

# Towards understanding the breaking and coalescence of bitumen emulsions for cold asphalt

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Digital Object Identifier (DOI): [dx.doi.org/10.14311/EE.2016.402](https://doi.org/10.14311/EE.2016.402)

## ABSTRACT

*Cold mix asphalt (CMA) emulsion based technology is a potential option to replace traditional hot mix asphalt due to environmental benefits and less energy consumption of producing it. However, there are some issues concerned with CMA, for instance, pre-mature coalescence of bitumen emulsions while mixing with minerals or aggregates, which might need more attention to improve the performance of CMA. Actually, the adhesion between the binder and the aggregate surface is largely dependent on the breaking process of bitumen emulsions and the water push-out from the mixtures. This breaking process helps to predict the materials behavior as well as the long term mechanical performance of the mixtures; however, the exact nature of the breaking mechanism of bitumen emulsion is not completely understood until today. The objective of this research is to develop understanding of the structural changes during the phase separation and coagulation stages of the bitumen emulsion. Wettability of bitumen was analyzed by changing the substrate climate conditions. Moreover, this study was extended with the addition of emulsifier and other additives to the binder itself as well as to the water phase. Similar kinds of experiments were setup for exploring the coalescence of bitumen drops in water and emulsifier with other additives.*

*Keywords: Cold Mix Asphalts, Bitumen Emulsions, Coalescence, Breaking Mechanism, Wettability, Surface Free Energy.*

**Keywords:** Adhesion, Cohesion, Cold Asphalt, Emulsions, Testing

# Toward understanding breaking and coalescence of bitumen emulsions for cold mix asphalts

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## ABSTRACT

Cold mix asphalt (CMA) emulsion based technology is a potential option to replace traditional hot mix asphalt due to environmental benefits and less energy consumption of producing it. However, there are some issues concerned with CMA, for instance, pre-mature coalescence of bitumen emulsions while mixing with minerals or aggregates, which might need more attention to improve the performance of CMA. Actually, the adhesion between the binder and the aggregate surface is largely dependent on the breaking process of bitumen emulsions and the water push-out from the mixtures. This breaking process helps to predict the materials behavior as well as the long term mechanical performance of the mixtures; however, the exact nature of the breaking mechanism of bitumen emulsion is not completely understood until today. The objective of this research is to develop understanding of the structural changes during the phase separation and coagulation stages of the bitumen emulsion. Wettability of bitumen was analyzed by changing the substrate climate conditions. Moreover, this study was extended with the addition of emulsifier and other additives to the binder itself as well as to the water phase. Similar kinds of experiments were setup for exploring the coalescence of bitumen drops in water and emulsifier with other additives.

**Keywords:** Cold Mix Asphalts, Bitumen Emulsions, Coalescence, Breaking Mechanism, Wettability, Surface Free Energy.

## 1. Introduction

Cold mix asphalt technology is attractive due to low emissions and in future that may lead to environmental benefits and cleaner production which is intended to minimize waste materials and reduced CO<sub>2</sub> emission [1]. Hot bitumen and water phase containing emulsifying agents are mixed by the application of mechanical energy to disperse the bitumen into small droplets [2-4].

The application of bitumen emulsions for pavements can be various, for example: spray applications like surface dressings or chip seals, fog seals, tack and prime coats or mixed with stone material as in slurries or micro surfacing and cold mix paving. Regardless of its application, there are two main requirements and controlling parameters of bitumen emulsions: 1) its stability (storage and chemical stability) and 2) its breaking or phase separation upon mixing with aggregates or existing asphalt concrete layers [5].

**1.1. Breaking & Coalescence**

Emulsions can destabilize through various processes such as sedimentation, creaming, Ostwald ripening, flocculation, coalescence and phase inversion. In this study, the main focus is towards flocculation and coalescence as the breaking processes. Flocculation is a reversible process whereby droplets stick together as agglomerates of droplets, without losing their individual integrity. However, coalescence is a breaking process of emulsions in which droplets merge together into bigger ones. Bitumen emulsions start breaking or rupturing when come into contact with aggregates, and a phase separation by flocculation and coalescence should quickly occur that leads to partial loss of water in emulsion as illustrated in Figure 1a. Coalescence is categorized as the last step in the breaking process of bitumen emulsions. A continuous film of bituminous binder is developed during coagulation that covers the aggregates completely or partially followed by curing or setting of the binder, which eventually determines the mechanical strength of the cold asphalt mixture. Good adhesion can be achieved in the case of complete wetting of aggregates by the bitumen and a poor adhesion will be achieved if there is a pre-mature coalescence away from the surface or water is still present at the interface as presented in Figure 1b.

