

## CHAPTER III

### RESULTS AND DISCUSSION

We have investigated the rheological and optical properties of emulsion as a function of aging time and solute concentrations. The systems studied were:

1. CTAC/FA = 0.7/y (y = 2.0-8.0%)
2. CTAC/FA/HEC = 0.7/y/z (y = 2.0- 8.0% ; z = 0-1.5 %)
3. CTAC/FA/Modified HEC = 0.7/y/z (y = 2.0- 8.0% ;  
z = 0- 1.5 %)
4. CTAC/FA = 1.05/y (y = 2.0-8.0%)
5. BTAC/FA = 0.7/y (y = 2.0-8.0%)
6. BTAC/FA = 1.05/y (y = 2.0-8.0%)

In each system, we will discuss results of certain concentrations since the behavior is similar.

#### 3.1 Effect of Aging Time on Emulsion Structure

Emulsion samples were characterized using a fluid rheometer for the determination of rheological properties in terms of aging time, CTAC, FA, HEC, Modified HEC, and BTAC concentrations.

### 3.1.1 Emulsion of CTAC/FA Systems

We investigated CTAC/FA emulsion systems at the following concentrations:

1)  $CTAC/FA = 0.7/y$

2)  $CTAC/FA = 1.05/y$

where  $y = 2.0, 2.3, 2.8, 3.3, 3.8, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0,$

$7.5, 8.0.$

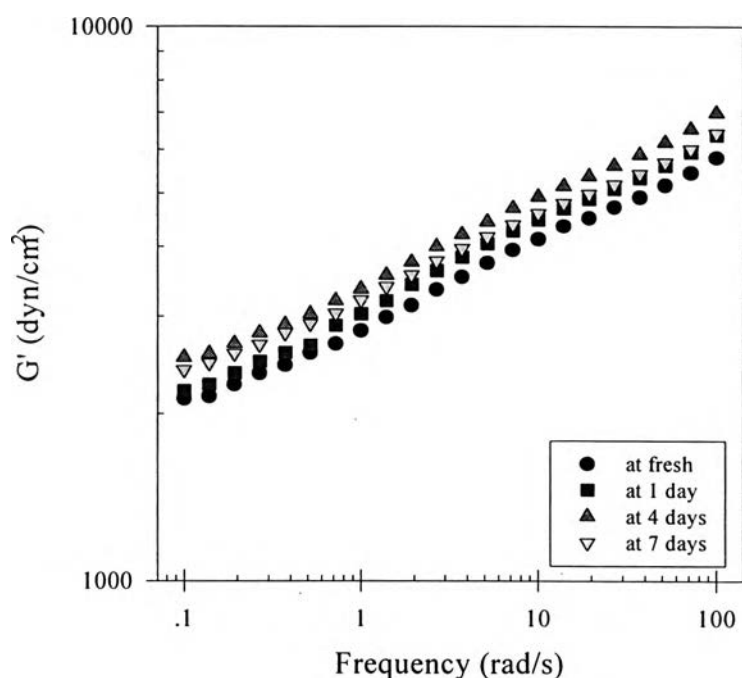


Figure 3.1a Double logarithmic plot of storage modulus against frequency of CTAC/FA = 0.7/3.3% as a function of aging time.

Figure 3.1a shows the frequency-dependent storage modulus of CTAC/FA = 0.7/3.3% mixtures as a function of aging time at room temperature. It can be seen that the storage modulus increases at every frequency with aging time starting from the end of sample preparation (at fresh) until the aging time is equal 7 days. The storage modulus at 7 days is

slightly smaller than that from 4 days. Data suggests that the system possibly reaches the equilibrium state after aging for 7 days.

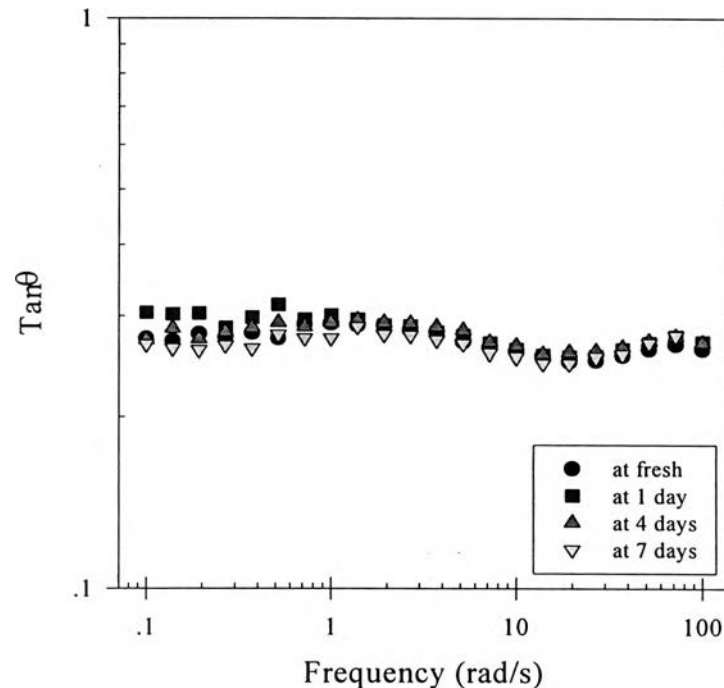


Figure 3.1b Double logarithmic plot of  $\tan\theta$  against frequency of CTAC/FA = 0.7/3.3% as a function of aging time.

Figure 3.1b shows  $\tan\theta$  versus frequency of CTAC/FA = 0.7/3.3% mixtures as a function of aging time.  $\tan\theta$  remains nearly the same at high frequency with aging time. It decreases slightly at low frequency. This implies that the emulsion elasticity increases as a result of some structure formation. The behavior of emulsion changes from viscous or liquid-like to solid-like. At 7 days or at equilibrium,  $\tan\theta$  has the lowest value which can be referred to as the equilibrium solid-like behavior.

Figure 3.2a shows the viscosity of the same CTAC/FA emulsion system versus shear rate as a function of aging time. The viscosity profiles show a pronounced pseudoplastic or shear-thinning behavior. Viscosity at any shear rate increases with aging time and reaches the equilibrium at about 7

days. *Sherman (1991)* found that the viscosity of emulsion can also increase with aging when the dispersed particles of an emulsion aggregate. Initially CTAC and FA can form the lamellar liquid crystalline phase by penetration of CTAC into molten FA. Later the unreacted CTAC penetrate slowly into the crystalline alcohol to form additional network structure as reported by *Barry and Eccleston (1973)*. The larger the lamellar structures, the higher the viscosity. So the viscosity increases with time.

