

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Cetyltrimethyl Ammonium Chloride (CTAC)

Cetyltrimethyl ammonium chloride ($C_{16}H_{33}N(CH_3)_3Cl$) obtained from Unilever Thai Holdings, Ltd. was used as the cationic surfactant without further purification. CTAC used in this study was in a commercially available product form of 50% concentration in 36% of isopropyl alcohol and 14% of water, which appears as a yellowish viscous liquid. The molecular weight of CTAC was 319.5 g/mol . The structure of CTAC is shown in Figure 3.1

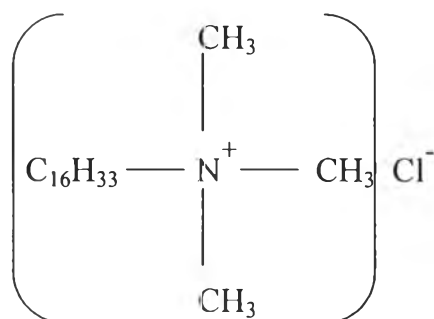


Figure 3.1 The chemical structure of CTAC.

3.1.2. Behenyltrimethyl Ammonium Chloride (BTAC)

Behenyltrimethyl ammonium chloride ($C_{22}H_{45}N(CH_3)_3Cl$) was obtained from Unilever Thai Holdings, Ltd. and used as another type of cationic surfactant. It was used without further purification. BTAC used in this study was in a commercially available product form of at 85% concentration. It appeared as white solid. The molecular weight of BTAC was 403.5 g/mol. The structure of BTAC is shown in Figure 3.2.

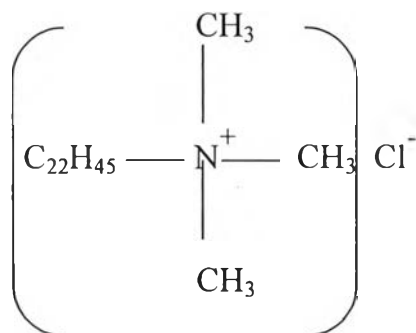


Figure 3.2 The chemical structure of BTAC.

3.1.3 Fatty Alcohol (FA)

The fatty alcohol (FA) is the mixture of 15% of cetyl alcohol ($\text{CH}_3(\text{CH}_2)_{15}\text{OH}$) and 85% of stearyl alcohol ($\text{CH}_3(\text{CH}_2)_{16}\text{OH}$) so it can be called cetostearyl alcohol. It can be used as a thickener, a coemulsifier, a stabilizer, an opacifier for cosmetics and topical pharmaceutical emulsions. The physical state is white pellet and the melting point is around 53°C . The molecular weight of cetyl alcohol and stearyl alcohol was 242 and 268 g/mol respectively. It was obtained from Unilever Thai Holdings, Ltd.

3.1.4 Hydroxyethyl Cellulose (Natrasol) (HEC)

Hydroxyethyl cellulose is a nonionic water - soluble polymer derived from cellulose. It was used as a thickening agent or a rheology modifier and was obtained from Unilever Thai Holdings, Ltd. Its solubility characteristics allow easy dispersion in hot or cold water. The physical state of HEC is white granular powder. The structure of HEC is shown in Figure 3.3.

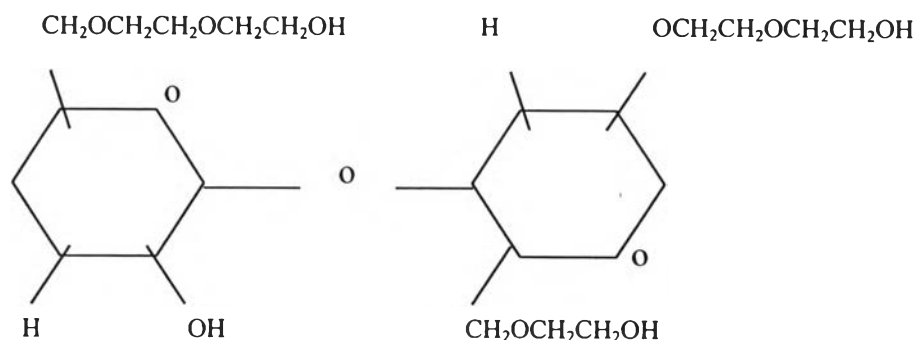


Figure 3.3 The chemical structure of Hydroxyethyl cellulose.

3.1.5 Deionized Distilled Water

Deionized distilled water was used as the pure solvent without further filtering or purification.