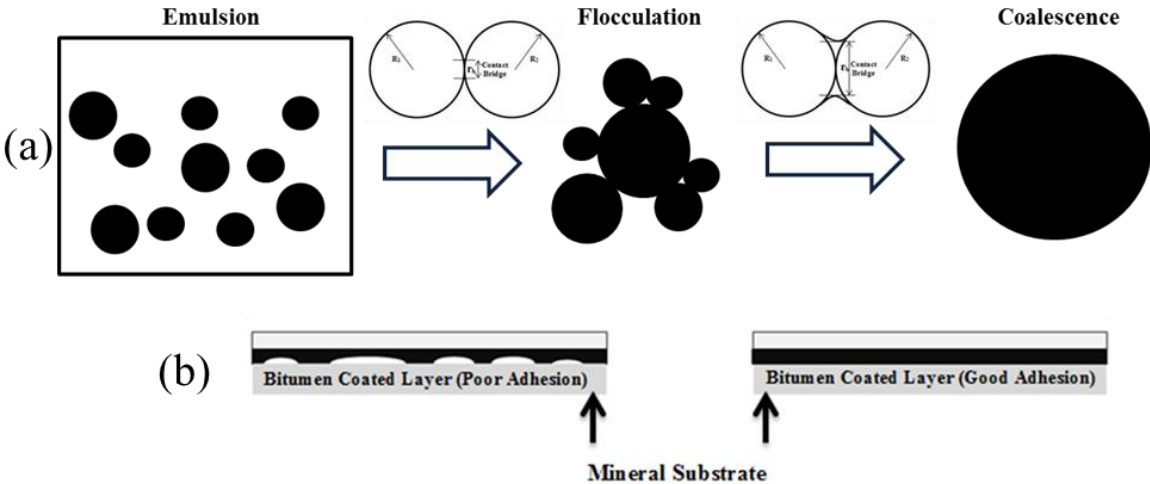


Figure 1. a). Coalescence process in bitumen emulsion, b). and their interactions with aggregates

Two drops of certain radius ‘R’ approach each other with the negligible initial velocities, which touch and form a tiny contact bridge due to Van der Waals interactions. This bridge contact length ‘r<sub>b</sub>’ quickly expands under the influence of interfacial stress, as illustrated in Figure 1a, and finally merges into a larger drop.

Several researchers [6-9] proposed that breaking of bitumen emulsion has a resemblance to the classical sintering process known in ceramics, latex paints and aerogels. After adding a breaking additive or destabilizing agent to the emulsion, a gel or network forms, which further contracts and become a separate phase. According to Frenkel’s theory, two oil drops diffuse into each other by a shape relaxation that is mainly driven by the surface tension [10]. The characteristic time for shape relaxation is controlled by a competition between surface tension and viscous dissipation and can be represented as (1);

$$\tau_{relaxation} \propto \frac{\eta R}{\gamma} \tag{1}$$

where  $\eta$  is the droplet viscosity,  $R$  is the characteristic radius of the droplet and  $\gamma$  is the droplet surface tension.

The main purpose of this study is to develop an understanding toward breaking and coalescence mechanisms in bitumen emulsions for improving the quality of cold asphalt.

## 1.2. Theoretical Background of Surface Tension, Surface Energy and Surface Free Energy

The term *surface tension* is used for liquids and the notion of a “contractile skin” on liquid surface is an integral part of surface tension which is due to intermolecular force. It is more usual to use the idea of *Surface Tension* rather than *Surface energy*, even though they refer to the same dimensional quantity. The fundamental relationship between surface curvature and surface tension was developed by Young and Laplace which is known as Laplace Equation (2);

$$\Delta p = p_2 - p_1 = \gamma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \quad (2)$$

Where  $R_1$  and  $R_2$  are the principle radii of the curvature,  $\gamma$  is surface tension and  $\Delta p$  is the hydrostatic pressure on the surface, which can be calculated by the difference of pressure within the liquid and without the liquid surface. The net inward force on the surface of a liquid makes the surface act as if it was an elastic skin that constantly tries to decrease its area.

Thermodynamically, surface tension is an excess quantity and represents extra energy as compared to the bulk phase which can be defined by Equation (3)

$$\gamma = \left( \frac{\partial F^s}{\partial A} \right)_{T,n} = \left( \frac{\partial F}{\partial A} \right)_{T,V,n} \quad (3)$$

Where  $A$  is surface area,  $V$  is the volume,  $n$  is amount in moles absorbed,  $F^s = (U^s - TS^s)$  is the Helmholtz free energy of the surface,  $U^s$  represents internal energy of the surface,  $T$  is absolute temperature and  $S^s$  is the entropy of the surface.

Surface energy is the work per unit area done by the force that creates the new surface. Surface energy (4) and surface free energy (5) are defined, respectively, as

$$u^s = \frac{U^s}{A} \quad (4)$$

$$f^s = \frac{F^s}{A} \quad (5)$$

As discussed before, surface tension is energy in excess, so surface free energy is not numerically equivalent to the surface tension as illustrated by Gibbs (6) as follows,

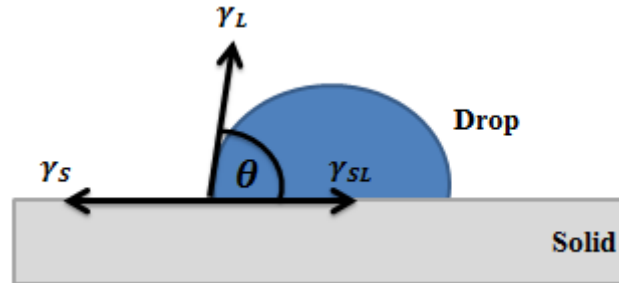
$$\gamma = f^s - \sum_i \Gamma_i \mu_i^s \quad (6)$$

Where  $i$  represent the component, and in a one component system (e.g pure liquid in contact with its own vapors), surface tension is numerically equal to the surface free energy [11].

