CHAPTER II
EXPERIMENTAL SECTION

2.1 Materials

Cationic surfactants

1) Cetyltrimethyl ammonium chloride

Cetyltrimethyl ammonium chloride (CTAC) 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 isopropyl alcohol 36% and water 14%, which appears as a yellowish viscous liquid. The structure of CTAC is shown in Figure 2.1.
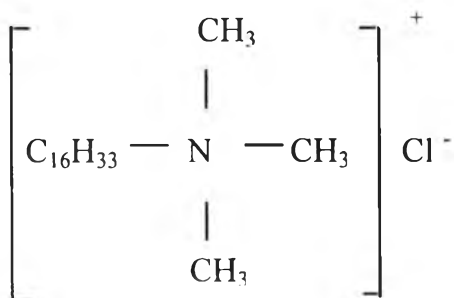
$$\left[C_{16}H_{33} - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{N}} - CH_3 \right]^{+} \quad Cl^{-}$$

Figure 2.1 The chemical structure of CTAC.

2) Behenyltrimethyl ammonium chloride

Behenyltrimethyl ammonium chloride (BTAC) 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 a white solid. The structure of BTAC is shown in Figure 2.2.
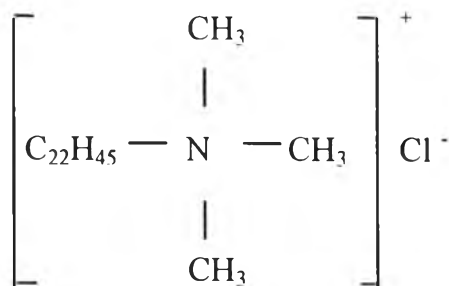
$$\left[C_{22}H_{45} - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N}} - CH_3 \right]^{+} Cl^{-}$$

Figure 2.2 The chemical structure of BTAC.

Fatty alcohol

The fatty alcohol (FA) is the mixture of cetyl and stearyl alcohol containing 15% of cetyl and 85% of stearyl alcohol. Its melting point is equal to 53.0 °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 (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 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 2.3.
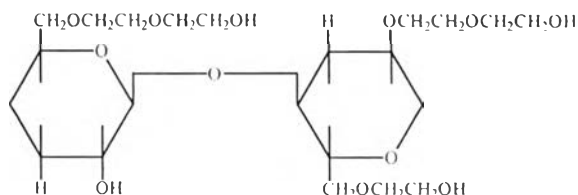

Figure 2.3 The structure of Hydroxyethyl cellulose.