3.2 Equipment

3.2.1 Laser Scanning Microscope (LSM)

The LSM or Laser scanning microscope is a new method for morphological studies in polymer science. The laser-scanning microscope improves the resolution of a conventional light microscope by replacing the light source with a scanning laser and by introducing a pinhole in the backfocal plane. It is a powerful tool for obtaining detailed three-dimensional information of morphologies. To operate the LSM, a laser is scanned horizontally over the sample and the beam is redirected by a beam splitter and is focused on the sample with the scanner and the objective lens. A pinhole located in the focal plane in front of the detector ensures that only light reflected and very narrow focal plane will reach the detector. The pinhole effectively suppresses light emanating from other planes passing through the photodetector, so that it greatly improves the limited depth of photo normally available with optical microscopes (Alexander, 1997).

The LSM 410 inverse laser scan microscope, from Zeiss

Inc., was used to investigate the structure of emulsion. This microscope can be regarded as one of the most important emulsion characterization tool. It can give information about relative amounts of oil, water, and solids including the structure of an emulsion system. It is based on the Axiovert 100, 135 or 135M microscope family. This microscope allows conventional microscope techniques using the usual contrast methods such as bright field, dark field, differential interference contrast, phase contrast, fluorescence and polarization.

Basic LSM System. This system consists of a beam scan system, a detector unit and a control computer.

Laser Unit. This part consists of one or two internal lasers.

Axiovert 100, 135 or 135 M microscope equipment. These are used for transmitted light, supplemented by the corresponding optical equipment and by various lighting units with the affiliated power supply units.

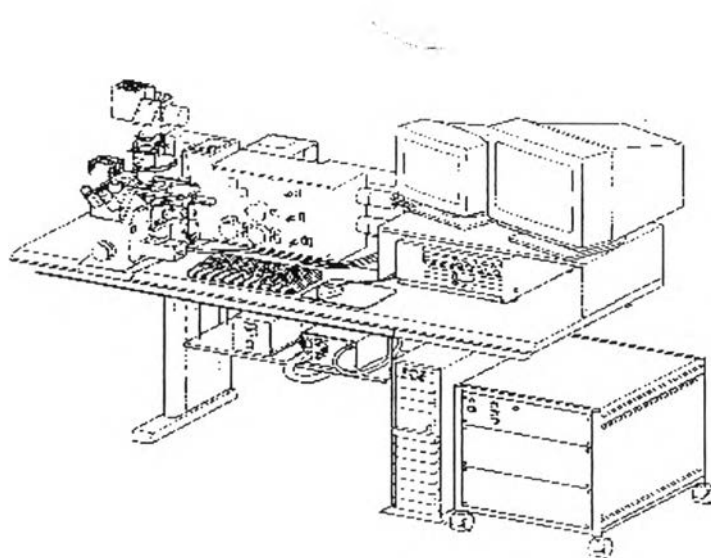


Figure 3.4 The general view of the LSM system.

The basic principle of LSM involves the transmitted-light and the scanner system. In laser scanning microscope a small aperture is placed in the plane where rays coming from a particular plane in the object from a point. This plane is called the confocal plane. A light detector is placed behind the

aperture. The aperture selects one point (x, y) in the plane, and also cuts out most of the light coming from other planes in the specimen. If the illumination is focused onto the selected point in the object, then information comes from the point only. Scanning the illumination and the confocal aperture together over x and y builds up a scanned image of the selected plane.

3.2.2 Rheometer

The fluid rheometer, model ARES, from Rheometric Scientific Inc., was used to measure the rheological properties of emulsion in oscillatory and steady state modes. Figure 3.5 shows a most common rheometer, a cone and plate rheometer. The test material is contained between a cone and plate, with the angle between the cone and plate being small ($<4^\circ$). In this work, a cone-and-plate rheometer with a diameter of 50 mm, a cone angle of 4° and gap size of 0.050 ± 1 mm was used. The apparatus consists of 2 circular disks, a stationary upper plate and an oscillating lower plate, separated by a thin gap where the sample is placed. The bottom plate oscillates at a frequency at a specified strain. The top plate is held stationary and connected to a transducer, which measures the torque. Torque can be converted to shear stress and other viscoelastic properties such as storage modulus (G'), loss modulus (G''), etc. as functions of frequency.

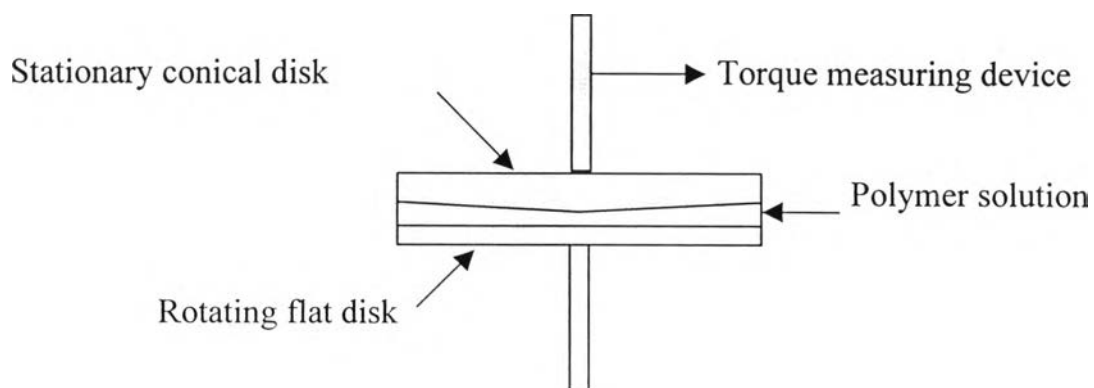


Figure 3.5 The cone and plate rheometer.