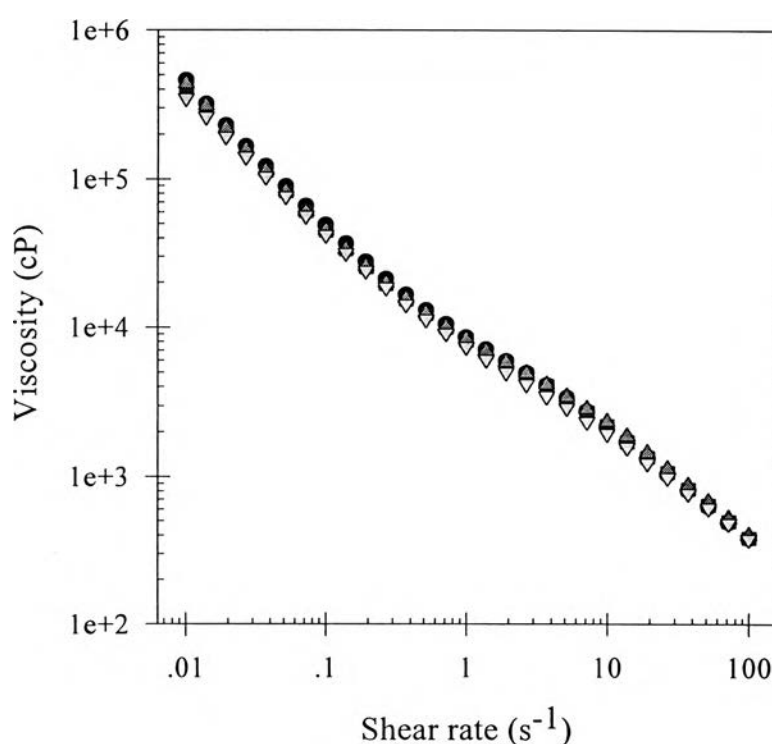


Figure 3.2a Double logarithmic plot of viscosity against shear rate of CTAC/FA = 0.7/3.3% as a function of aging time.

Figure 3.2b shows the stress-strain curves as a function of the aging time. They do not show the yield stress because of its liquid-like behavior in this system. The stress profiles increase with time, and show greater degree of elasticity of the emulsion when aged.

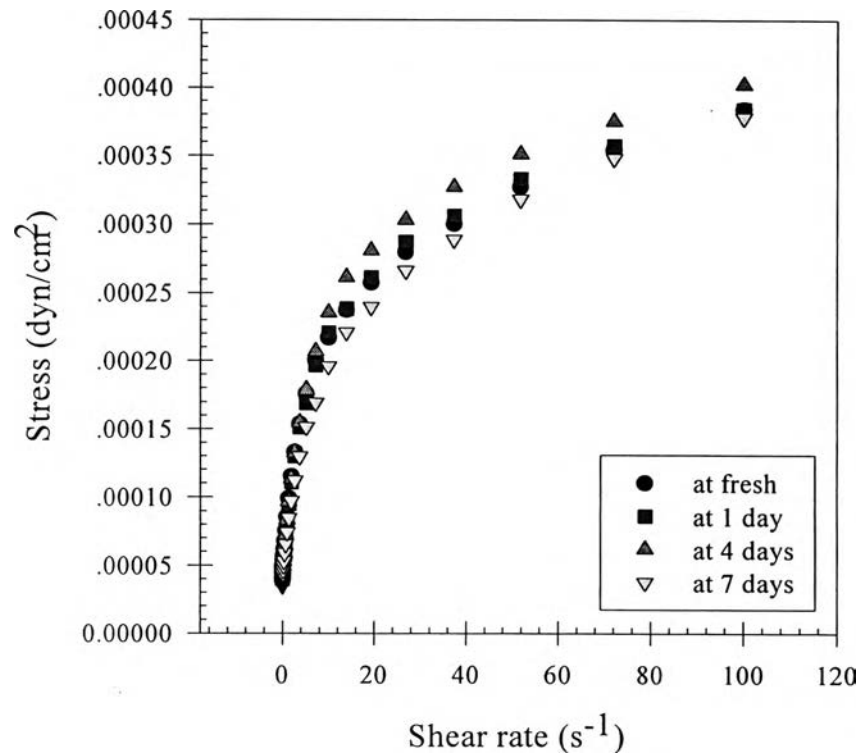


Figure 3.2b Plot of stress against shear rate of CTAC/FA = 0.7/3.3%.

The optical properties were characterized by a laser scanning microscope for monitoring the changes in emulsion structure. In the absence of FA, the cationic surfactant or 0.7%CTAC solution is viscoelastic (*Hoffmann, 1994*). Rod-like micelles were found and seen. Addition of FA induces the formation of lamellar structure. LSM micrographs showed the rod-like to lamellar transition in the CTAC/FA system as shown in figures 3.3 a-e. On microscopic examination of a liquid emulsion of cetostearyl alcohol in mineral oil and cetomacrogol 1000 in water, *Talman and Rowan (1986)* found filaments which they assumed to be cetostearyl alcohol complexed with the surfactant in the aqueous phase. The filaments are referred to as the rigid structural units or three-dimensional gel network which was later reported by *Munzel and Amann (1989)*.

