

CHAPTER II

EXPERIMENTAL SECTION

2.1 Materials

Cationic surfactants

1) Cetyltrimethyl ammonium chloride

Cetyltrimethyl ammonium chloride or CTAC obtained from Unilever Thai Holdings, Ltd. was used as the cationic surfactant. It was used without further purification. CTAC used in this study was obtained from a commercially available product at 50% concentration in isopropyl alcohol which appears as a yellowish viscous liquid. The structure of CTAC is shown in figure 2.1

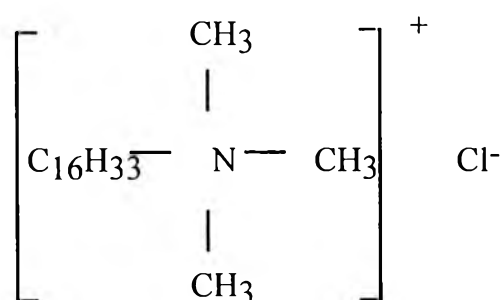


Figure 2.1 The chemical structure of CTAC.

2) Behenyltrimethyl ammonium chloride

Behenyltrimethyl ammonium chloride or BTAC was used as another type of cationic surfactant and obtained from Unilever Thai Holdings, Ltd. It was used without further purification. BTAC used in this study was

obtained from a commercially available product at 85% concentration. It appears as a white solid. The structure of BTAC is shown in figure 2.2

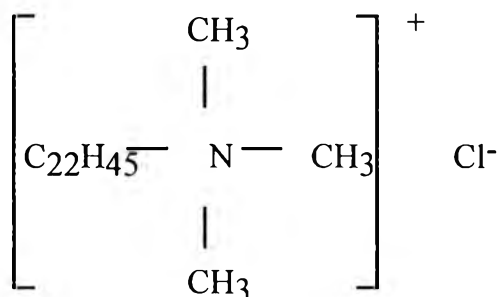


Figure 2.2 The chemical structure of BTAC.

Fatty alcohol

The fatty alcohol is the mixture of cetyl and stearyl alcohol containing 15% of cetyl and 85% of stearyl alcohol. Its melting point is equal to 48.5 °C. It was used as a component in the formation of lamellar phase and was obtained from Unilever Thai Holdings, Ltd.

Polymers

1) Hydroxyethyl cellulose

Hydroxyethyl cellulose or HEC is a nonionic water soluble polymer derived from cellulose. It was used as a thickening agent or rheology modifier and was obtained from Unilever Thai Holdings, Ltd.. Its solubility characteristics allows easy dispersion in hot or cold water. The physical state of HEC is white granular powder. The structure of HEC is shown in figure 2.3

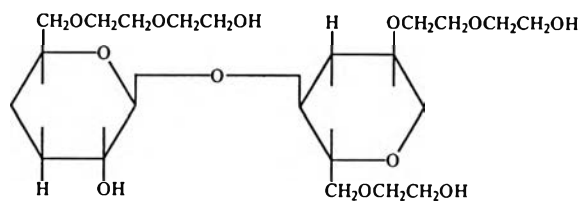


Figure 2.3 The structure of Hydroxyethyl cellulose.

2) Modified hydroxyethyl cellulose

Modified hydroxyethyl cellulose was obtained from Unilever Company. Hydrophobic C16 alkyl chains are attached to the backbone chain of HEC. It was also used as a thickening agent. The structure of Modified hydroxyethyl cellulose is shown in figure 2.4

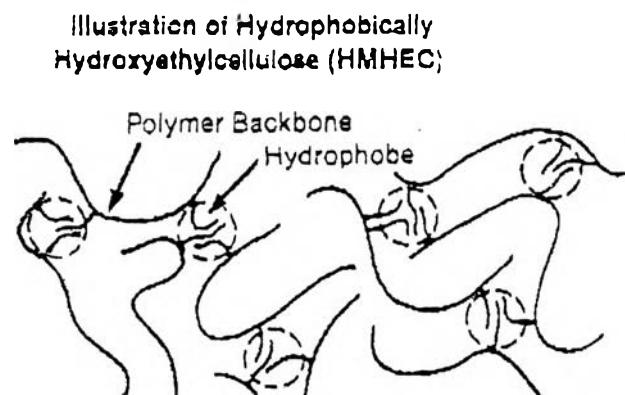


Figure 2.4 The structure of modified hydroxyethyl cellulose.