The Rheometer was used to measure the rheological behavior of material. There are two different methods available: static method or steady state method dynamic and method or oscillatory strain method. Static tests involve the imposition of a steady state strain rate (or stress). Dynamic tests involve the application of a harmonically varying strain.

3.2.2.1 Steady State Method

The steady state mode measures viscosity as functions of strain rate. The equations for viscosity (η), shear stress (σ), shear rate ($\dot{\gamma}$), first normal stress difference at small angles (α) of Newtonian fluids are

$$\eta = (3\alpha M)/(3R^3) \quad (3.1)$$

$$\sigma = (3M)/(2\pi R^3) \quad (3.2)$$

$$\dot{\gamma} = dv/dr = \omega/\alpha \quad (3.3)$$

$$\sigma_{11} - \sigma_{22} = -2F_N/(\pi R^2) \quad (3.4)$$

where M is the torque needed to turn the cone, R is the radius of the cone, v is the linear velocity, r is the distance from the axis, ω is the cone rotational frequency, F_N is the total force normal to fixed plate and $\sigma_{11} - \sigma_{22}$ is the first difference normal stress.

3.2.2.2 Dynamic Method

$$\text{Let } \gamma(t') = \gamma_0 \exp(i\omega t') \quad (3.5)$$

where i is $\sqrt{-1}$, ω is frequency and γ_0 is strain amplitude. The corresponding strain rate is given by

$$\dot{\gamma}(t') = i\omega\gamma_0 \exp(i\omega t') \quad (3.6)$$

In oscillatory shear, a complex shear modulus G^* is defined as

$$\sigma(t) = G^*(\omega)\gamma(t) \quad (3.7)$$

$$G^* = G' + iG'' \quad (3.8)$$

where G' is storage modulus (or dynamic rigidity) which indicates the solidity and G'' is loss modulus, which indicates the fluidity

The more convenient complex representation of the oscillatory motion as an alternative to the complex shear modulus, can be defined as "complex viscosity" (η^*) or the ratio of the shear stress σ to the rate of shear $\dot{\gamma}$.

$$\sigma(t) = \eta^* \cdot \dot{\gamma}(t) \quad (3.9)$$

$$\eta^* = \eta' - i\eta'' \quad (3.10)$$

where η' is dynamic viscosity ($G'' = \eta'\omega$) and η'' is storage viscosity ($G' = \eta''\omega$).

The alternative method of characterizing rheology is to plot G' and the loss angle (δ), $\tan\delta$ can be defined as G'' divided by G' which represents the ratio of fluidity to elasticity.

3.3 Experimental Conditions

3.3.1 Conditions in Microscope Measurement

Each sample was placed on a glass slide and covered by a cover glass. The specimen was then placed on the objective lens in order to measure the structure of emulsion. The measurement was performed in transmitted-light mode and using the confocal plane to reconstruct an image. The magnification was 1000 times: 10 magnification for the objective lens and 100 magnification for eyes piece lens. The picture was taken at the pinhole of 10 and the enlargement of 7.

3.3.2 Conditions in Oscillatory Measurements

3.3.2.1 *Dynamic Strain Sweep Default Test*

Usually, the rheological properties of viscoelastic material are independent of strain up to a critical strain. Beyond this critical strain level, the material behavior is nonlinear and the moduli decline. Thus, measurement of the strain amplitude dependence of the storage and loss

moduli is usually the first step taken in characterizing the viscoelastic behavior. For example, a strain sweep is used to establish the extent of the linearity of the viscoelastic response of a material.

The measurements were performed by the Fluid Rheometer using the cone-n-plate geometry with a cone angle of 4° and a diameter of 50 mm. The gap range was 0.050 ± 1 mm. The experiments were carried out at the frequency of 1.0 rad/s, at the temperature of $26 \pm 1^\circ\text{C}$. Initial strain and final strains were equal to 0.1 and 100%, respectively. For these measurements, the level of strain was determined in order to ensure that measurements were made within the linear viscoelastic regime.

3.3.2.2 *Dynamic Frequency Sweep Default Test*

After the fluid linear viscoelastic regime has been established by a strain sweep, its structure can be further characterized using a frequency sweep at a strain below the critical strain. This provides more information about rheological properties at different lengths on time scales. In the dynamic frequency sweep mode, measurements were made over a range of oscillation frequency at a constant oscillation amplitude and temperature.