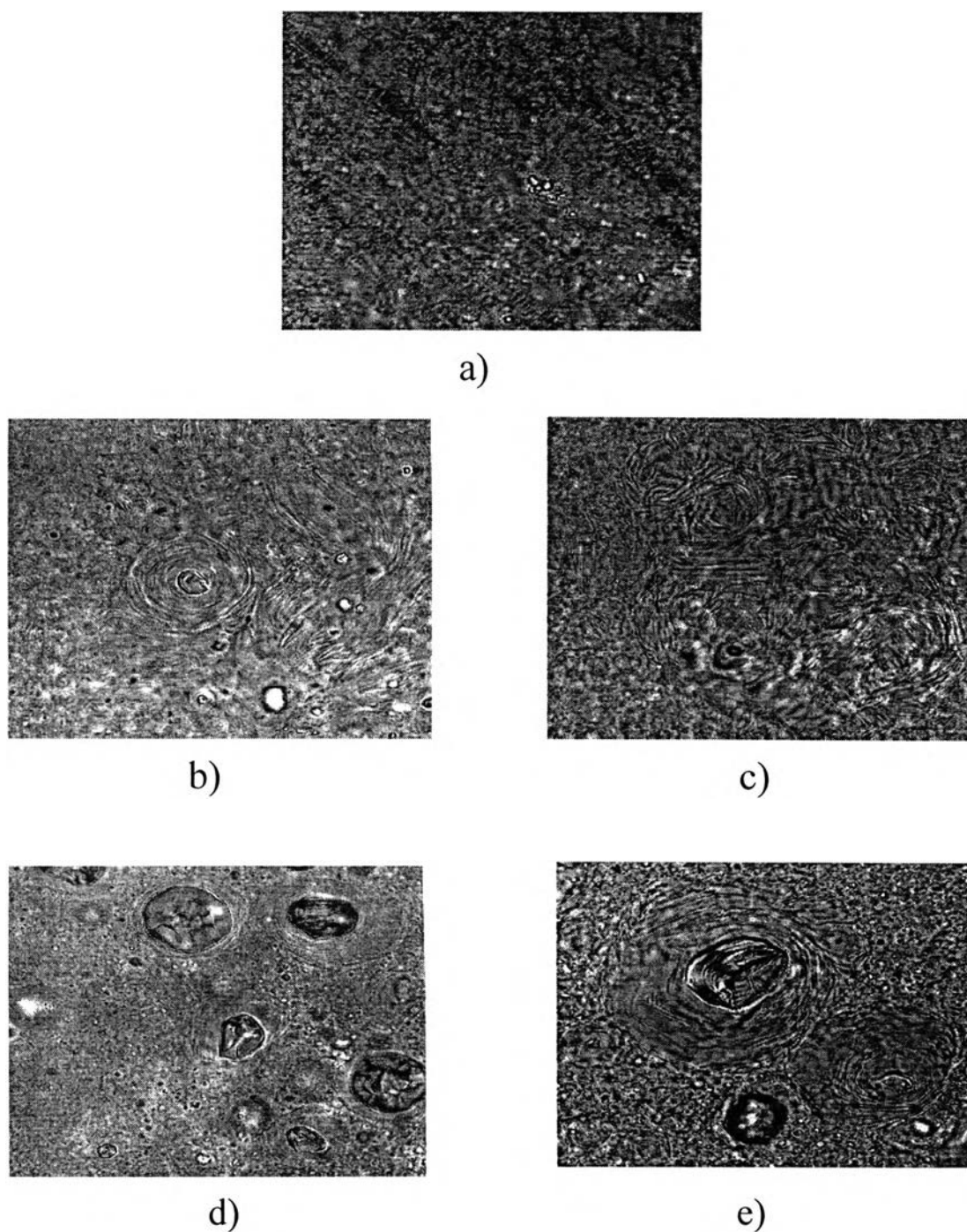


Figure 3.3 Micrograph of CTAC and CTAC/FA = 0.7/y systems:

a) CTAC system; b) FA = 3.3% at 1 day; c) FA = 3.3% at 7 days; d) FA = 8.0% at 1 day; e) FA = 8.0% at 7 day.

The micrographs of CTAC and CTAC/FA system are shown in figure 3.3. Figure 3.3a shows the rod-like micelles of the CTAC system. On addition of FA, the lamellar formation occurs as shown in figure 3.3b-e. It can be seen that the lamellar structure increase their sizes with aging time in both low and high FA concentration. For the mixtures with low FA concentration, it can not be noticed that there are FA left in the middle of structures while for high FA concentration mixtures, we observe that they exhibit excess crystalline FA.

### 3.1.2 Emulsion of CTAC/FA/HEC Systems

We investigated CTAC/FA/HEC emulsion systems at the following concentrations:

1) CTAC/FA/HEC = 0.7/y/z

2) CTAC/FA/HEC = 1.05/y/z

where  $y = 2.3, 3.3, 4.0$  ;  $z = 0.1, 0.3, 0.5, 0.7, 1.0, 1.2, 1.5$ .

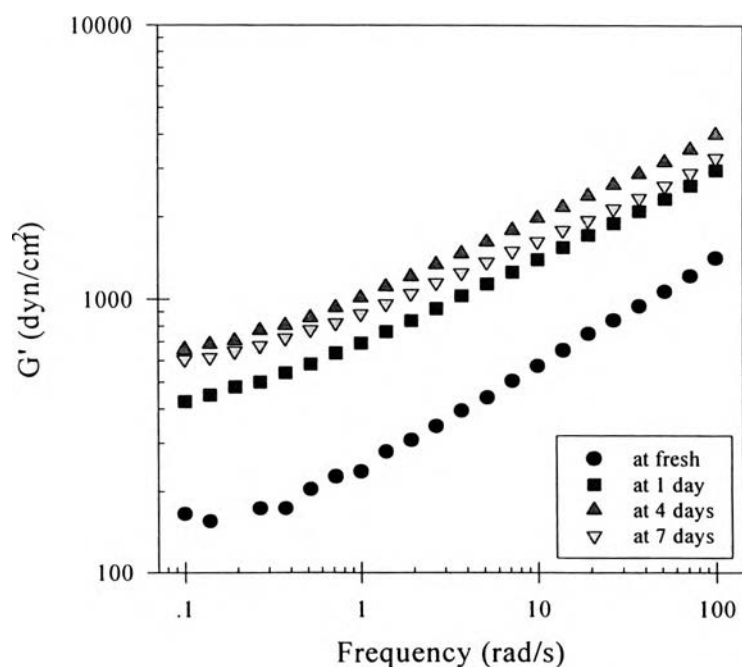


Figure 3.4a Double logarithmic plot of storage modulus against frequency of CTAC/FA/HEC = 0.7/3.3/0.3% as a function of aging time.