Solvent

Deionized distilled water was used as the pure solvent 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, while 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

```
┌─────────────────┐              ┌──────────────────────────┐
│  Fatty Alcohol  │              │  The main mixture (water)│
└─────────────────┘              └──────────────────────────┘
        │ heated to 75 °C                    │
        ▼                                     │ heated to 75 °C and stirred
┌─────────────────┐                          │ by the blade mixer at 110 rpm
│ Adding the CTAC │                          │
└─────────────────┘                          │
        │ heated to 75 °C and stirred        │
        │ by glass rod until it was melt     │
        ▼                                     │
┌─────────────────┐  poured into the main mixer
│  The mixture of │ ──────────────────────►  │
│  CTAC/FA        │                           │
└─────────────────┘                          ▼
                              ┌──────────────────────┐
                              │  Emulsion of TAC/FA  │
                              └──────────────────────┘
                                         │ stirred at   210 rpm for 15
                                         │ minutes  cooled  down  by
                                         │ turning off the hot plate and
                                         │ adding  more  water,  stirred
                                         │ further for 10 minutes at 110
                                         │ rpm
                                         ▼
                              ┌──────────────────────┐
                              │ Emulsion of CTAC/FA  │
                              └──────────────────────┘
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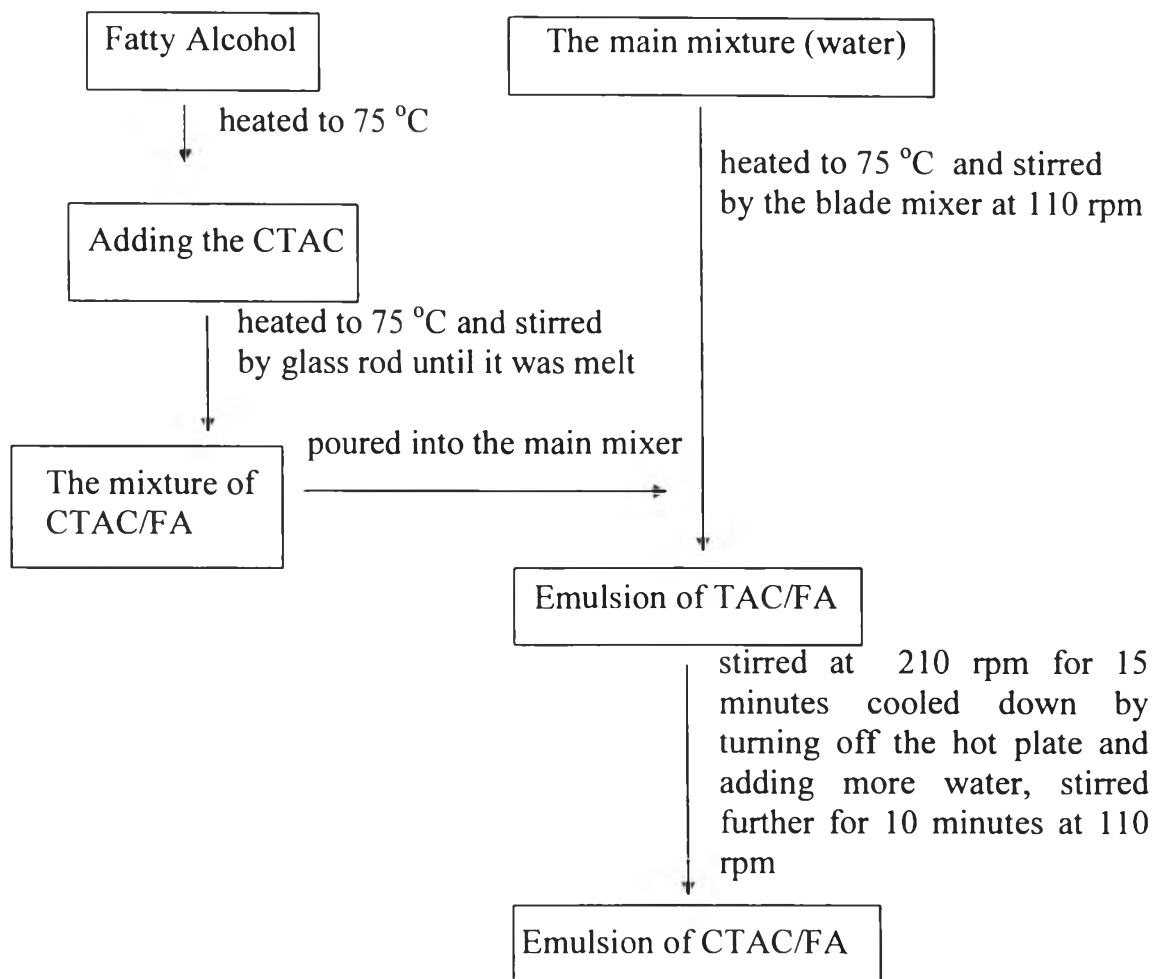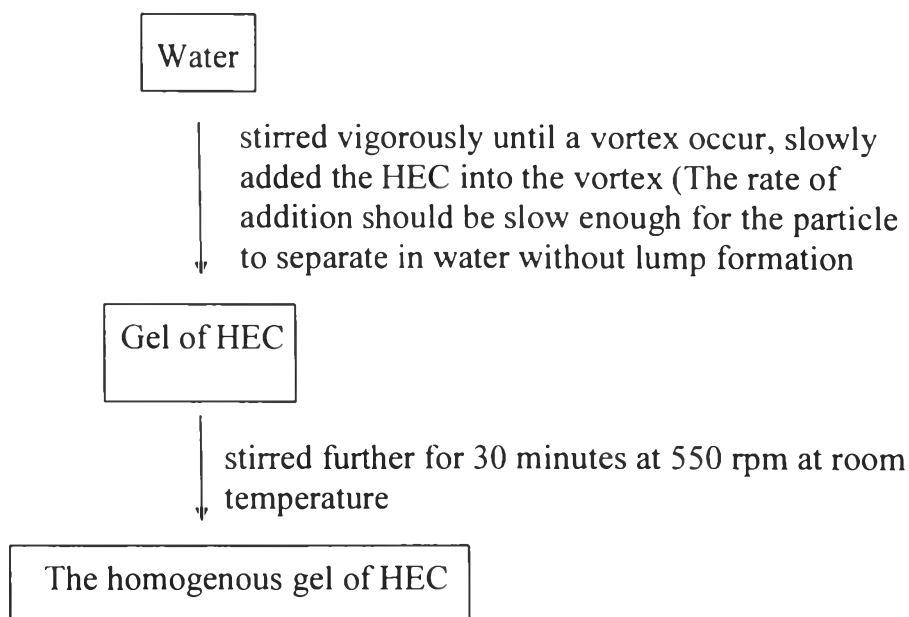
2.2.2 Sample preparation of solution of HEC

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