The measurements were performed by the Fluid Rheometer using the cone-n-plate geometry with a cone angle of 4° and a diameter of 50 mm. The gap range was 0.050 ± 1 mm. The experiments were carried out at the temperature of $26 \pm 1^\circ\text{C}$. Initial frequency and final frequency were equal to 100 and 0.1%, respectively. The value of strain used was chosen to be within the linear viscoelastic regime. In these measurements, G' , G'' , $\tan\theta = G''/G'$, η'' were determined as a function of frequency.

3.3.3 Conditions in Steady Shear Measurement (Steady Rate Sweep Test)

The measurements were performed by a Fluid Rheometer using the cone-n-plate geometry with a cone angle of 4° and a diameter of 50 mm. The gap range was 0.050 ± 1 mm. The experiments were carried out at the temperature of 26 ± 1 °C. Initial rate and final rates were equal to 0.01 and 100 1/s, respectively. The data mode was time based. Time delay and measurement times were 0.1 and 1 sec, respectively. The direction was clockwise, only one direction per measurement. In these measurements, flow curve of viscosity versus shear rate or viscosity versus stress was obtained.

3.4 Data Analysis

In this work we investigate three important parameters which were entanglement storage modulus (G_N^0), Bingham stress (τ_B) and zero shear viscosity (η_0). G_N^0 could be defined as the storage modulus at 100 rad/sec. It is referred to the dynamic entanglement network of emulsions. Bingham stress is force per area required to initiate the flow of emulsions. It was obtained from the plot of stress versus strain rate and extrapolated to zero shear rates. Zero shear viscosity is defined as the viscosity at zero shear rates. In this work, it was the estimated value at the shear rate 0.01 sec^{-1} .

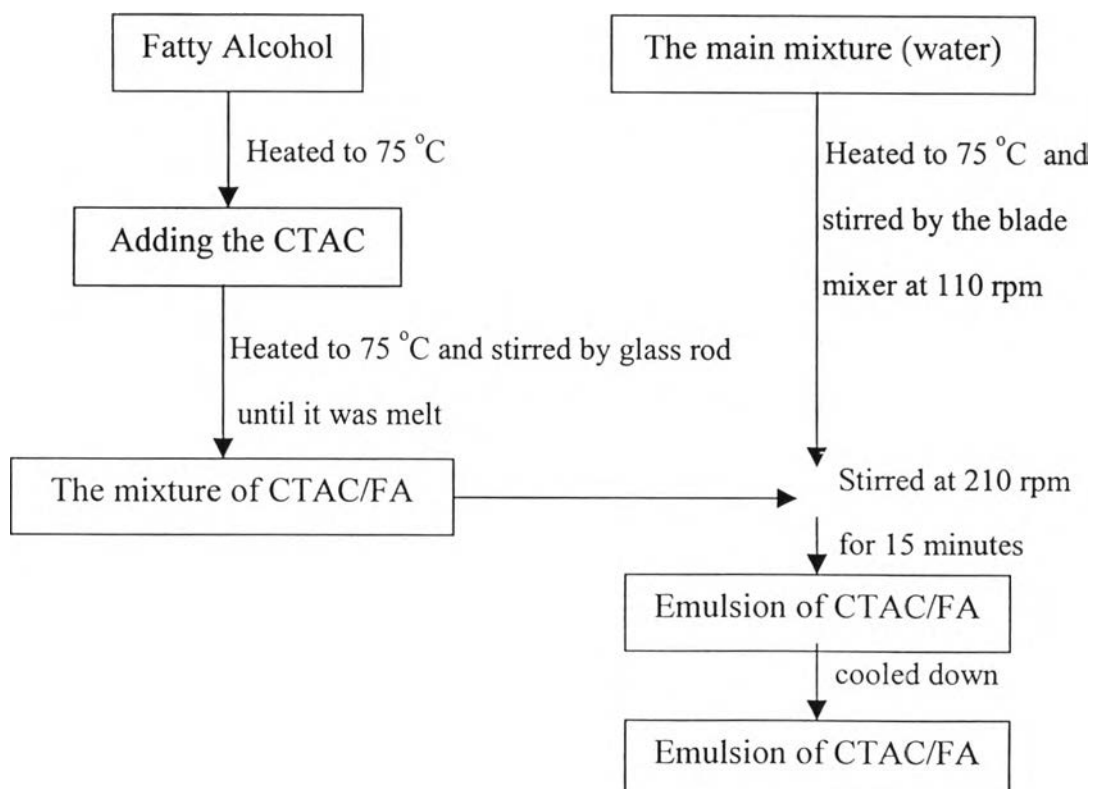
3.4 Methodology

3.4.1 Sample Preparation of Emulsion of CTAC/FA

The main mixture was heated to 75 °C. Then the fatty alcohol was heated to 75 °C before adding CTAC. A glass rod was used to stir the mixture until it was melted. After that the mixture was poured into a main mixer beaker consisting of water at 75 °C. A blade mixer at a slow speed of 110 rpm homogenized the whole mixture about 1-2 minutes before the speed was changed to 210 rpm for a period of 15 minutes.