The direct measurement of surface energy of a solid is for practical reasons not a very common practice and usually indirect methods are used to measure surface energies of solids. These methods include contact angle measurements, gas adsorption, inverse gas chromatography and micro calorimetry. Each method describes the surface energy parameters. Among all, Sessile drop contact angle measurement is the most economical, easy to operate and less time consuming method. In this method, a liquid drop of a probe liquid is

placed on the surface of a solid substrate and when the drop becomes static or sessile then contact angle is measured. Later on, this contact angle is used for surface energy calculations.

Surface energy ' $\gamma$ ' is the amount of work required to create a unit area of a given materials in a vacuum, or in other words, surface energy or interfacial energy quantifies the disruption of intermolecular bonds that occur when a surface is created. Young-Laplace developed a relation (7) between contact angle and surface energy, as below;



$$\gamma_s = \gamma_{SL} + \gamma_L \cos\theta \quad (7)$$

Where  $\gamma_s$  is solid surface energy,  $\gamma_L$  is liquid surface energy,  $\gamma_{SL}$  is solid-liquid interface energy and  $\theta$  is contact angle. Fowkes developed a theory to calculate the component of surface energy from the known surface tension as shown below (8); (D represents the dispersive component of surface energy);

$$\gamma_{SL} = \gamma_s + \gamma_L - 2\sqrt{(\gamma_s^D * \gamma_L^D)} \quad (8)$$

Later on, Fowkes uses the above relationship (8) combined with Young's Equation (7), to create an Equation (9) based upon the contact angle.

$$\cos\theta = 2\sqrt{(\gamma_s^D) * [1/\sqrt{\gamma_L^D}] - 1} \quad (9)$$

By plotting the contact angle versus the known dispersive surface energy of the liquid, this equation can be used to find the dispersive surface energy of the solid, which is the slope of the line. The polar component is also found using a linear regression relationship. Fowkes extended Equation (9) to include the polar components of surface energy as shown below in Equation (10).

$$\gamma_{SL} = \gamma_s + \gamma_L - 2[\sqrt{(\gamma_s^D * \gamma_L^D)} + \sqrt{(\gamma_s^P * \gamma_L^P)}] \quad (10)$$

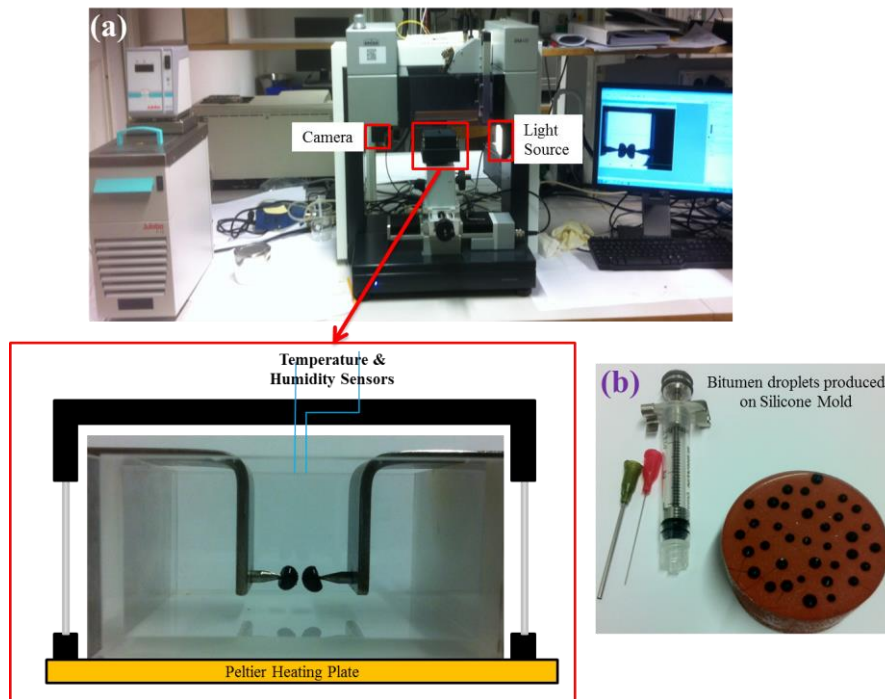
In the Sessile drop method, a minimum of two probe liquids with known surface tensions are required to get the dispersive and polar components of surface free energy. In this paper, three probe liquids water, formamide and diiodo-methane have been selected for the investigation of surface free energy and contribution of surface interactions [12].

## 2. Methodology

### 2.1. Test Set-up

The method to study coalescence in bitumen emulsions proposed in this study is also based on an optical approach, but its setup is significantly simplified in comparison to the light scattering and light transmission methods. Similar to the micro-pipette and vesicle methods described earlier [13-14], the proposed test is also based on bring two droplet in proximity of each other to study their coalescence, but under a more controlled set-up. The basic experimental setup for studying coalescence process in bitumen emulsions is shown in Figure 2. As it can be seen from the Figure 2a, the set-up consists of a camera, a light source and a climate chamber with optical transparent walls. In addition to these, the test setup contains a

transparent glass container, two L-shaped probes hooked with a vertical support of the glass container, temperature and humidity sensors and a Peltier heating panel that is connected to the temperature bath. Bitumen drops of 1-4 mm size are attached with L-shaped probes and brought into contact with each other for the coalescence to happen. The transparent glass container is filled with the relevant solvents (water phase with and without additives).