```
        ┌──────────┐
        │  Water   │
        └──────────┘
             │    stirred vigorously until a vortex occur, slowly
             │    added the HEC into the vortex (The rate of
             │    addition should be slow enough for the particle
             ↓    to separate in water without lump formation
       ┌────────────┐
       │ Gel of HEC │
       └────────────┘
             │    stirred further for 30 minutes at 550 rpm at room
             ↓    temperature
   ┌───────────────────────────┐
   │ The homogenous gel of HEC │
   └───────────────────────────┘
```
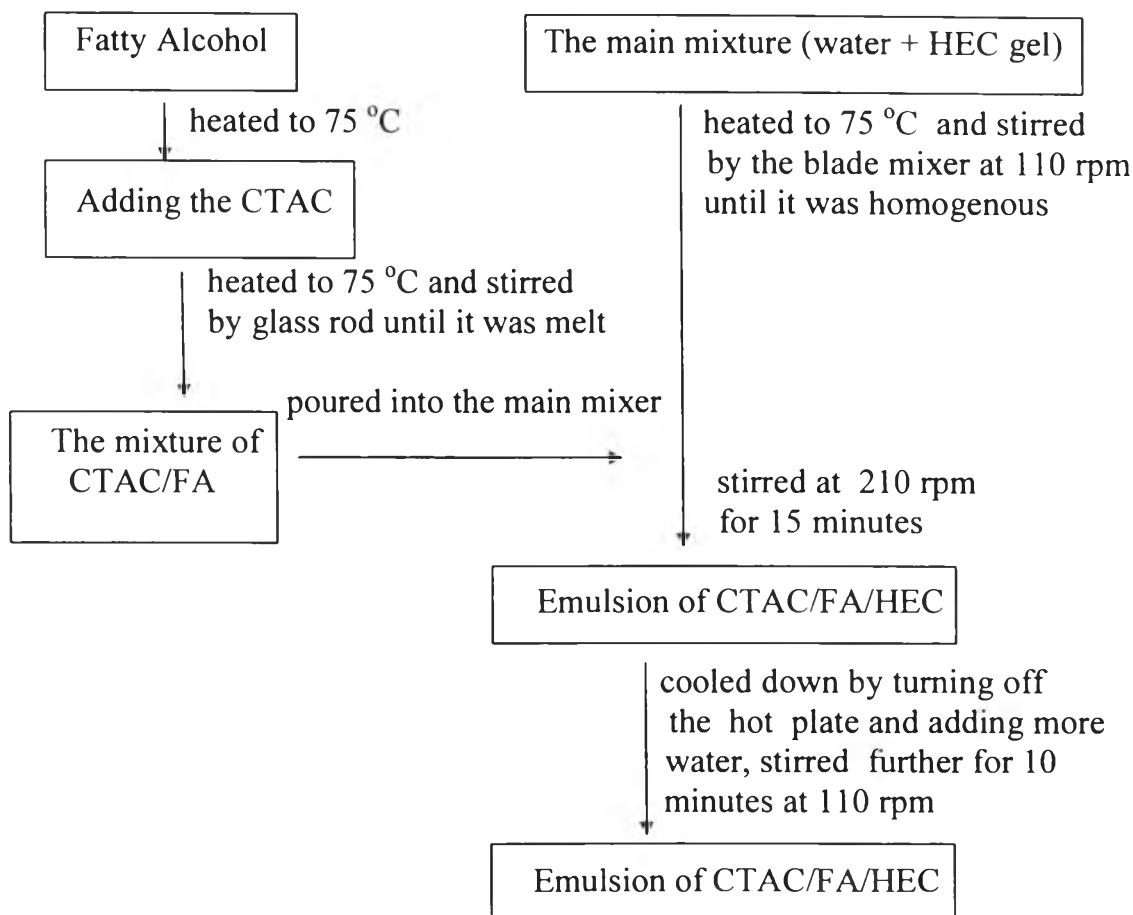
2.2.3   Sample preparation of emulsion of CTAC/FA/HEC

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 was 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.

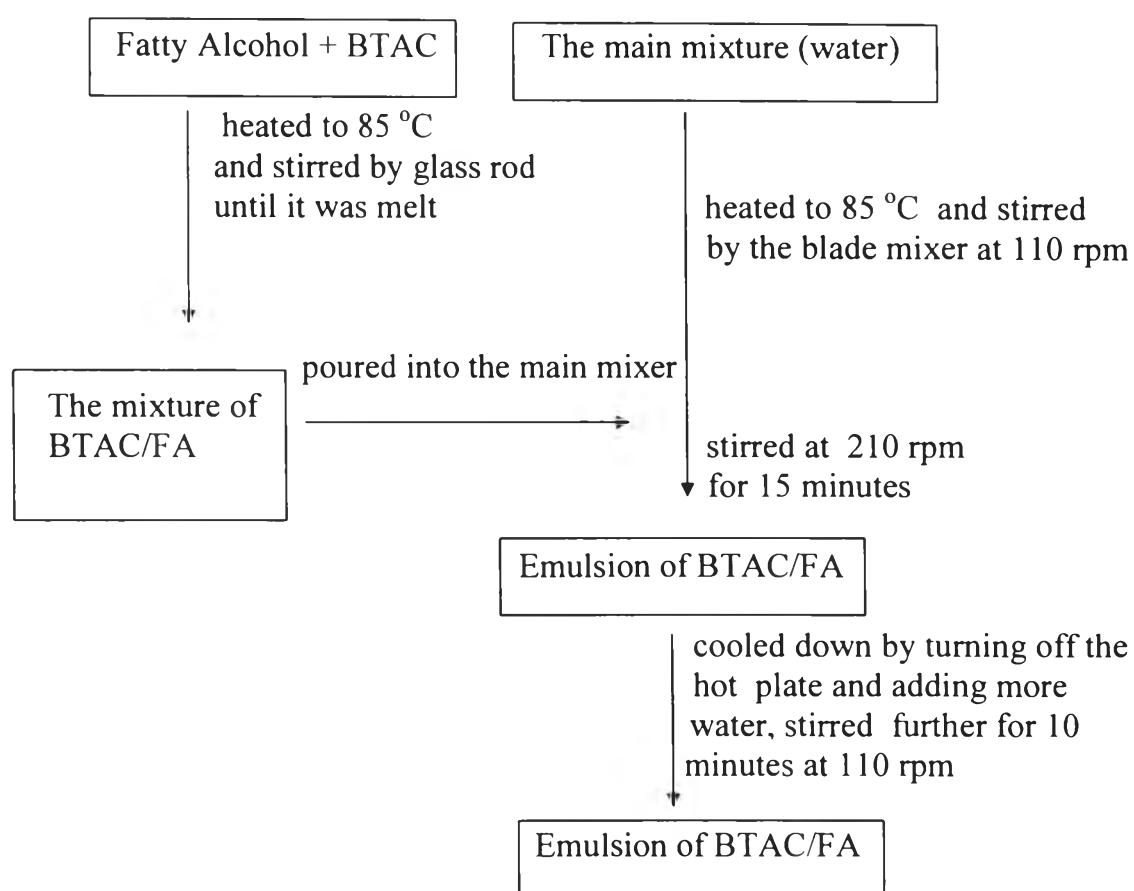**Flow chart diagram of preparation of emulsion of CTAC/FA/HEC**