Once the emulsion of CTAC/FA started to form, the heater was turned off and more water was added, whose temperature was controlled at 45 °C, and then it was cooled down. The mixture was stirred at a slow speed of 110 rpm for a period of 10 minutes. Finally an emulsion of CTAC/FA was obtained at room temperature.

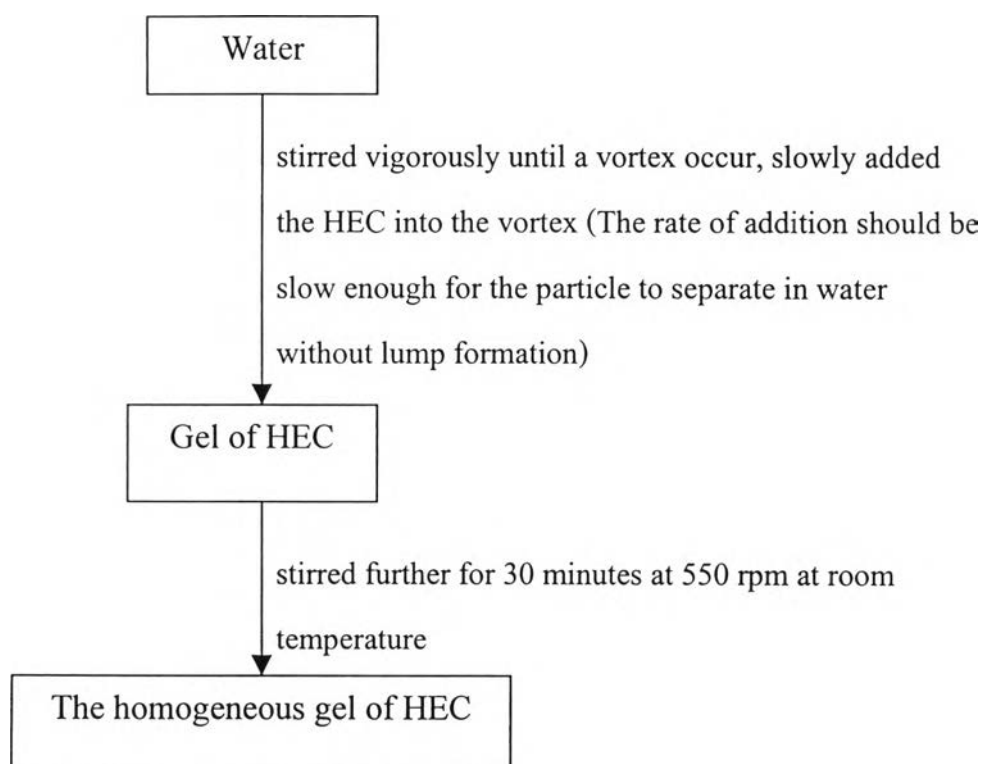
Diagram 3.1: Sample Preparation of Emulsion of CTAC/FA.



3.4.2 Sample Preparation of Solution of HEC

Water was stirred vigorously until a vortex occurred. Then powder of HEC was slowly added into the vortex. The rate of addition was slow enough for the particles to disperse in water without lump formation. A blade mixer using a high speed of 550 rpm for 30 minutes homogenized the mixture of water and HEC. Finally the gel of HEC was obtained at room temperature.

Diagram 3.2: Sample Preparation of Solution of HEC.