Solvent

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

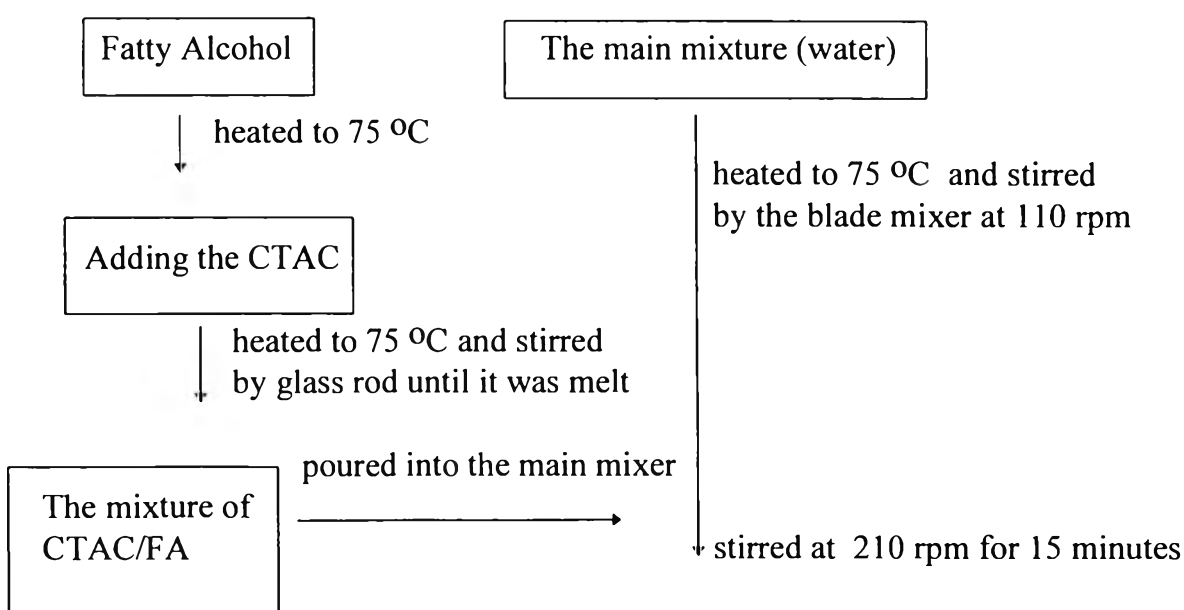
2.2 Methodology

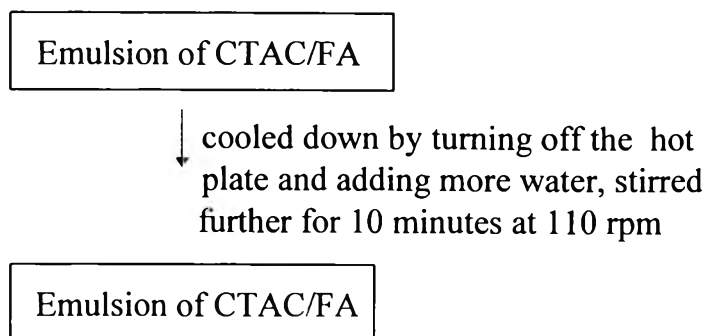
2.2.1 Sample preparation of emulsion of CTAC/FA

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

Once the emulsion of CTAC/FA started to form. It was cooled down by turning off the heater and adding more water, whose temperature was controlled at 45 °C. 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.