```
┌─────────────────┐                    ┌──────────────────────────────────┐
│  Fatty Alcohol  │                    │  The main mixture (water + HEC gel) │
└─────────────────┘                    └──────────────────────────────────┘
        │ heated to 75 °C                         heated to 75 °C and stirred
        ▼                                          by the blade mixer at 110 rpm
┌─────────────────┐                                until it was homogenous
│  Adding the CTAC │
└─────────────────┘
        │ heated to 75 °C and stirred
        │ by glass rod until it was melt
        ▼            poured into the main mixer
┌─────────────────┐
│  The mixture of │ ─────────────────────►
│  CTAC/FA        │                                stirred at 210 rpm
└─────────────────┘                                for 15 minutes
                              ┌──────────────────────────────┐
                              │  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      │
                              └──────────────────────────────┘
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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.

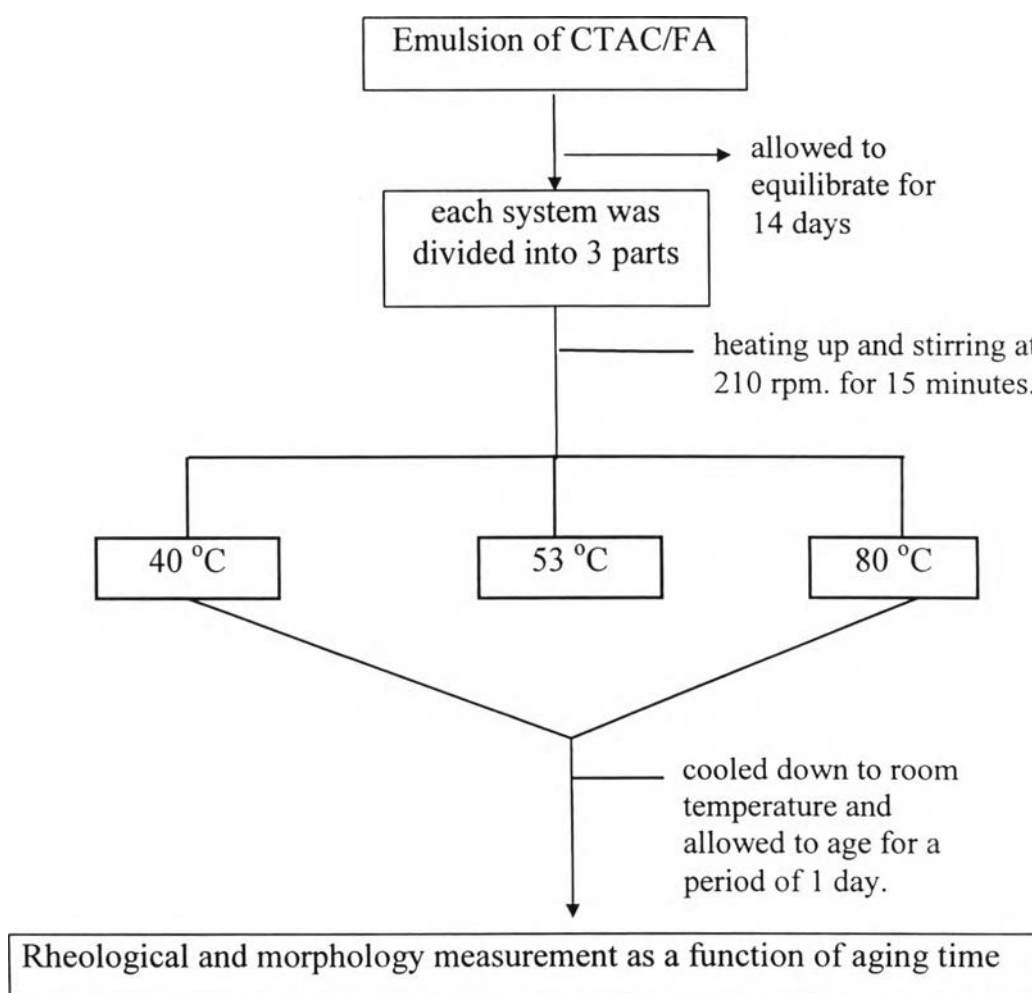**Flow chart diagram of preparation of emulsion of BTAC/FA**

```
┌──────────────────────┐      ┌──────────────────────────┐
│ Fatty Alcohol + BTAC │      │ The main mixture (water) │
└──────────────────────┘      └──────────────────────────┘
         │ heated to 85 °C                  │
         │ and stirred by glass rod         │ heated to 85 °C  and stirred
         │ until it was melt                │ by the blade mixer at 110 rpm
         ▼                                  │
┌──────────────────┐  poured into the main mixer
│ The mixture of   │  ──────────────────────►    │
│ BTAC/FA          │                             │ stirred at 210 rpm
└──────────────────┘                             ▼ for 15 minutes
                    ┌────────────────────┐
                    │ Emulsion of BTAC/FA │
                    └────────────────────┘
                              │ cooled down by turning off the
                              │ hot plate and adding more
                              │ water, stirred  further for 10
                              │ minutes at 110 rpm
                              ▼
                    ┌────────────────────┐
                    │ Emulsion of BTAC/FA │
                    └────────────────────┘
```

2.2.5   Sample preparation of emulsion of CTAC/BTAC/FA

The fatty alcohol and BTAC were heated to 85 °C together 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 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 CTAC/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/BTAC/FA was obtained at room temperature.