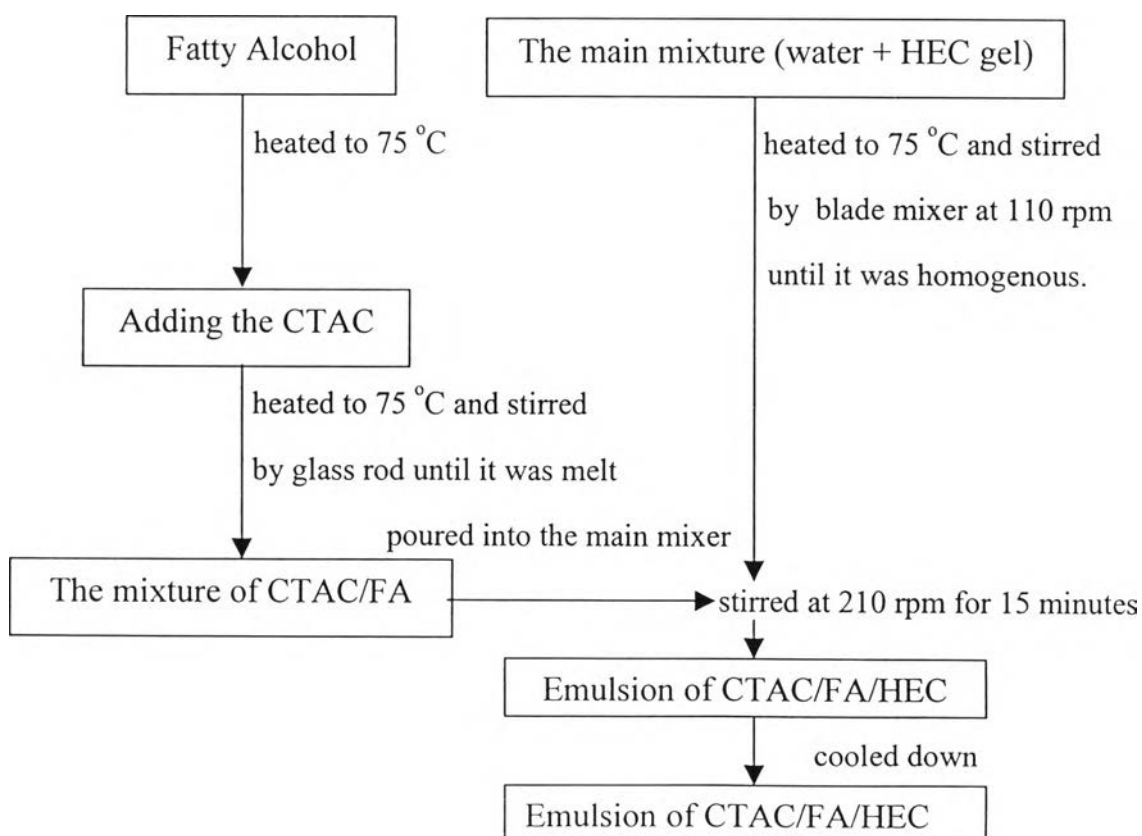


3.4.3 Sample Preparation of Emulsion of CTAC/FA/HEC

The fatty alcohol was heated to 75 °C before adding CTAC. A glass rod was used to stir the mixture until it was melted. Then the mixture was poured into a main mixer beaker consisting of water and HEC gel then it was homogenized at 75 °C. A blade mixer at a slow speed of 110 rpm then homogenized the whole mixture about 1-2 minutes before the speed was changed to 210 rpm for a period of 15 minutes.

Once the emulsion of CTAC/FA/HEC started to form, the heater was turned off and more water was added, whose temperature was controlled at 45 °C, and then it was cooled down. The mixture was stirred at a slow speed of 110 rpm for a period of 10 minutes. Finally an emulsion of CTAC/FA/HEC was obtained at room temperature.

Diagram 3.3: Sample Preparation of Emulsion of CTAC/FA/HEC.