**Figure 2. a).** An experimental setup for studying coalescence process of bitumen droplets and **b).** formation of bitumen droplet on Silicone Mold.

## 2.2. Formation of Bitumen Droplets

Bitumen samples are heated in the oven to form a flowing liquid (160 °C to 180 °C depending on bitumen grade) and then with the help of different sizes of the syringe needles, droplets of different diameters are produced at the surface of silicon rubber as it has nonstick surface for bitumen (presented in Figure 2b). After this, rubber surface containing bitumen droplets is placed in a refrigerator at -20 °C for 2-3 hours to stabilize the bitumen drops.

## 2.3. Coalescence Experiment

The two bitumen droplets are brought in contact with each other to analyze coalescence in different environments. In the setup, both drops are separately connected with two L-shaped probes and when these probes are placed in a water phase container, the drops are far away from each other initially. These two drops are brought together manually in a way that they are almost touching each other but in reality these drops are separated approximately by a very small distance (order half  $\mu\text{m}$ ). After bringing two drops in contact to each other, relaxation process starts naturally. Coalescence times vary for different binder grades, droplet size, test temperature, type of emulsifier, additives (salts and salt concentrations, adhesion promoters etc.), variation in pH and different solvents. Moreover, these parameters affect the



stability of bitumen emulsions or in other words influence the coalescence process in bitumen emulsions, such as softer binder grade coalesce faster than hard one. Similarly, droplet size and temperature also influence the relaxation time. Major part of this work is submitted to *TRB Annual Meeting 2016* [15] and *Journal of Colloids and Surfaces-A* [16].

## 2.4. Materials

In this study, an emulsion grade of unaged and unmodified straight run bitumen from Nynas Bitumen AB with penetration grades 160/220, 70/100 and 50/70 were used to demonstrate the feasibility, efficiency and applicability of the new proposed experimental method. The basic physical properties for three grades of Nynas bitumen are shown in Tables 1.

**Table 1.** Properties of three different grades of bitumen

Bitumen Grade	Penetration (mm/10)		Softening point (°C)		Dyn. Viscosity (Pa.s) @ 60°C	Kin. Viscosity (mm <sup>2</sup> /s) @ 135°C	Fraass breaking point (°C)
	Min	Max	Min	Max			
50/70-N	50	70	46	54	145	295	-8
70/100-N	70	100	43	51	90	230	-10
70/100-I	86		46.4		-	181	-
160/220-N	160	220	35	43	30	135	-15
160/220-Q	205		39.2		-	225	-
160/220-R	180		40.1		-	202	-

To simulate the emulsion environment, Redicote EM44® from AkzoNobel was added to the water phase in the experiment by 1.0 wt%. Redicote EM44 is basically an amine based (*N*-tallow alkyltrimethylene-diamine, but containing additional functional groups) standard emulsifier for rapid and medium setting cationic bitumen emulsions.

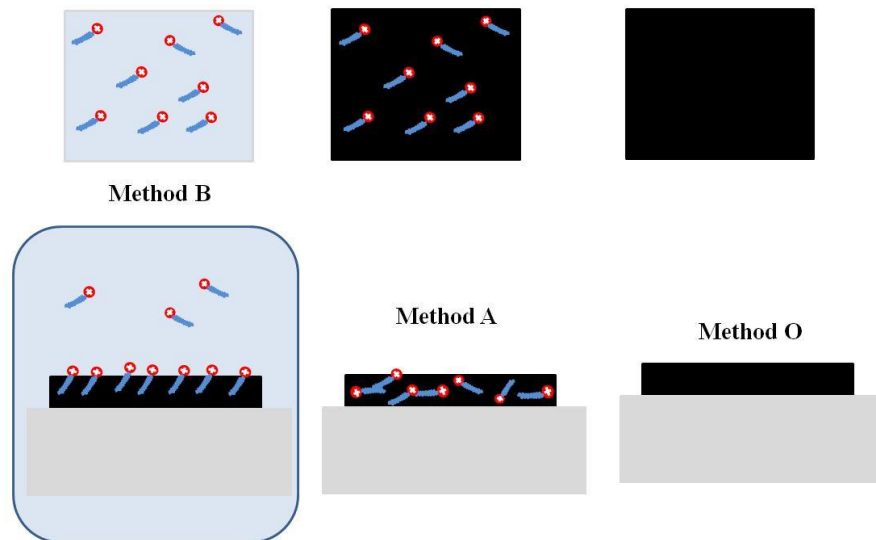
## 2.5. Sample Preparation for Binders Surface Free Energy

Bitumen surfaces were prepared in different ways by adding additives to bitumen and water phase separately, as shown in Figure 3, for the characterization of surface free energy measurements, and compared them with the unmodified or untreated surface.

**Method O.** Unmodified pure bitumen was heated 80 to 90 °C above softening point and then spread over the glass slides. Coated samples were cooled down at ambient temperature for an overnight in the fuming hood under cover, protecting the surface from dust particles.