Flow chart diagram of preparation of emulsion of CTAC/FA

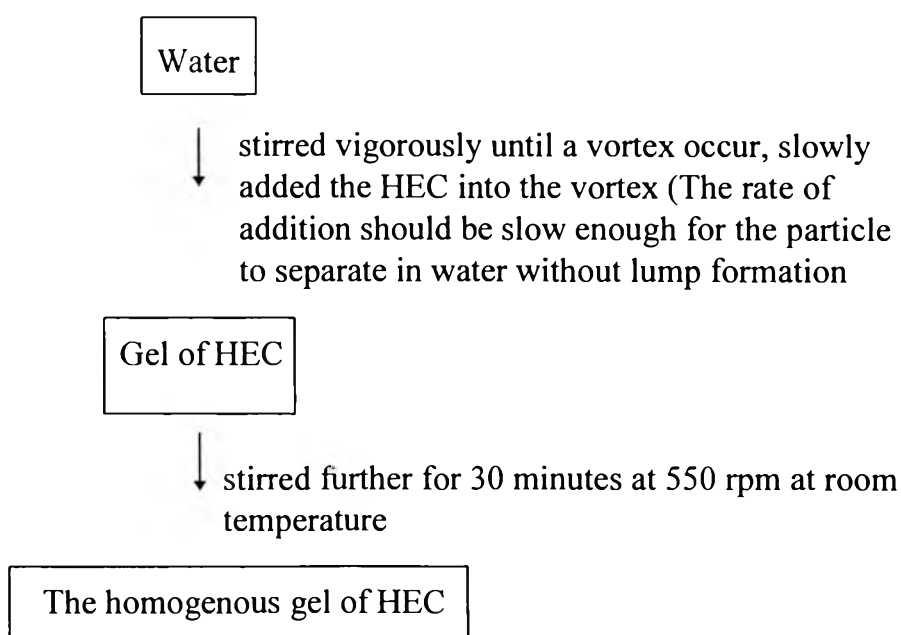




2.2.2 Sample preparation of solution of HEC

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

Flow chart diagram of preparation of solution of HEC

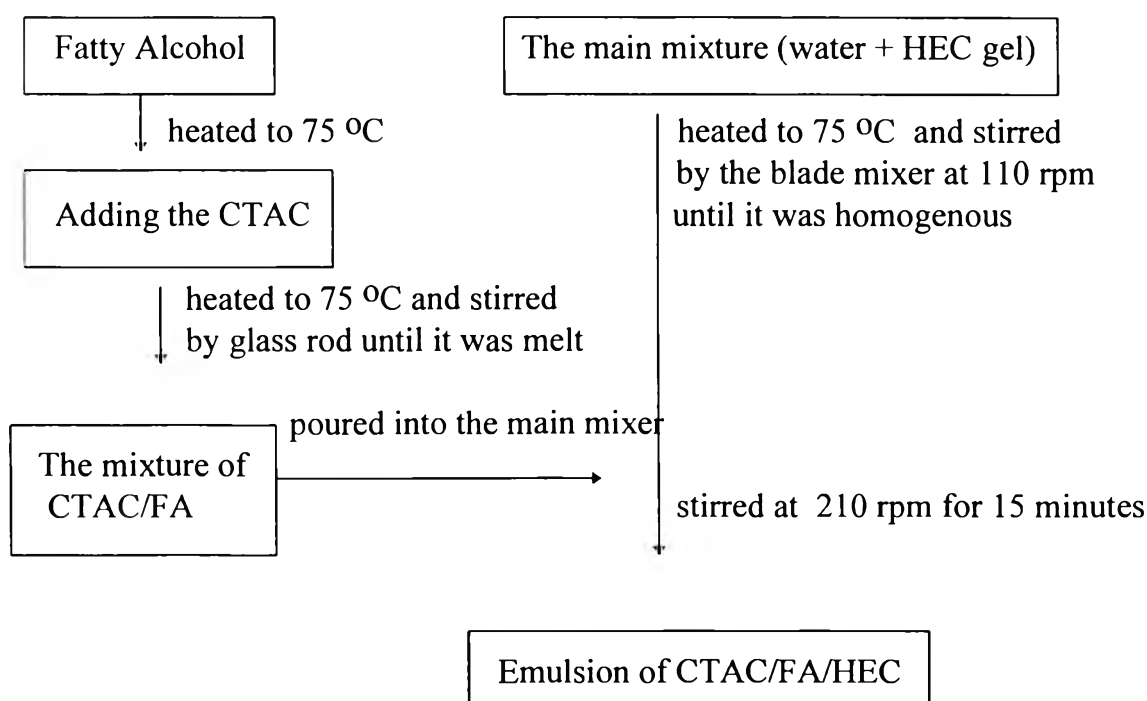


2.2.3 Sample preparation of emulsion of CTAC/FA/HEC

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

Once the emulsion of CTAC/FA/HEC started to form. It was cooled down by turning off the heater and adding more water, whose temperature was controlled at 45 °C. 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.