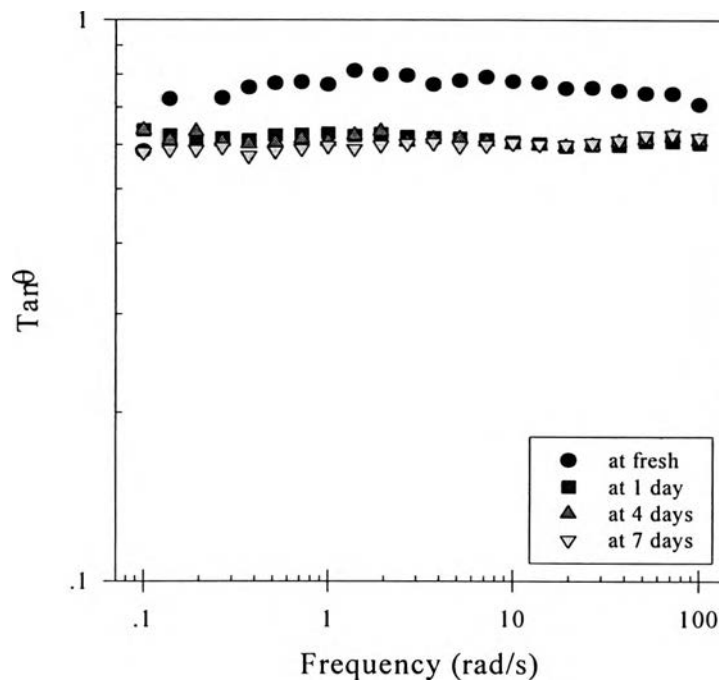


Figure 3.4b Double logarithmic plot of  $\tan\theta$  against frequency of CTAC/FA/HEC = 0.7/3.3/0.3% as a function of time.

Figure 3.4a shows the storage modulus versus frequency of the CTAC/FA/HEC system. The storage modulus dramatically increases at all frequency from the fresh solution to 1 day and the changes only slightly from 4 days to 7 days of aging. This occurs because the polymer can change the rate of lamellar phase formation via the interaction between the polymer and the cationic surfactant. For the system with polymer, the formation of lamellar occurs more slowly than in the system without polymer. The storage modulus of the system without polymer (figure 3.1a) is higher than the system with polymer (figure 3.4a) around 10 times.

Figure 3.4b shows the plot of  $\tan\theta$  against frequency of the same system. Similarly,  $\tan\theta$  sharply decreases from fresh to 1 day. Between 1 to 7 days  $\tan\theta$  remains nearly the same at all frequency.



Figures 3.5a and 3.5b show, respectively the viscosity and stress plotted versus shear rate. Both viscosity and stress increase at a given shear rate with aging time. We observe a Newtonian plateau of the viscosity profile for the fresh solution only. Non-Newtonian behavior occurs at low shear rate with aging of the solution. Figure 3.5b indicates an apparent yield stress whose value grown with aging time.

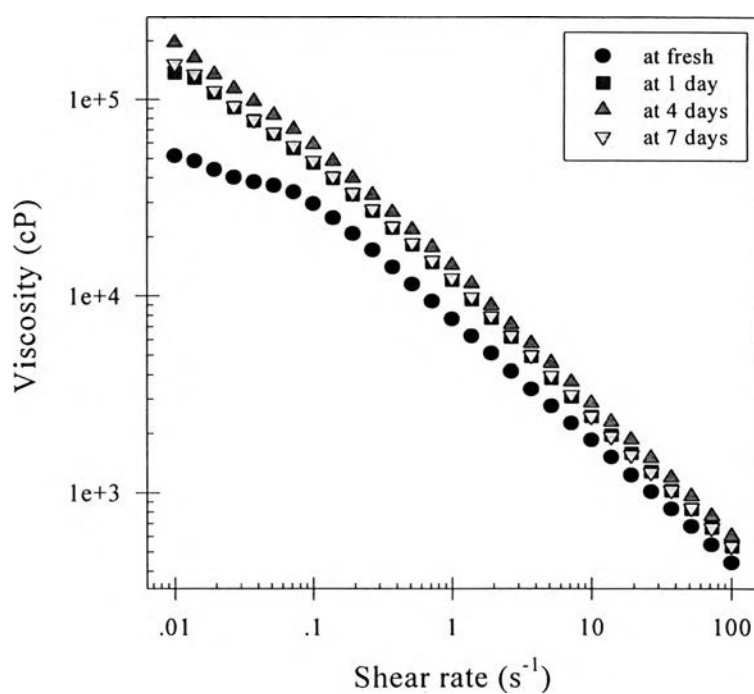


Figure 3.5a Double logarithmic plot of viscosity against shear of CTAC/FA/HEC = 0.7/3.3/0.3% as a function of aging time.

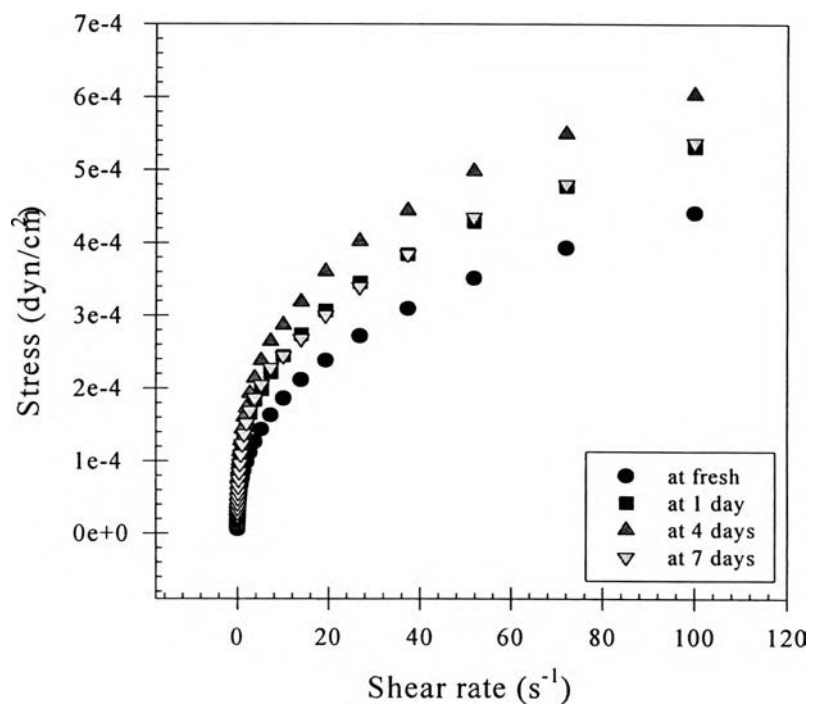


Figure 3.5b Plot of stress against shear rate of CTAC/FA/HEC = 0.7/3.3/0.3%.