**Method A.** Bitumen (160/220, 70/100, and 50/70) was heated and then additives were mixed according to weight percentages (EM44 1%, Wetfix 0.8%) with the pure bitumen. After mixing additives, hot bitumen was coated on the glass slides and samples were put in the chamber for overnight for cooling. Then cooled surfaces were investigated for surface energy measurement using contact angle methods.

**Method B.** Two step processes. In the first step, samples of pure unmodified bitumen were prepared as method-o. In the second step, the next day, samples were placed in water solutions containing EM44 (1%) and Wetfix (0.8%) for 3 days. Then samples were taken out from the water phase solutions containing emulsifier (one separate solution) and wetfix (another separate solution), and then washed the sample surfaces with distilled water and let them dry in fuming hood for 48 hrs. The surface energies of dried samples were measured using contact angle methods.

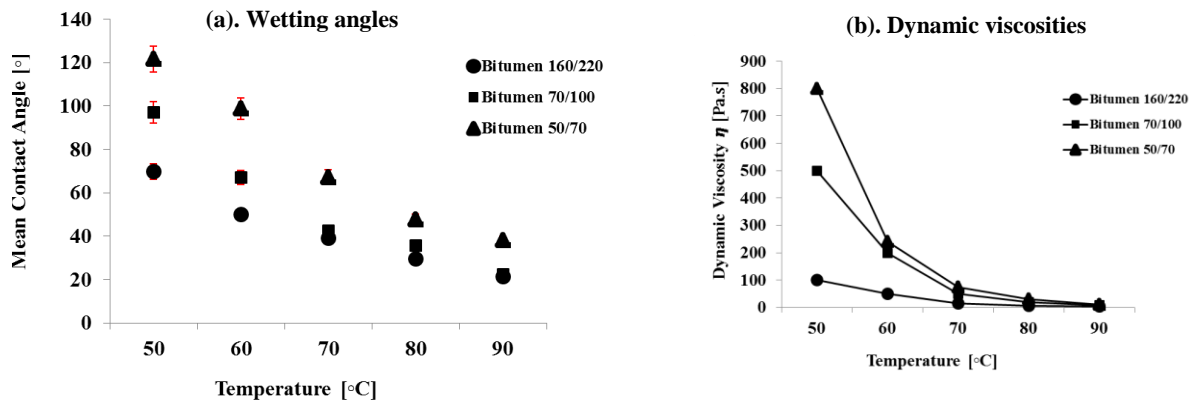


**Figure 3.** Three different ways to prepare binder surfaces with and without additives modifications. *Method O*-pure binder heated 80-90 °C above softening point and the spread over glass slide, *Method A*-different additives like emulsifier and wet fix were added in the pure binder and then spread over glass slide, and *Method B*- additives were dissolved in water and pure binder or method O samples were dipped in water phase containing emulsifier and wetfix (an adhesion promoter from AkzoNobel).

### 3. Results and Discussions

The characteristic relaxation time of the bitumen is strongly dependent on the physical and chemical properties of the bitumen. For this reason, the wettability profiles of three bitumen grades were analyzed at different temperatures by contact angle methods using KRÜSS DSA100 equipment. All temperature measurements were repeated three times to check the time of equilibrium and angles were measure at certain time frames for all the samples. From this, it is clearly seen in Figure 4 that, as expected, wettability is enhanced at high temperature and with softer grade of the binder.





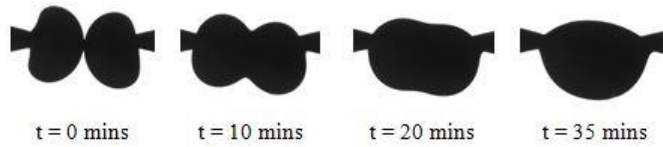
**Figure 4.** a). Contact / wetting angles at different temperatures, b). Dynamic viscosities of three bitumen grades.

In Figure 4a, the measured mean contact angles are plotted for the three bitumen grades at different temperatures. All the contact angle measurements were performed after drop deposition and contact angles were recorded at 3 minutes of deposition time frame, however, these do not ensure equilibrium time scale. Equilibrium time scales will be different for each binder at different temperatures. From the behavior of each bitumen grade it can be seen that the wettability behavior with respect to temperature, follow similar trend to that of viscosity as presented in Figure 4b. The wetting angles of these bitumen grades at different temperatures can be compared with their respective viscosities. The kinetics of shape relaxation of bitumen droplets can be related to the different physio-chemical parameters such as viscosity and surface energy of the bitumen, as well as droplet size (see equation 1).