Flow chart diagram of preparation of emulsion of CTAC/FA/HEC



↓ cooled down by turning off the hot plate and adding more water, stirred further for 10 minutes at 110 rpm

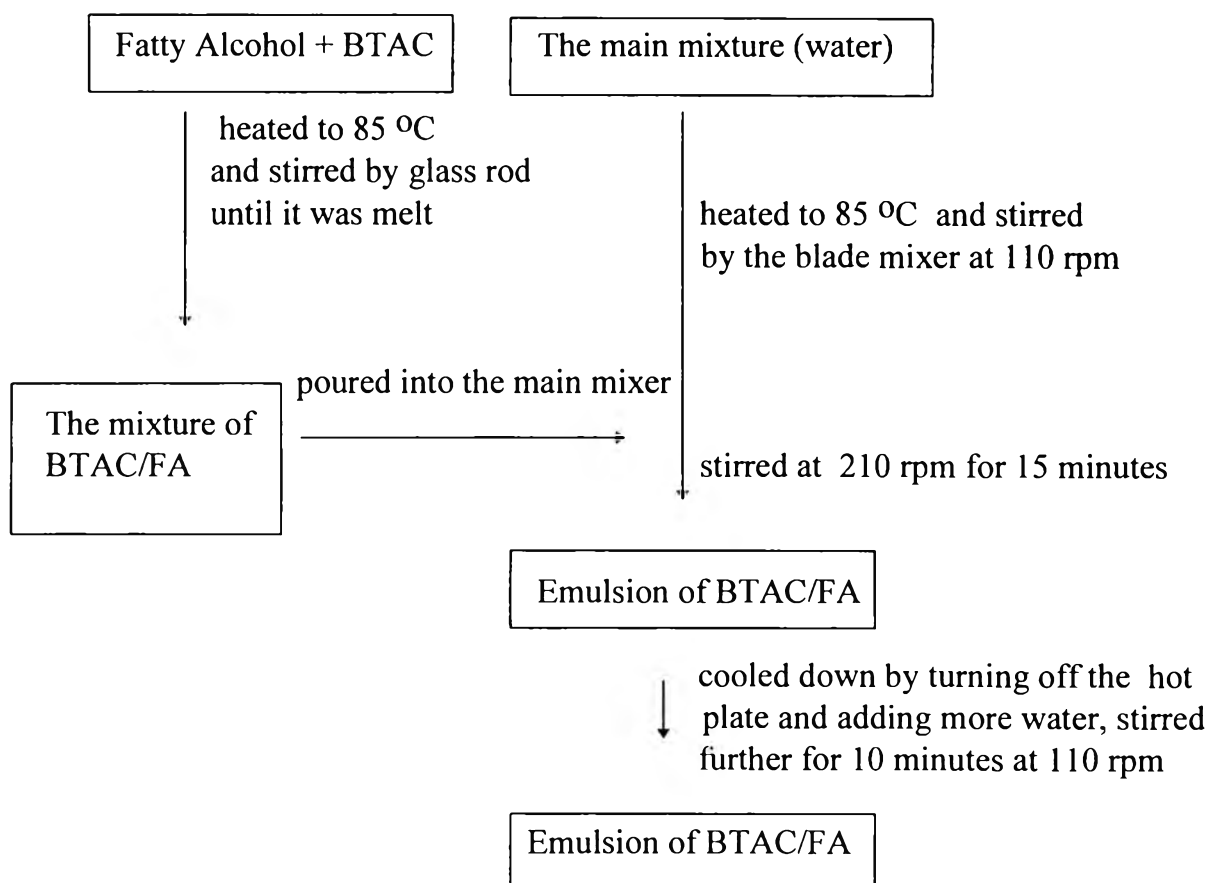
Emulsion of CTAC/FA/HEC

2.2.4 Sample preparation of emulsion of BTAC/FA

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

Once the emulsion of BTAC/FA started to form. It was cooled down by turning off the heater and adding more water, whose temperature was controlled at 45 °C. 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.