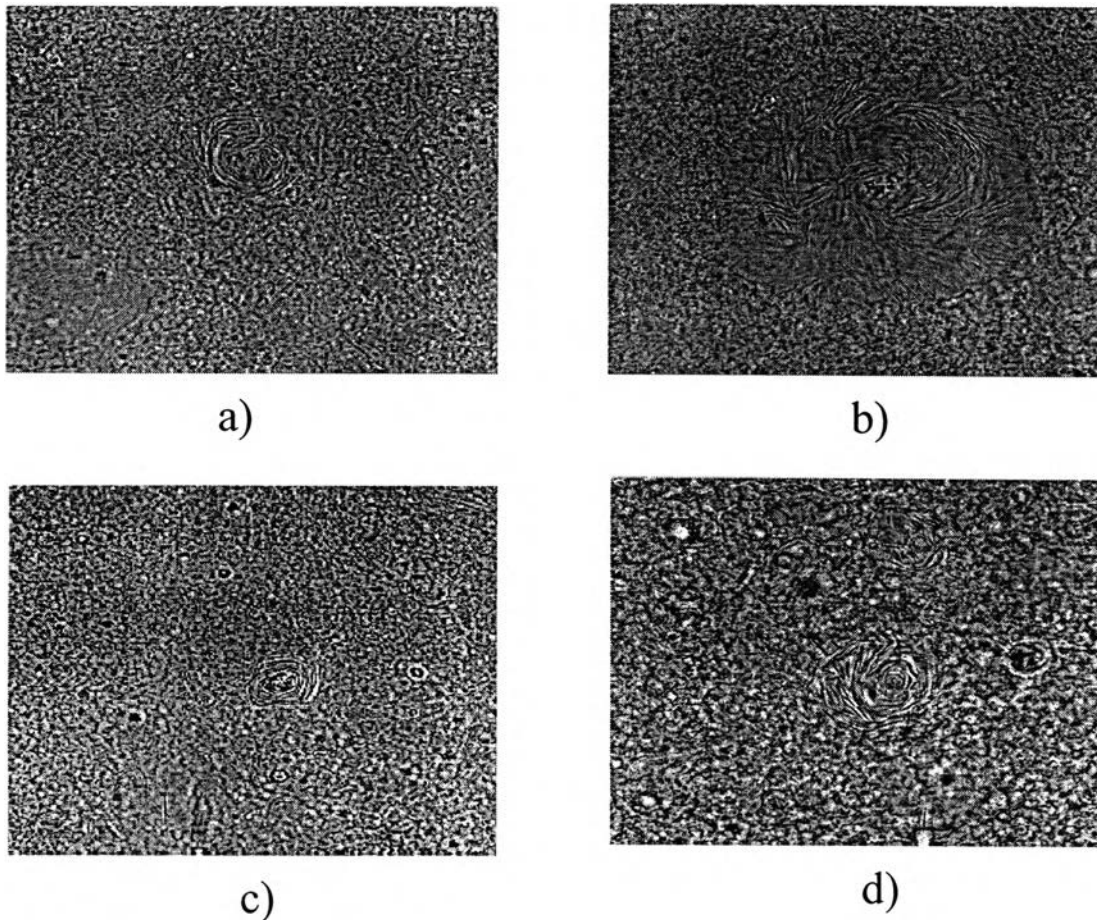


Figure 3.6 Micrograph of CTAC/FA/HEC = 0.7/3.3/z systems:

- a) HEC = 0.075% at 1 day; b) HEC = 0.075% at 7 days;
- c) HEC = 0.7% at 1 day; d) HEC = 0.7% at 7 days.

From micrographs of figure 3.6, the growth of lamellar phase occurs with aging time at both low and high HEC concentrations. For low HEC concentration there is a large amount of lamellar phase relative to mixtures of high HEC concentration, in terms of size and number of lamellar unclussions. This occurs probably because the polymer chain of HEC will interfere with the formation of lamellar phase via the interaction of HEC and CTAC. The change in structure for this emulsion contributes to changes in rheological properties that have been previously shown. The rheological properties such as the decreasing in  $\tan\theta$  showing that the emulsion becomes

more solid-like behavior. The more the lamellar phase, the higher the solid-like behavior.

### 3.1.3 Emulsion of CTAC/FA/modified HEC Systems

We have investigated CTAC/FA in the presence of modified HEC at the following concentrations:

1) CTAC/FA/modified HEC = 0.7/y/z

where  $y = 2.3, 3.3, 4.0$  ;  $z = 0.1, 0.3, 0.5, 0.7, 1.0, 1.2, 1.5$ .

The differences between HEC and modified HEC systems are not only the appearance of emulsion but also the rheological and optical properties. The texture of HEC system is more stringy and easily flow, whereas modified HEC system is not stringy and difficult to flow.

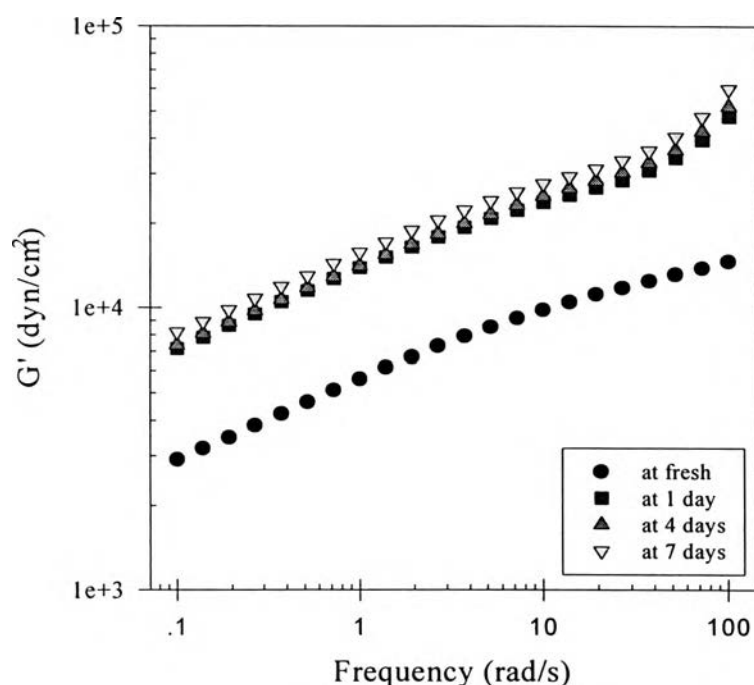


Figure 3.7a Plot of storage modulus against frequency of CTAC/FA/modified HEC = 0.7/3.3/0.7% as a function of aging time.