Flow chart diagram of preparation of emulsion of CTAC/BTAC/FA
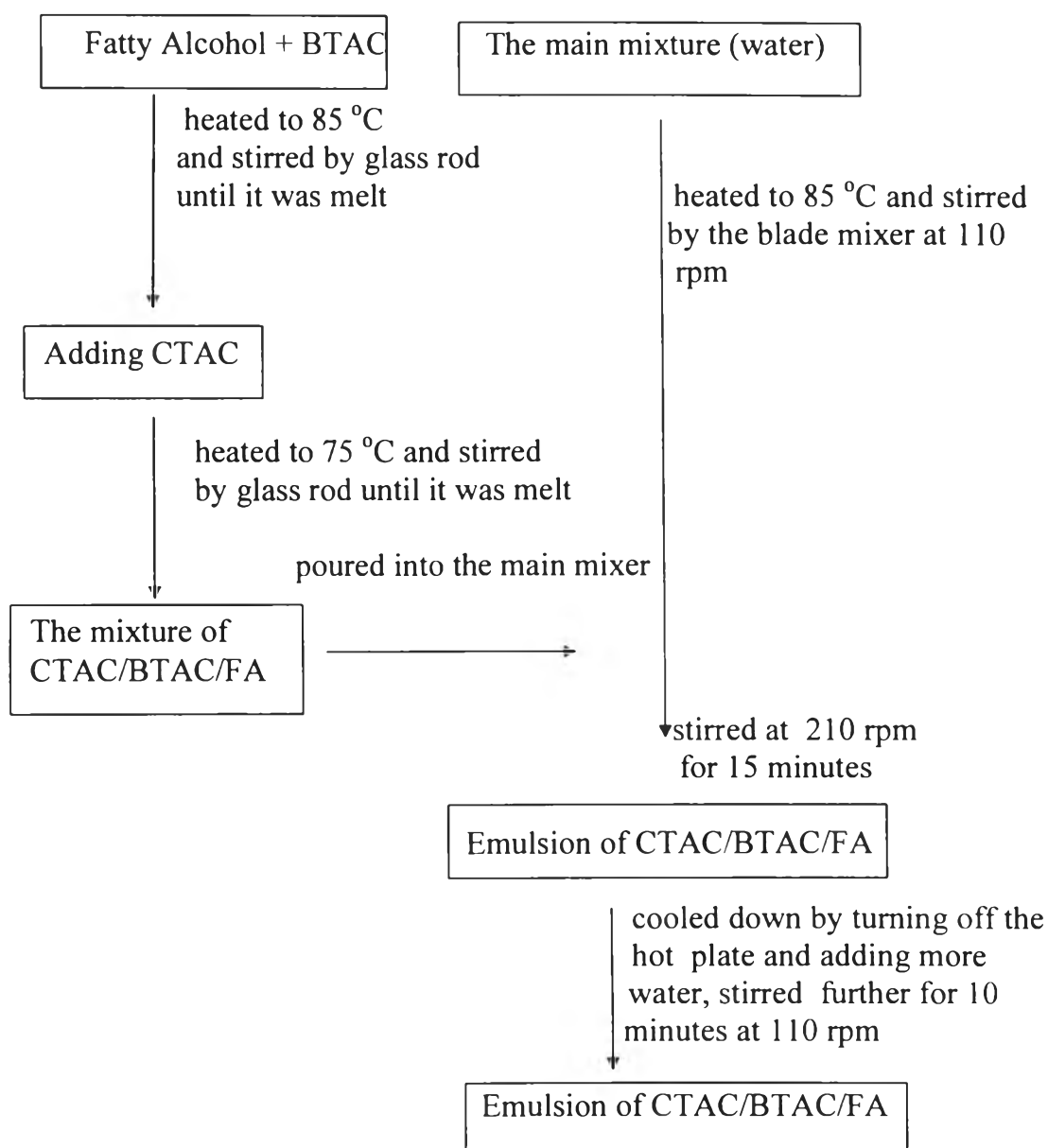
2.2.6 Sample preparation of emulsion for studying effect of annealing

In order to study the effect of annealing. The emulsion was heated to 40, 53, and 85 °C respectively. The emulsion was then stirred by the blade mixer at a slow speed of 110 rpm for a period of 15 minutes. Finally, the emulsion was cooled down to room temperature and allowed to equilibrate for 1 day before measuring the rheological properties as a function of aging time.