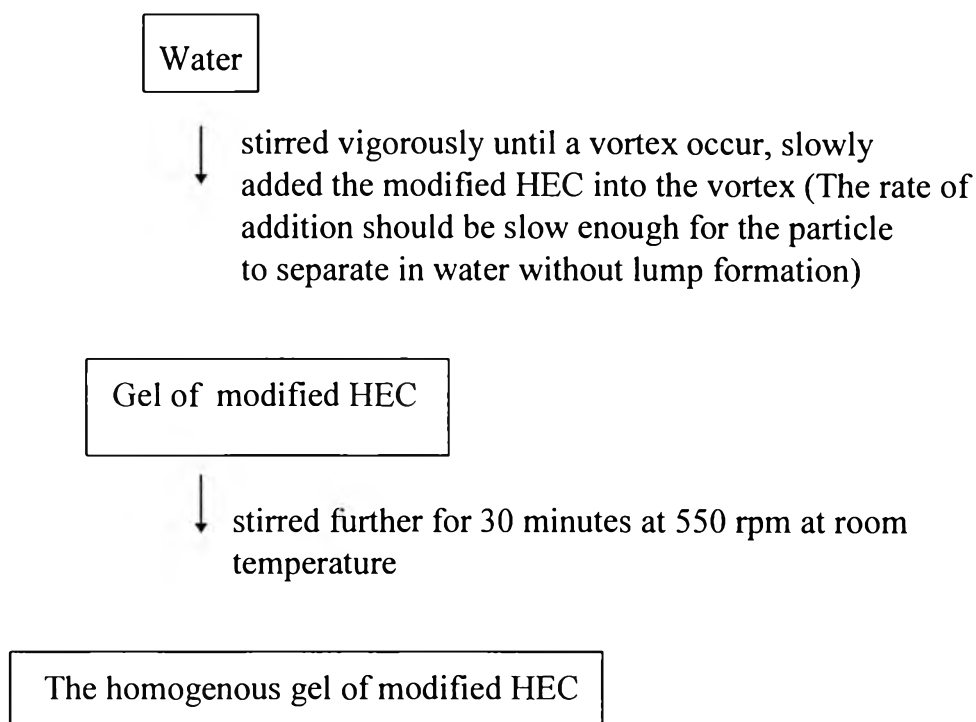
Flow chart diagram of preparation of emulsion of BTAC/FA



2.2.5 Sample preparation of solution of modified HEC

Water was stirred vigorously until a vortex occurred. Then powder of modified HEC was slowly added into the vortex. The rate of addition should be slow enough for the particles to disperse in water without lump formation. The mixture of water and modified HEC was homogenized by a blade mixer using a high speed of 550 rpm for 30 minutes. Finally the gel of HEC was obtained at room temperature. Unlike HEC solution which appears stringy during flow, Modified HEC dispersion was not stringy and appeared “Blob-like” during flow.