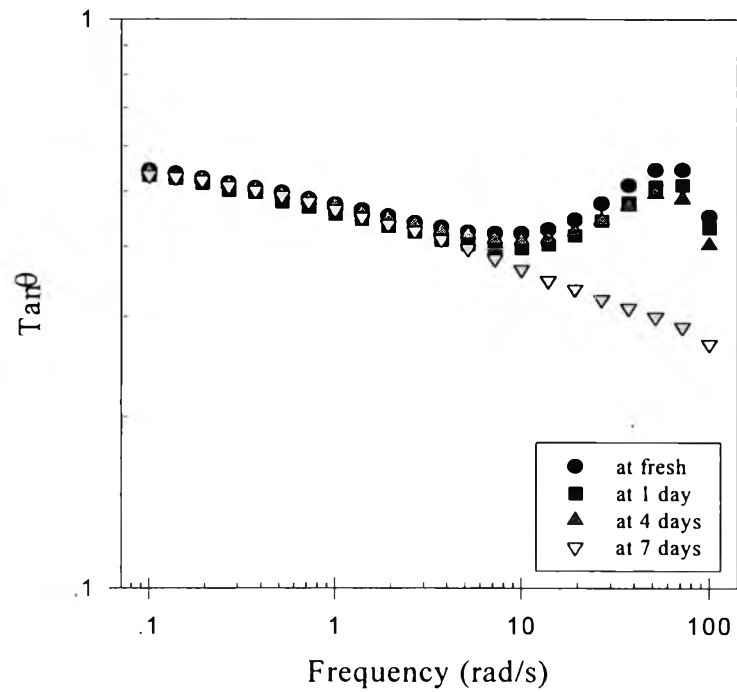


Figure 3.7b Plot of  $\tan\theta$  against frequency of CTAC/FA/modified HEC = 0.7/3.3/0.7% as a function of aging time.

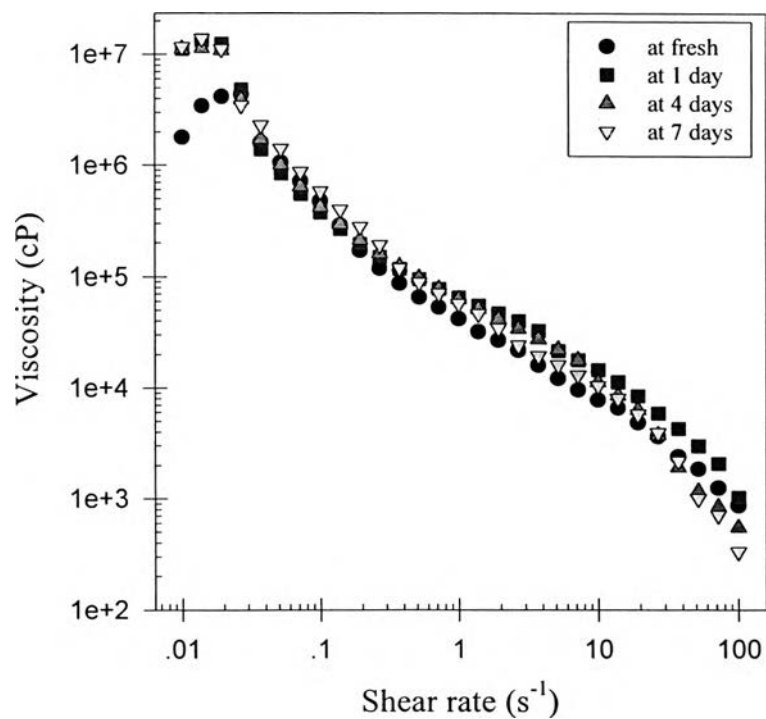


Figure 3.8 Plot of viscosity against shear rate of CTAC/FA/modified HEC = 0.7/3.3/0.7% as a function of aging time.

Figures 3.7a and 3.7b show the storage modulus and  $\tan\theta$  plotted versus frequency for CTAC/FA/modified HEC = 0.7/3.3/0.7% system. The storage modulus in figure 3.7a increases substantially from fresh to 1 day. We note the apparent plateaus at 1 to 7 day over the frequency range of 5 - 30 rad/s. In figure 3.7b,  $\tan\theta$  at low frequency remain nearly the same but at high frequency there is a reduction in  $\tan\theta$ . This can be interpreted as a build up in elasticity of emulsion. At high frequency, we probed only a part of the lamellar structure. In the aged emulsion, the formation of interconnected of lamellar structure or network occurs. This may be the reason for the decrease in  $\tan\theta$  at high frequency.

Figure 3.8 shows the plot of viscosity against shear rate. The viscosity also shows the shear-thinning behavior and increases with aging time at all shear rate. In modified HEC emulsion system has much higher viscosity at low shear rate than HEC emulsion system. Because in modified HEC system the lamellar structure can occur the interconnected between each other while HEC system the lamellar phase can not occur due to the interaction of HEC and CTAC which induce chain expansion.