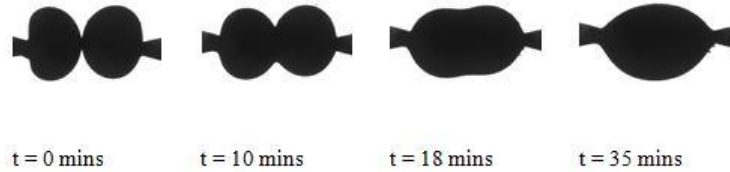
### 3.1. Coalescence of Bitumen Drops in Water

A horizontal drop approaching scheme was selected instead of a vertical approach to overcome buoyancy effects in water environment [16]. In Figure 5, three different sample of bitumen 160/220 from different origin were investigated for droplet coalescence at 40 °C in a water phase with (pH=2.1), containing Redicote EM44. The relaxation time of bitumen droplets (size  $\approx$  2-3mm) was hereby found almost similar for two binders N and Q, but bitumen R coalesced faster as compared to others. Bitumen R has intermediate kinematic viscosity as compared to bitumen N and bitumen Q. However, binder R has lower penetration than binder Q. The early stage of coalescence represents neck formation and it was very rapid as compared to the last stages of the coalescence process.

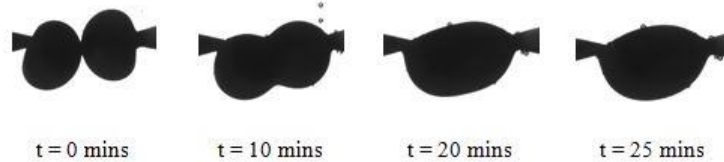
**Bitumen 160/220-N** [water + Redicote EM44 @ pH 2.1, Temperature 40 °C]



**Bitumen 160/220-Q** [water + Redicote EM44 @ pH 2.1, Temperature 40 °C]



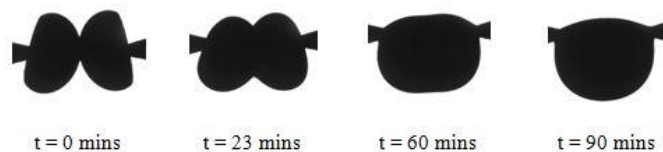
**Bitumen 160/220-R** [water + Redicote EM44 @ pH 2.1, Temperature 40 °C]



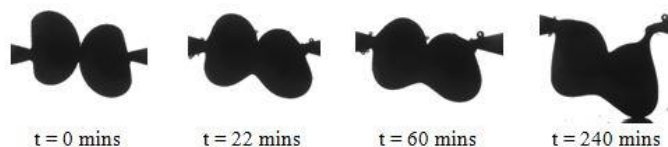
**Figure 5.** Coalescence of bitumen 160/220 (bitumen with different origin) droplets [water + Redicote EM44 @ pH 2.1, Temperature 40 °C]

The presence of surfactants or surface active molecules at the interface also changes the surface tension and their variation in concentration give rise to surface tension gradients. Moreover, the contraction or expansion of the interface may also affect the concentration of surfactants, which lead to varying surface tension. In the early stage of coalescence, during neck opening, droplet interfaces contract and if emulsifiers are present then such interface shrinkage will increase their concentration, which will result in reducing surface tension. However, high concentration of surfactant usually above critical micelle concentration (CMC) and a small variation in surface area will not change the surface tension.

**Bitumen 70/100-N** [water + Redicote EM44 @ pH 2.1, Temperature 40 °C]



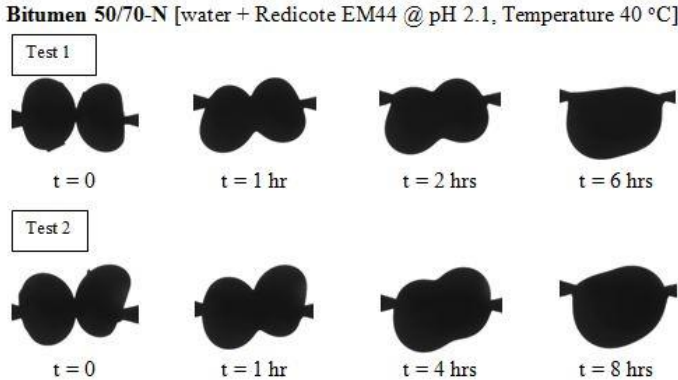
**Bitumen 70/100-I** [water + Redicote EM44 @ pH 2.1, Temperature 40 °C]



**Figure 6.** Coalescence of bitumen 70/100 (bitumen with different origin) droplets [water + Redicote EM44 @ pH 2.1, Temperature 40 °C]

The hydrodynamics of droplet coalescence of binder 70/100 can be observed in Figure 6, where two bitumen samples from different origin were tested. Water phase composition and test temperature were fixed similar to bitumen 160/220. It can be observed that relaxation times of two bitumen samples with same penetration grades but different origin are not the

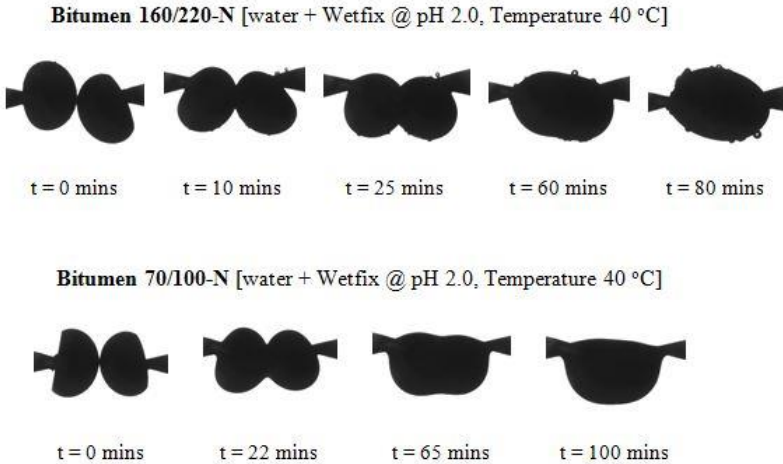
same. Moreover, binder 70/100-I did not coalesce completely and sedimentation was happening.