Flow chart diagram of preparation of solution of modified HEC

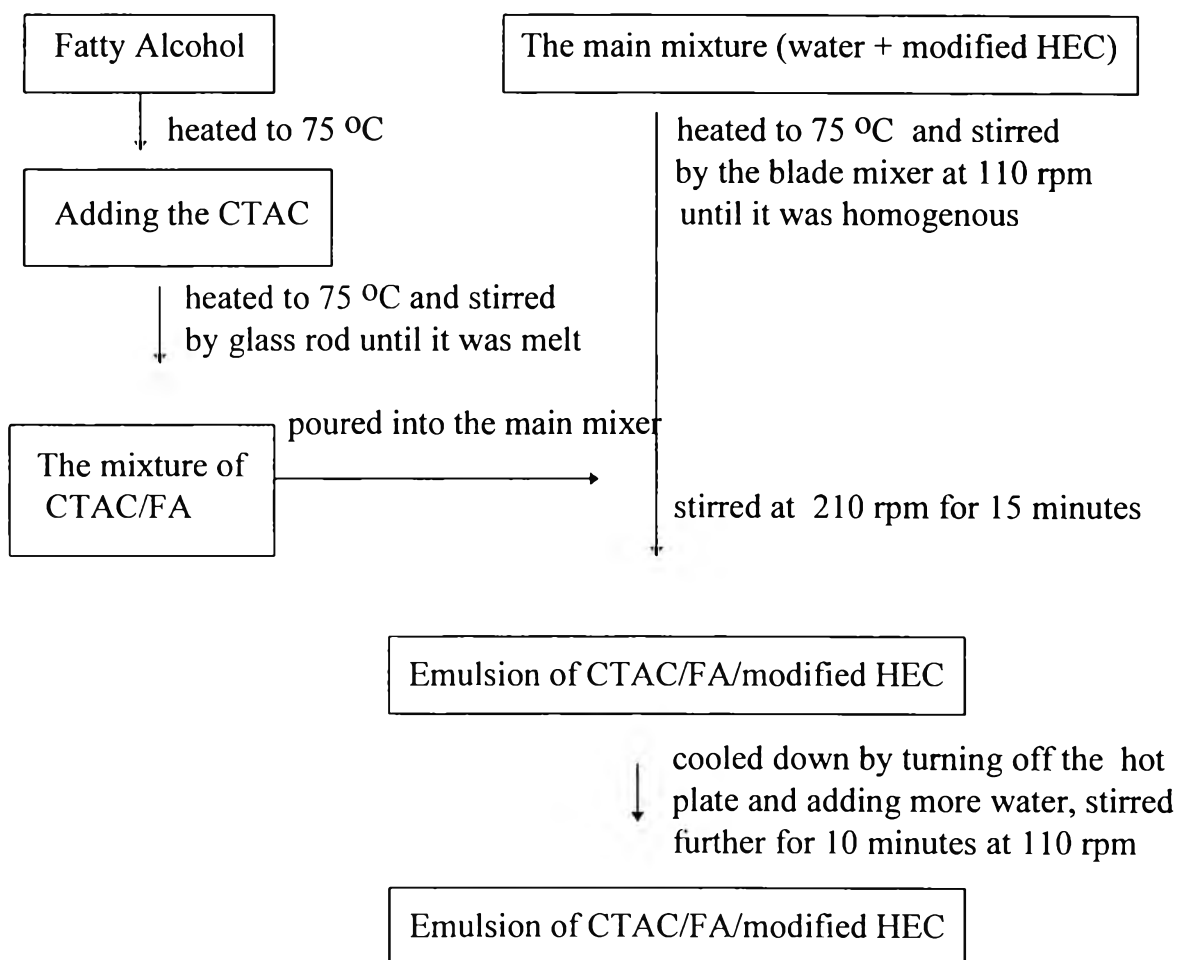


2.2.6 Sample preparation of emulsion of CTAC/FA/modified HEC

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

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

Flow chart diagram of preparation of emulsion of CTAC/FA/modified HEC



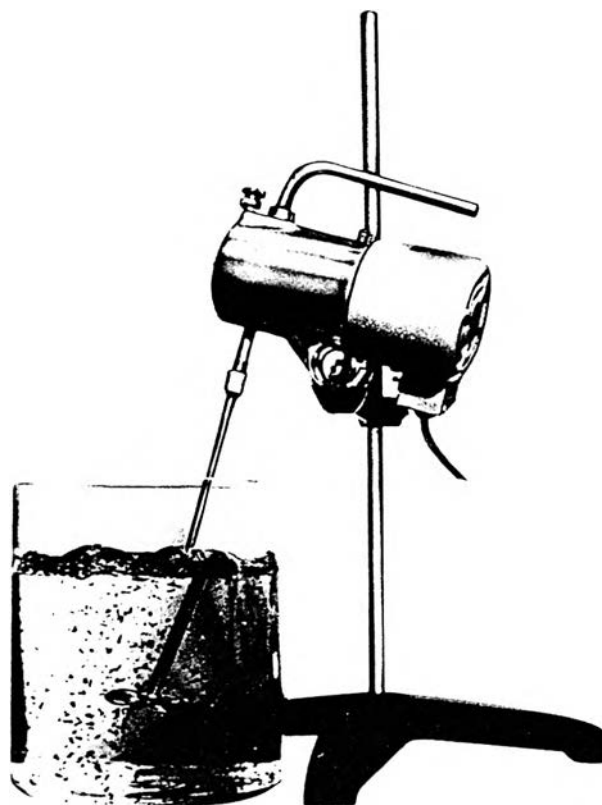


Figure 2.5 The propeller or blade mixer.