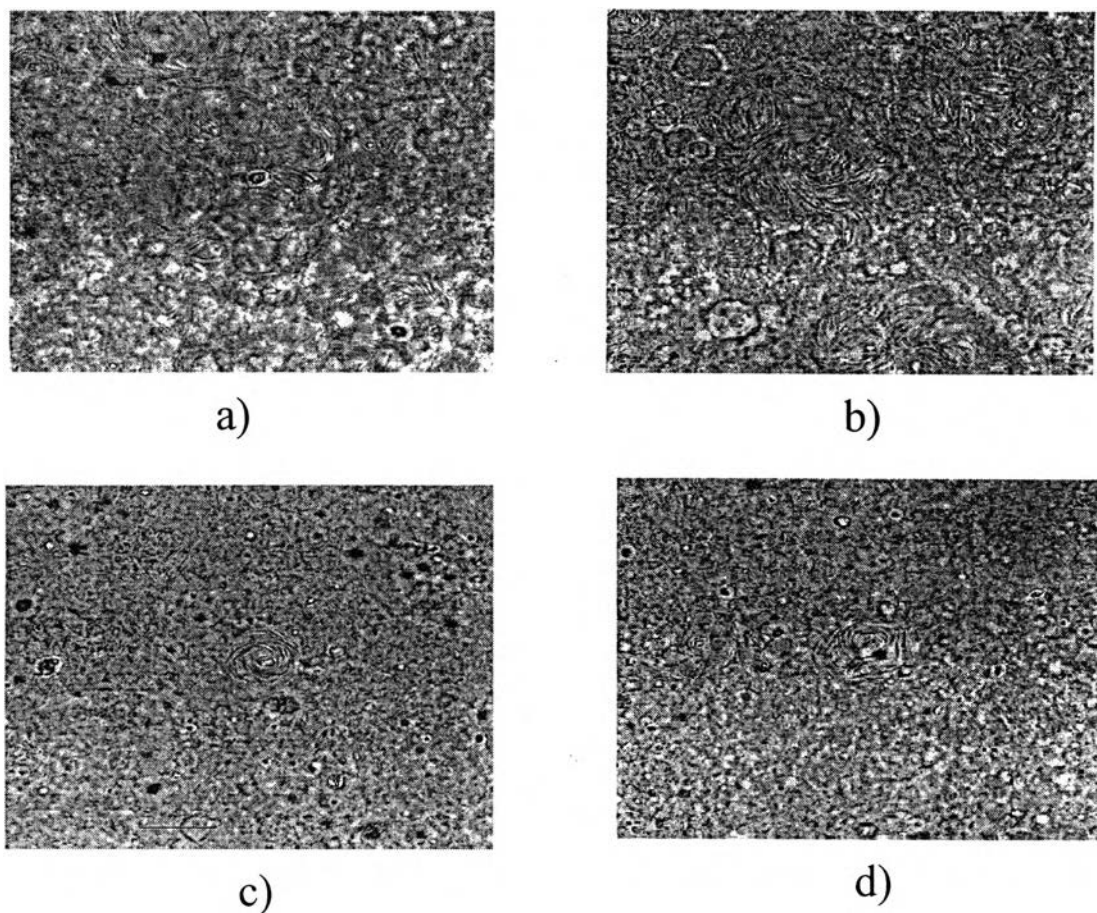


Figure 3.9 Micrograph of CTAC/FA/modified HEC = 0.7/3.3/z systems:

a) modified HEC = 0.075% at 1 day; b) modified HEC = 0.075% at 7 days; c) modified HEC = 0.7% at 1 day; d) modified HEC = 0.7% at 7 days.

From micrographs of figure 3.9, it can be seen that the lamellar phase size increases with aging time and also lamellar phases become interconnected with each other to form a network structure which can be observed at low modified HEC concentration. At high modified HEC concentration, it is difficult to see the lamellar phase at 1 day because the polymer chain of modified HEC interrupt the interaction of CTAC and FA to form lamellar structure, we can observe only the small lamellar structure. But

for aged emulsion the growth of lamellar structure occurs for both modified HEC concentrations.

### 3.1.4 Emulsion of BTAC/FA Systems

Again, we have investigated BTAC/FA emulsions system at following concentrations:

1) BTAC/FA = 0.7/y

2) BTAC/FA = 1.05/y

where  $y = 2.0, 2.3, 2.8, 3.3, 3.8, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0$ .

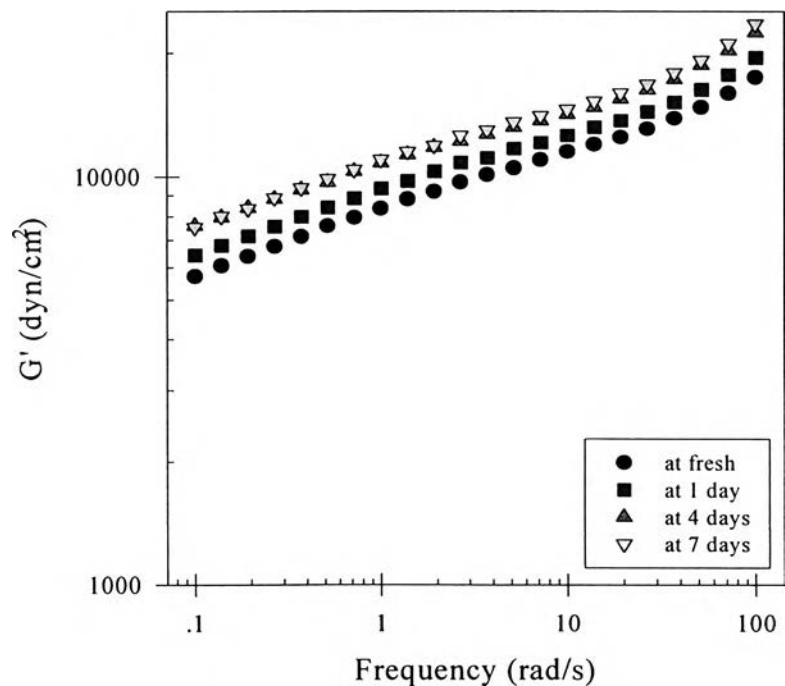


Figure 3.10a Double logarithmic plot of storage modulus against frequency of BTAC/FA = 0.7/3.3% as a function of aging time.



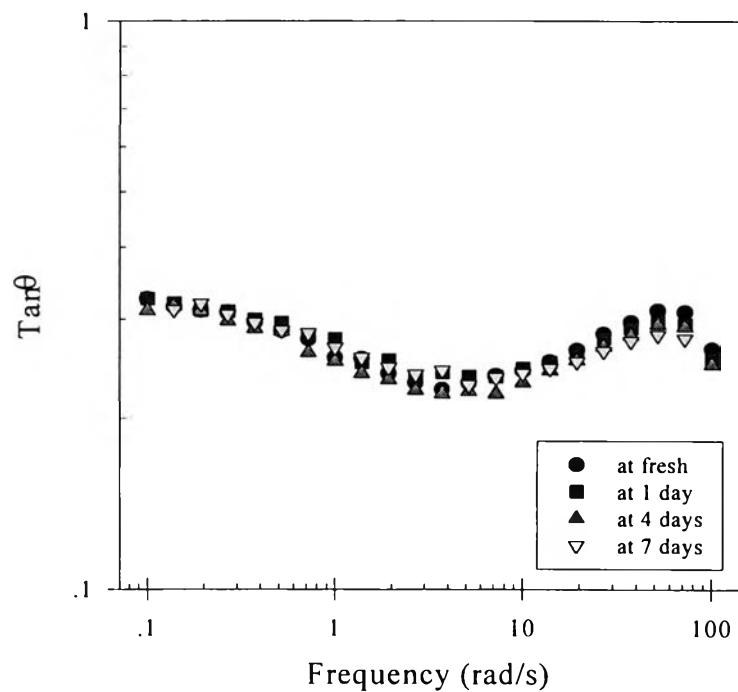


Figure 3.10b Double logarithmic plot of  $\tan\delta$  against frequency of BTAC/FA = 0.7/3.3% as a function of aging time.