**Figure 7.** Coalescence of bitumen 50/70 droplets [water + Redicote EM44 @ pH 2.1, Temperature 40 °C]

Figure 7 represents relaxation of harder penetration grade (50/70) of bitumen. Two different droplets with small variation in droplet size resulted in different relaxation time. It can be evaluated from the results shown in Figures 5-7, that softer grade binder coalesce fast as compared to a harder one.

Wetfix N from AkzoNobel is an adhesion promotor used in bituminous mixtures both in hot mix and cold mix applications. In Figure 8, water phase was prepared with Wetfix instead of EM44 and other conditions were kept the same. Two different bitumen grades of the same base binder were investigated for coalescence experiment. Coalescence or cohesive forces were slowed down with Wetfix addition for both binders grades, which promote adhesive properties.



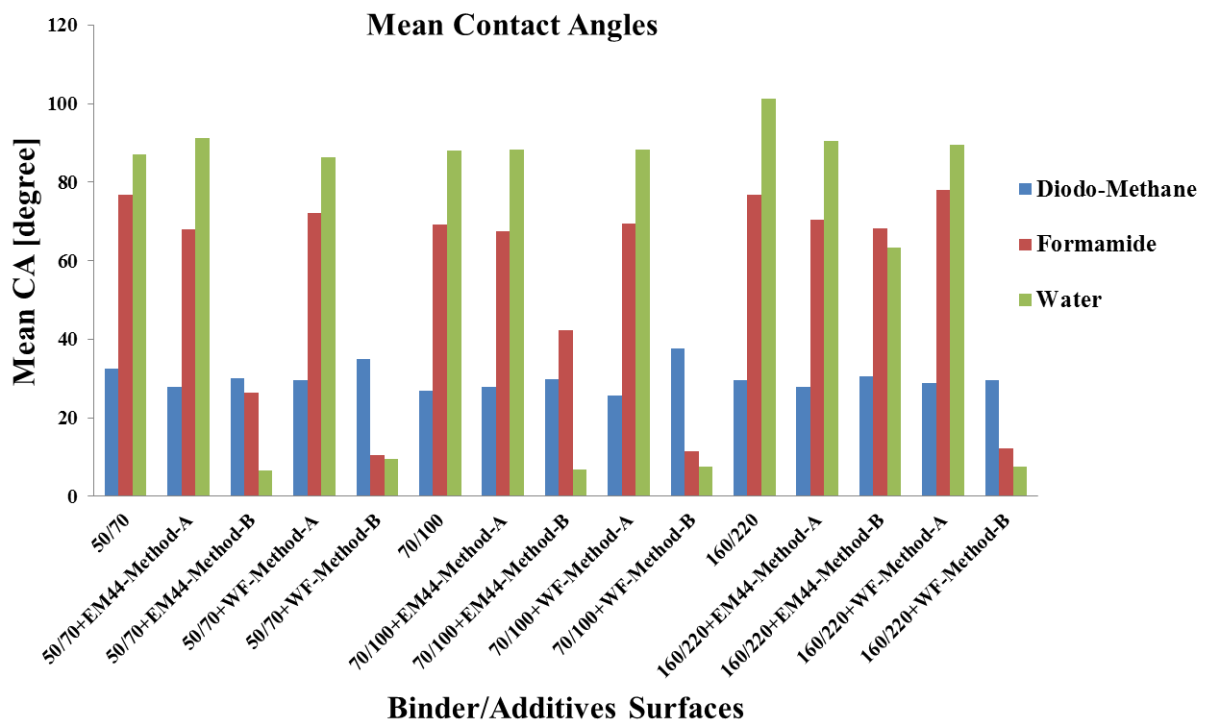
**Figure 8.** Coalescence of two different bitumen grades of same base binder droplets [water + Wetfix @ pH 2.0, Temperature 40 °C]

These relaxation experiments can be related to the Frenkel’s concept of viscous sintering and according to this theory, the time of relaxation is directly proportional to the ratio between viscosity and surface tension of each bitumen grade, which can be observed here as well. The droplet shrinkage is very rapid in the early stages of coalescence and bridge contact ‘ $r_b$ ’ grows linear with time for all three binders, which also agrees with the Finite Element based

theoretical calculations of Martinez et.al [17]. Moreover, if ratios between surface energy and viscosity ( $\gamma/\eta$ ) of each binder are compared, soft binder will have higher values as compared to the harder binder grade, which explains the extremely fast and extremely low relaxation process, respectively.