2.3 Apparatus

2.3.1 Laser Scanning Microscope

The LSM 410 inverse laser scan microscope from Zeiss Inc., was used. Laser scanning microscope were used to investigate the structure of emulsion . This microscope can be regarded as the single most important emulsion characterization tool. It can give the 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 using the usual contrast methods such as bright field, dark field, differential interference contrast, phase contrast, fluorescence and polarization.

Basic LSM system : It is based on beam scan system, detector unit, control computer including keyboard, mouse and color monitor for display and control monitor.

Laser unit : This part consists of one or two internal lasers.

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

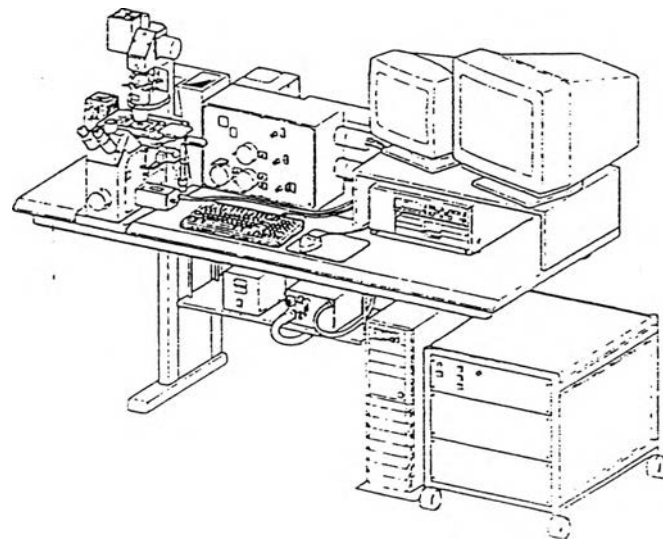


Figure 2.6 General view of the LSM system.

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 (see in figure 2.7). The plane is called 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.

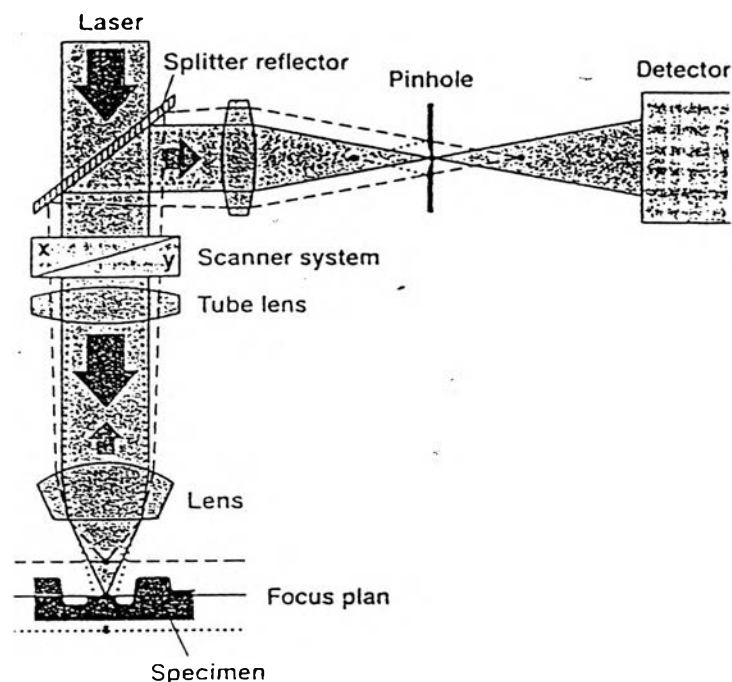


Figure 2.7 Schematic of LSM.

2.3.2 Rheometer

The fluid rheometer, model ARES, is from Rheometric Scientific Inc., was used to measure the rheological properties of emulsion in oscillatory and steady-state mode. It is a strain controlled instrument. The base system (see figure 2.9) consists of the test station, power chassis, and host computer. In this thesis, cone-and-plate rheometer was used. This apparatus consists of 2 circular disks, stationary upper plate and oscillating lower plate, separated by a thin gap where the sample is placed. The bottom plate will oscillate at frequency at a specified strain. The top plate is held stationary and the torque is measured by a transducer. Torque can be converted to shear stress and other viscoelastic properties such as storage modulus, loss modulus, tangent, etc.