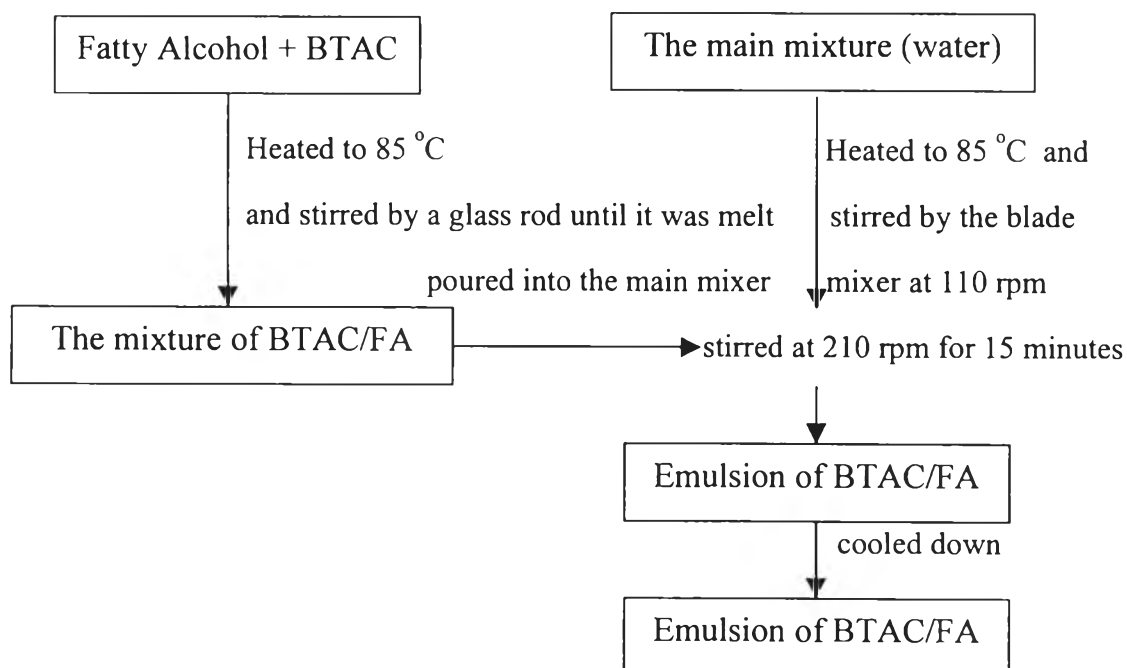


3.4.4 Sample Preparation of Emulsion of BTAC/FA

The Fatty alcohol and BTAC were mixed and heated at 85 °C together. A glass rod was used to stir the mixture until it was melted. Then the mixture was poured into a main mixer beaker consisting of water at 85 °C. A blade mixer at a slow speed of 110 rpm homogenized the whole mixture about 1-2 minutes before the speed was changed to 210 rpm for a period of 15 minutes.

Once the emulsion of BTAC/FA started to form, the heater was turned off and more water was added, whose temperature was controlled at 40 °C, and then it was cooled down. The mixture was stirred at a slow speed of 110 rpm for a period of 10 minutes. Finally an emulsion of BTAC/FA was obtained at room temperature.

Diagram 3.4: Sample Preparation of Emulsion of BTAC/FA.

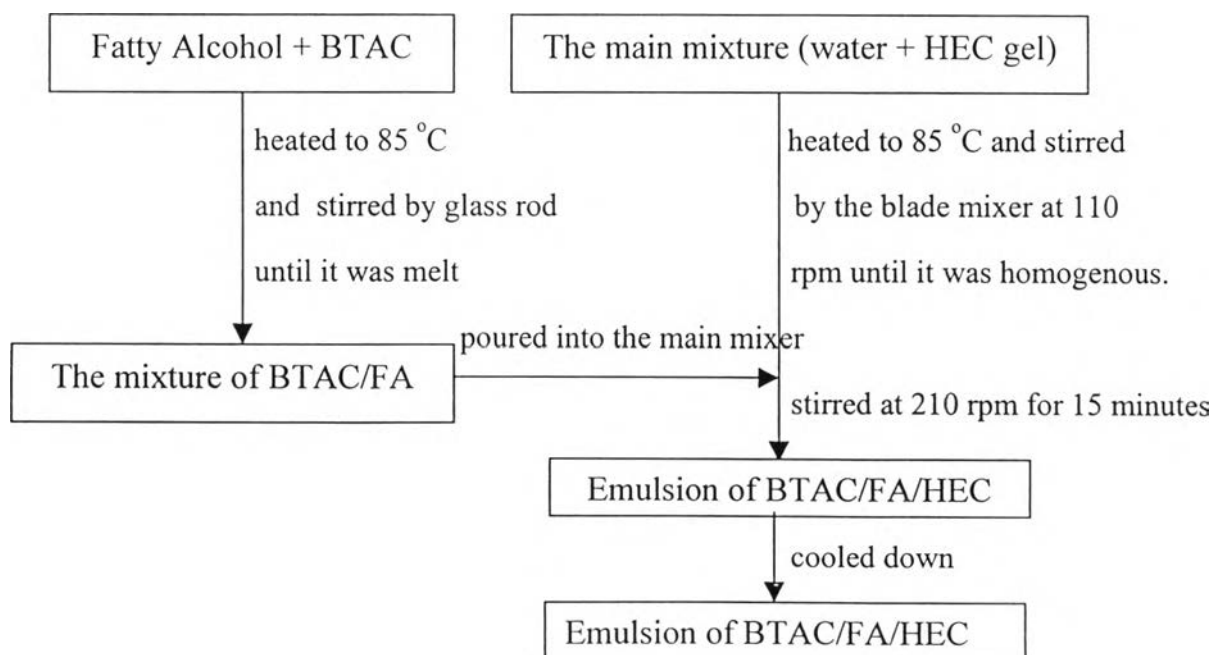


3.4.5 Sample Preparation of Emulsion of BTAC/FA/HEC

The fatty alcohol and BTAC were heated to 85 °C. A glass rod was used to stir the mixture until it was melted. Then the mixture was poured into a main mixer beaker consisting of water and HEC gel then it was homogenized at 85 °C. A blade mixer at a slow speed of 110 rpm then homogenized the whole mixture about 1-2 minutes before the speed was changed to 210 rpm for a period of 15 minutes.

Once the emulsion of BTAC/FA/HEC started to form, the heater was turned off and more water was added, whose temperature was controlled at 45 °C, and then it was cooled down. The mixture was stirred at a slow speed of 110 rpm for a period of 10 minutes. Finally an emulsion of BTAC/FA/HEC was obtained at room temperature.