Flow chart diagram of preparation of emulsion for studying effect of annealing.

```
         ┌─────────────────────────┐
         │   Emulsion of CTAC/FA   │
         └─────────────────────────┘
                      │
                      │──────────────────► allowed to
                      ▼                     equilibrate for
         ┌─────────────────────────┐       14 days
         │   each system was       │
         │   divided into 3 parts  │
         └─────────────────────────┘
                      │
                      │──────────── heating up and stirring at
                      │             210 rpm. for 15 minutes.
          ┌───────────┼───────────┐
          ▼           ▼           ▼
     ┌────────┐  ┌─────────┐  ┌────────┐
     │ 40 °C  │  │ 53 °C   │  │ 80 °C  │
     └────────┘  └─────────┘  └────────┘
          └───────────┼───────────┘
                      │
                      │──────────── cooled down to room
                      │             temperature and
                      │             allowed to age for a
                      │             period of 1 day.
                      ▼
  ┌──────────────────────────────────────────────────────┐
  │ Rheological and morphology measurement as a function  │
  │ of aging time                                         │
  └──────────────────────────────────────────────────────┘
```

2.3 Apparatus

2.3.1 Laser Scanning Microscope

Laser scanning microscope is a new method for morphological studies in polymer science. The laser scanning microscope, which 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, is a powerful tool for obtaining detailed three dimensional information of morphologies. The LSM 410 inverse laser scan microscope from Zeiss Inc., was used. Laser scanning microscope was used to investigate the structure of emulsion. This microscope can be regarded one of the 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.
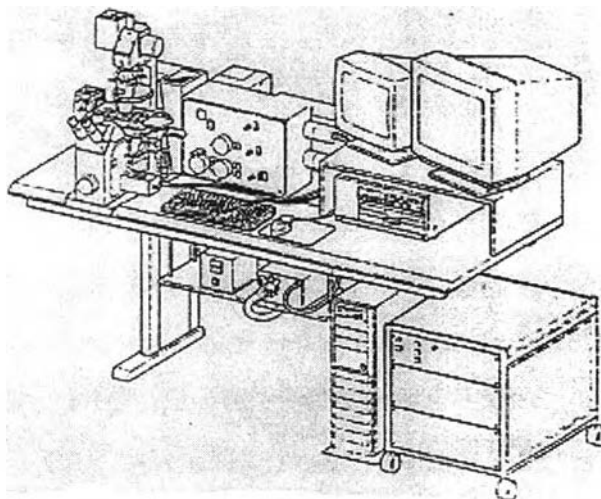
Figure 2.4 General view of the LSM system.

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 2.5). 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.
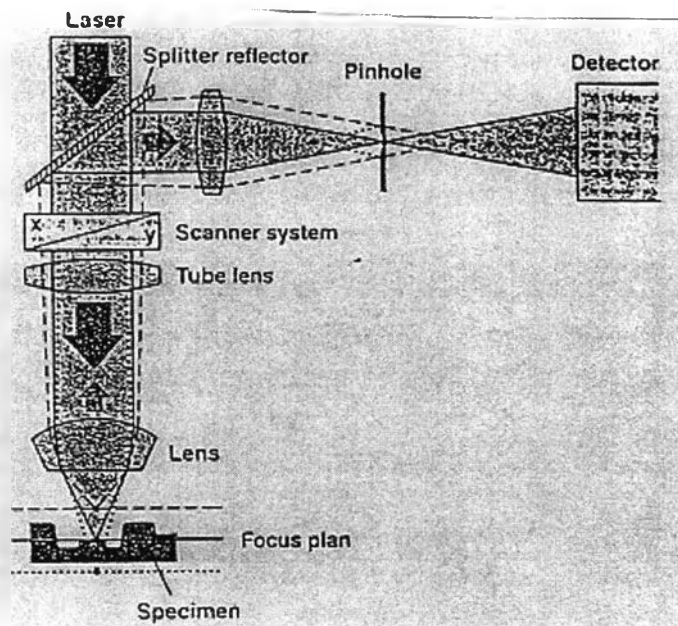
Figure 2.5 Schematic of LSM.

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 modes. It is a strain controlled instrument. The base system consists of the test station, power chassis, and host computer. In this thesis, cone-and-plate rheometer which has a diameter of 50 mm, a cone angle 4° and gap size 0.051 ± 1 mm was used. This 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 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.