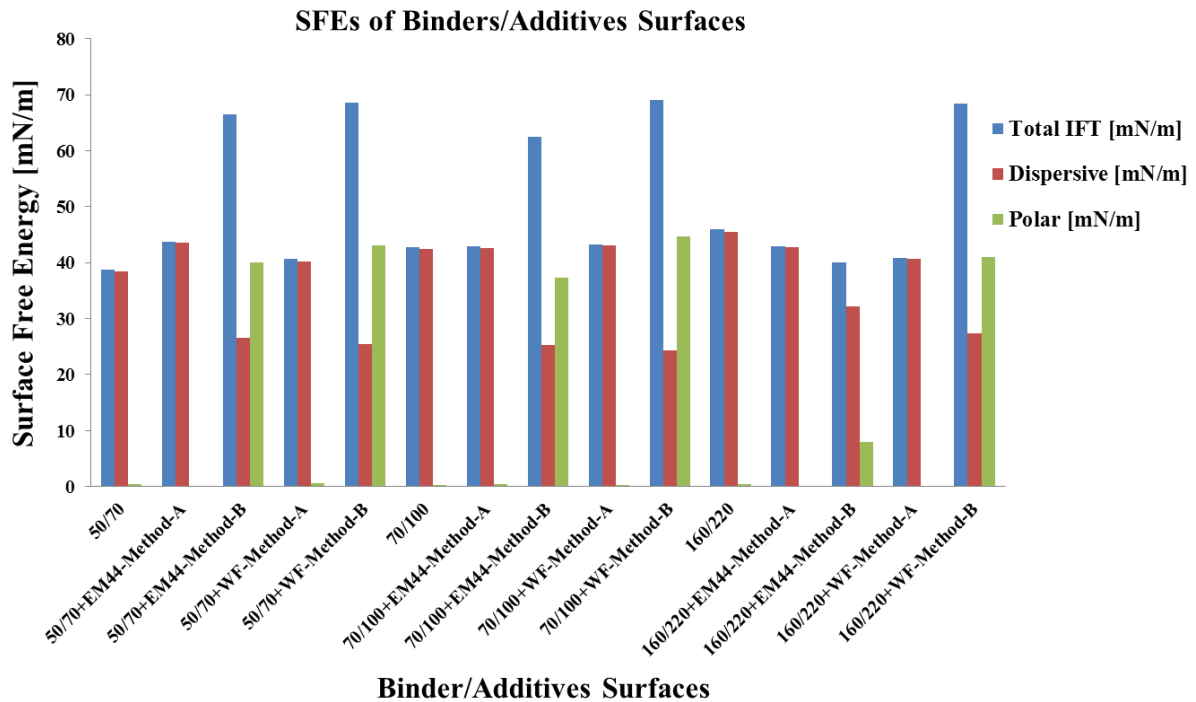
### 3.2. Surface Free Energy Calculations of Binder Surfaces

Sessile drop contact angle method was used to characterize the surfaces of different binders. Mean contact angles of three probe liquids are plotted in Figure 9 for straight run and modified binders with emulsifiers and adhesion promoters. There is not a big difference in mean contact angles among Method-O samples and Method-A samples. In case of method-B, contact angles of both polar probe liquids (formamide and water) drops decreased, however, contact angle of non-polar or dispersive probe liquid drop remained unaffected.



**Figure 9.** Mean contact angles of different probe liquids drops at bitumen surface prepared using different methods

The structure of an Emulsifier or surfactant molecule consists of two parts, a long carbon chain (8-18 C atoms) which is the lipophilic part that goes to the oil phase, and a polar or hydrophilic part that is soluble in water phase. Adding Emulsifier EM44 and Wetfix N to the bitumen phase (Method A), have not made any significant changes to the surface free energies of the binder. However, exposing bitumen surface to the water phase containing these additives (Method B) have brought a significant differences in the surface free energies of the binders as illustrated in Figure 10. These results indicate that solubility dynamics and kinetics of these additives are different in both phases



**Figure 10.** Surface Free Energies of different bitumen surfaces prepared using different methods

Moreover, it can also be observed that softer grade binder surface energies are much more sensitive to modifications using Method-B. These changes in surface free energies can be linked with the relaxation times, which have been evaluated and discussed so far. As a result, it can be said that coalescence is driven by viscous forces as well as surface free energies changes of the bitumen phase.

#### 4. Conclusions

Current study revealed that relaxation times are strongly dependent on the physical properties of the bitumen and this new test method enables a systematic investigation of the relevant parameters. The time of coalescence or relaxation ( $\tau_{\text{relaxation}}$ ) can be related to the viscosity, surface energy, size of the droplet and temperature. The initial droplet shrinkage for all three binders was more rapid in comparison to the later stages of the coalescence process, which is in agreement with theoretical models presented by different researchers.

- Wettability profiles of different binder grades at glass substrate showed that wettability is enhanced at high substrate temperature and with softer grade of the binder.
- Softer grade binders were coalescing faster as compared to harder grade binders. Relaxation times can be approximately compared by calculating the ratios between surface energy and viscosity ( $\gamma/\eta$ ) of each binder.
- Surface active species like emulsifiers and adhesion promoters are active and help to change the surface characteristic, if and only if added to the water phase.

- Coalescence is driven by viscous forces and surface free energies changes of the bitumen phase.

## Acknowledgement

This research work was sponsored by Nynas AB and performed at KTH Royal Institute of Technology, Sweden. The authors acknowledge Romain Balieu, Xiaohu Lu, Hilde Soenen and Måns Collin for valuable discussions and comments.

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