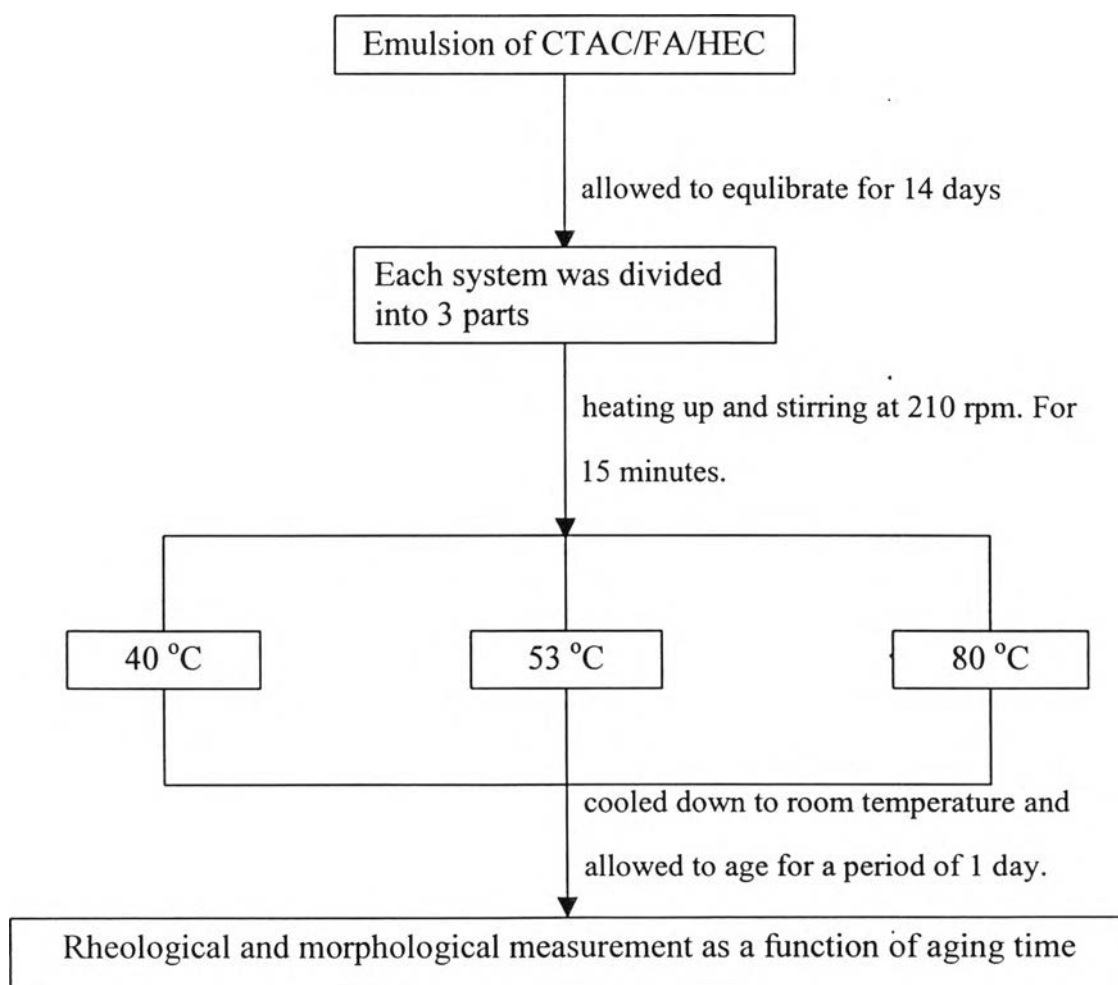
Diagram 3.5: Sample Preparation of Emulsion of BTAC/FA/HEC.



3.4.6 Sample Preparation of Emulsion for Studying Effect of Annealing Temperature

In order to study the effect of annealing. The emulsions were heated to 40, 53, and 80 °C respectively. The emulsions were then stirred by the blade mixer at a slow speed of 110 rpm for a period of 15 minutes. Finally, the emulsions were cooled down to room temperature and allowed to equilibrate for 1 day before measuring the rheological properties as a function of aging time.

Diagram 3.6: Sample Preparation of Emulsion to Study the Effect of Annealing Temperature.



3.4.7 Sample Preparation of Emulsion for Studying the Effect of Temperature

In this experiment, emulsions were prepared according to the preparation methods of CTAC/FA and BTAC/FA emulsions. Then they were allowed to age for 14 days. For each system, samples will be characterized for rheological properties at 26 °C, 35 °C, 45 °C and 80 °C.

3.4.8 Sample Preparation of Emulsion to Study the Effect of pH

In this experiment, emulsions were prepared according to the preparation methods of CTAC/FA and BTAC/FA emulsions. The emulsion was adjusted for pH at 3, 5, 7 and 9. The blade mixer at a slow speed of 110 rpm then was used to stir the emulsion for a period of 15 minutes. Finally, the emulsion was allowed to equilibrate for 14 day before measuring the rheological and optical properties.

Diagram 3.7: Sample Preparation of Emulsion to Study the Effect of pH.