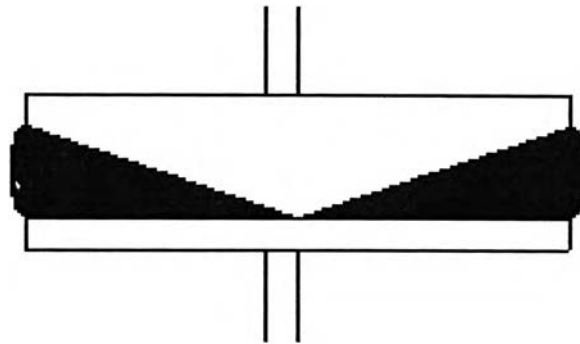


Figure 2.8 The cone-and-plate configuration.

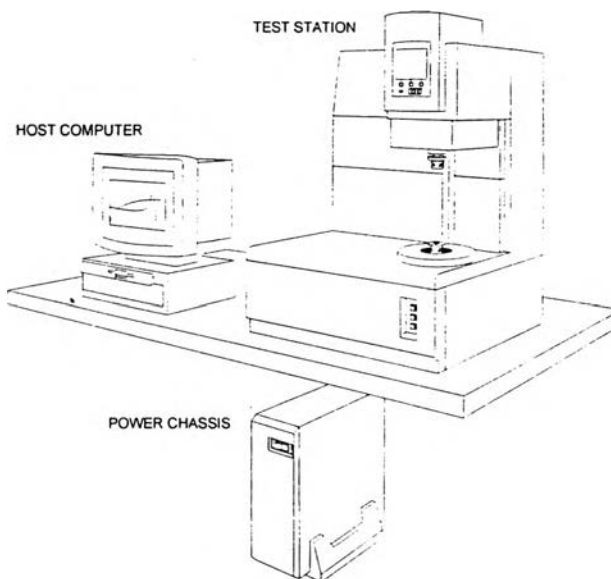


Figure 2.9 The Base System.

2.4 Experimental Conditions

2.4.1 Conditions in microscope measurement

Each sample was placed on a glass slide and covered by the cover glass. The specimen was then placed on the objective lens in order to measure the structure of emulsion. The measurement were performed in transmitted-light mode and used confocal to reconstruct an image. The

magnification is 1000 times, 10 magnification for the objective lens and 100 magnification for eyes piece lens. The picture were taken at the pin hole of 10 and enlargement of 7.

2.4.2 Conditions in oscillatory measurement

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's 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 a Fluid Rheometer using the cone-and-plate geometry with a cone angle of 4° and a diameter of 50 mm. The gap range was 0.051 ± 1 mm. The experiments were carried out at the frequency of 1.0 rad/s, at the temperature of 26 ± 1 °C. Initial strain and final strain were equal to 0.1 and 100 %, respectively. For these measurements, the level of strain was determined in order to ensure that all measurements were made within the linear viscoelastic regime.

2) Dynamic frequency sweep default test

After the fluid's 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 length scales. In the

dynamic frequency sweep mode measurements are made over a range of oscillation frequency at a constant oscillation amplitude and temperature.

Below the critical strain, the elastic modulus for a solid-like material is usually nearly independent of frequency which is expected for a solid-like material. The greater frequency dependent elastic modulus implies that the material is the more fluid-like material.

The measurements were performed by a Fluid Rheometer using the cone-and-plate geometry with a cone angle of 4° and a diameter of 50 mm. The gap range was 0.051 ± 1 mm. The experiments were carried out at the temperature of 26 ± 1 °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.

2.4.3 Conditions in steady shear measurement

1) Steady rate sweep default test

We would like to measure the flow properties of emulsion namely the viscosity as a function of shear or strain rate. For this measurement, the shear-thinning characteristic of emulsion is observed.

The measurements were performed by a Fluid Rheometer using the cone-and-plate geometry with a cone angle of 4° and a diameter of 50 mm. The gap range was 0.051 ± 1 mm. The experiments were carried out at the temperature of 26 ± 1 °C. Initial rate and final rate were equal to 0.01 and 100 1/s, respectively. The data mode was time based. Time delay and measurement time 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 constructed.