Cone-N-Plate Viscometer

Instrument: ARES

The cone-n-plate viscometer is widely used instrument for measurement of shear flow rheological properties of polymer solution. The principal features of this viscometer are shown schematically in Fig 2.6 The sample, whose rheological properties are to be measured, is trapped between the circular conical disk at the top and circular horizontal plate at the bottom. The plate is connected to the drive motor, which rotates the plate at various constant speeds. The shear rate can be assumed to be constant for any point within the gap.
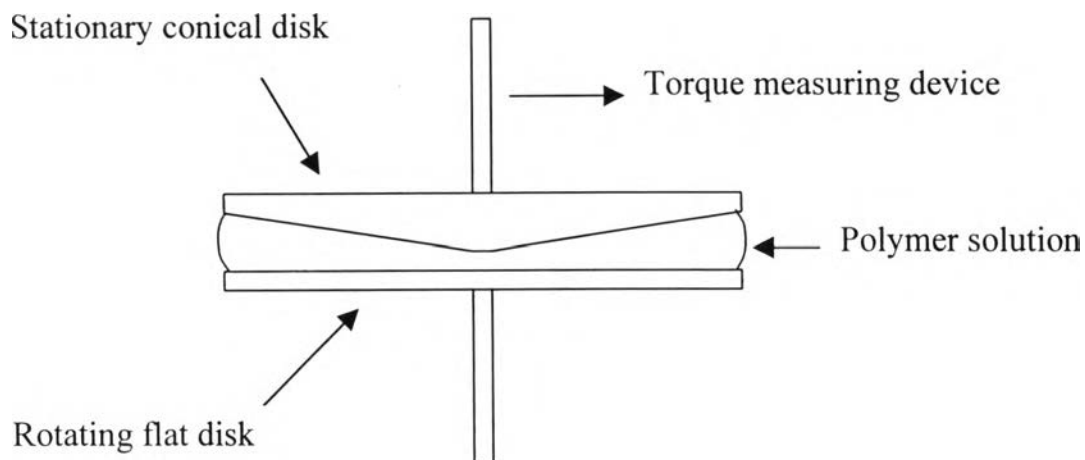
Figure 2.6 Schematic diagram showing the principal features of cone-n-plate

A. Shear Rate

For a constant speed of rotation of N rpm, the linear velocity ($v = \omega r$) is $2\pi rN/60$ cm/sec. Where ω is the angular velocity (rad/sec) and r is the

radial position in centimeters. Then gap height at r is $r\tan\theta_0$ where θ_0 is the cone angle. Hence, the shear rate in reciprocal seconds at r can be written as

$$\dot{\gamma} = \frac{2\pi N}{60 r \tan\theta_0} = \frac{\pi N}{30 \tan\theta_0} \approx \frac{\pi N}{30\theta_0} \qquad (2.1)$$

Because the cone angle is always maintained to be very small, the approximation of $\tan\theta_0 = \theta_0$ does hold well.

B. Shear Stress

The following expression defines the relationship between the measured torque and the shear stress:

$$T = 2\pi\tau_{21}\int_0^R r^2 dr = \frac{2}{3}\pi\overline{R}^3\tau_{21} \qquad (2.2)$$

Thus,

$$\tau_{21} = \frac{3T}{2\pi\overline{R}^3} \qquad (2.3)$$

The shear stress is then obtained in dyn/cm^3 when T is expressed in dyn/cm and $\overline{R}$ in cm. The ratio of Eq. (2.3) to Eq. (2.1) results in the apparent viscosity , expressed in poise.

C. Normal Stress Difference

The cone-n-plate configuration can be used for estimating the primary normal stress difference of the sample. If $\overline{p}$ is the pressure at the point on the plate in excess of that due to the atmosphere pressure, then it can be shown that the total normal force N_F on the plate is given by

$$N_F = \int_0^R 2\pi r\, \bar{p}\, dr \qquad (2.4)$$

which on the integration gives

$$N_F = \frac{\pi \bar{R}^2}{2} N_1 \qquad (2.5)$$

Thus,

$$N_1 = \frac{2N_F}{\pi \bar{R}^2} \qquad (2.6)$$

Using Eq. (2.1) and (2.6), a plot of the primary normal stress versus shear rate can be generated.

The shear stress and primary normal stress measurements can be made simultaneously on the sample when it is subjected to unidirectional rotation shear in the gap of cone-n-plate viscometer.

D. Oscillatory Shear

The cone-n-plate viscometer can be used for oscillatory shear measurements as well. In this case, the sample is deformed by an oscillating driver, which maybe mechanical or electromagnetic. The amplitude of the sinusoidal deformation by the small deformation of a relatively rigid spring or tension bar to which a stress transducer is attached. Because of the energy dissipated by the viscoelastic polymer melt, a phase difference develops between the stress and the strain. The complex viscosity behavior is determined from the amplitudes of the stress and strain and the phase angle between them. The results are usually interpreted in terms of the material functions η', G', G'', and others.

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 was 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 was 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-n-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 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.

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-n-plate geometry with a cone angle of 4 $^\circ$ 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 $^\circ$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'', tanθ = 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 was observed.

The measurements were performed by a Fluid Rheometer using the cone-n-plate geometry with a cone angle of 4 $^\circ$ 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 $^\circ$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 obtained.