphalt binders can be foamed and concomitant mixing and coating efficiency achieved is related to the surface tension of the binder. With regards to chemical additives, the ability of the additives to act as surfactants has been ascribed as the mechanism that facilitates coating at warm mix temperatures. The surfactant mechanism suggests a reduction in the surface tension of the binder with the addition of the chemical additive.

The objective of this study was to measure the dynamic surface tension of typical asphalt binders with and without chemical additives at several different temperatures typically associated with the production of hot and warm mix asphalt. The motivation of this study was that this information can be used to better understand the mechanisms of aggregate coating and influence of additives to promote mixing.

Three different binders were used in this study. Surface tensions of these binders were measured at several different temperatures in the range of 140°C and 170°C using the maximum differential bubble pressure method. Surface tensions were also measured by varying the rate of formation of the bubble surface from 0.1 bubbles per second to 1.0 bubbles per second as well as by incorporating three different types of chemical additives. Based on the results and analysis obtained from this study, the following conclusions can be drawn.

1. Asphalt binders have a surface tension that varies between 35 to 64 dynes/cm depending on the rate of surface formation, temperature and type of binder. The sur-

face tension of the binders reduced linearly with an increase in temperature. This is consistent with the behavior of several other liquids.

2. At any given temperature, the surface tension of asphalt binders is dependent on the source and type of the asphalt binder. For the binders tested, a difference of approximately 5 dynes/cm at any given temperature was observed. In terms of temperature, this difference could translate to approximately 15°C or more for a given value of surface tension. For example, if an equilibrium surface tension of 40 dynes/cm is desired then the PG 64-22 and PG 70-22 can achieve this surface tension at approximately 152°C whereas the PG 76-22 can achieve this surface tension at approximately 167°C.
3. Asphalt binders tend to have a significant “surfactant like” behavior even without any post production modifier or additive. In other words, the surface tension of the binders was shown to be strongly dependent on the rate of formation of the surface. This finding also indirectly lends more credence to the colloidal theory of asphalt binder. However, the binders also approached their equilibrium surface tension as the surface life approached approximately 10 seconds. This is much shorter than the typical times for which the binder remains in contact with the surface of the aggregate particle.
4. The three warm mix chemical additives used in this study did not result in any significant surfactant like behavior beyond what was already observed with unmodified asphalt binders. Given the number of proprietary warm mix additives that are currently available, this finding is limited to only three such additives that were included in this study.

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