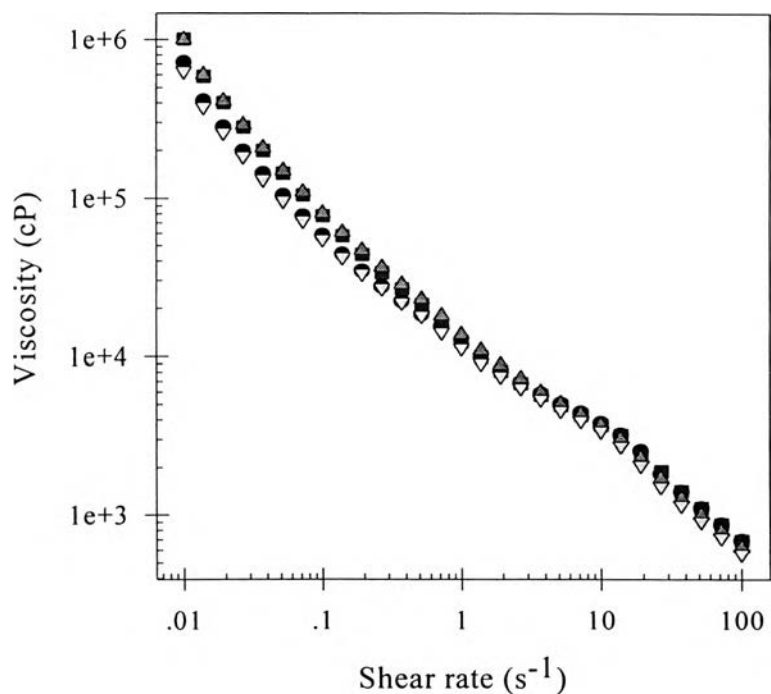


Figure 3.11a Double logarithmic plot of viscosity against shear rate of BTAC/FA = 0.7/3.3% as a function of aging time.

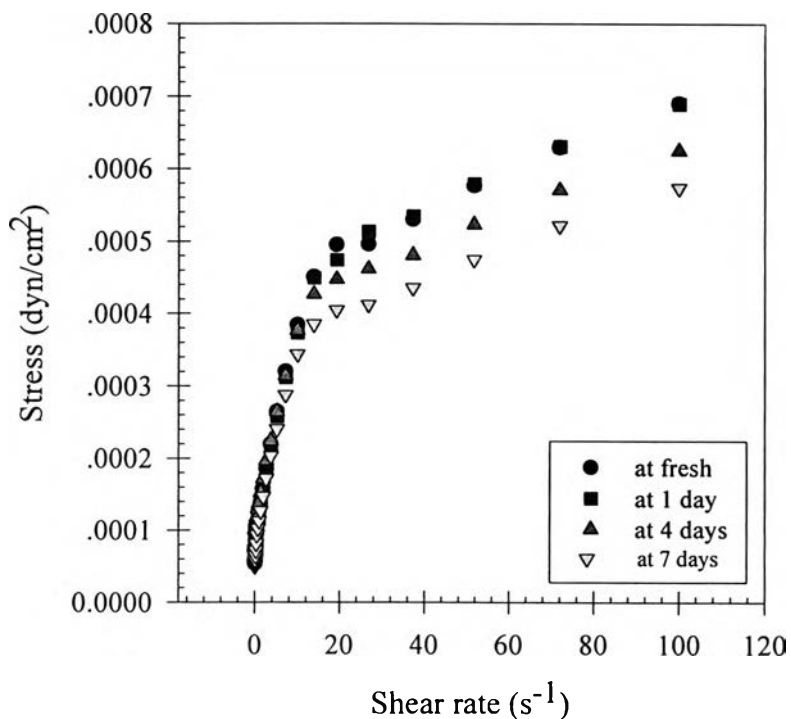


Figure 3.11b Plot of stress against shear rate of BTAC/FA = 0.7/3.3% as a function of aging time.

Figure 3.10a shows the storage modulus as a function of frequency of BTAC/FA system when aged. The system reaches an equilibrium state at 7 days. It can be seen that the storage modulus increases with aging time. For BTAC/FA system the storage modulus increases from  $5.0 \times 10^3$  to  $8.0 \times 10^3$  dyn/cm<sup>2</sup> while CTAC/FA system it increases from  $2.0 \times 10^3$  to  $2.5 \times 10^3$  dyn/cm<sup>2</sup>. Kevin (1994) reported that long-chain surfactant plays an important role in the thickening of the products.

Figure 3.10b shows that  $\tan\theta$  decreases very slightly with aging time. It indicates that the mixture becomes more elastic than viscous, similar to the CTAC/FA system.

Figure 3.11a shows the viscosity of BTAC/FA emulsion system versus shear rate as a function of aging time. The viscosity profiles show shear-thinning behavior. They show a slight shoulder at shear rates of 1-10 s<sup>-1</sup>.

It is hypothesized that these shoulder appear due to residue fatty alcohol particles. Because BTAC has more bulky hydrophobic group, the interaction time between BTAC and FA is longer when compared with the CTAC systems. Moreover BTAC consists of C-22 whereas CTAC consists of C-16 which has the same number of carbon in FA. So the interaction of CTAC and FA is more preferable to occur between each other than between BTAC and FA. Similar to the CTAC/FA system, viscosity increases with aging time and reaches the equilibrium at 7 days.

Figure 3.11b shows the stress-strain curves as a function of aging time. The stress profiles increase with time. They show a greater degree of elasticity of emulsion with aging time and increase in apparent yield stress with time.

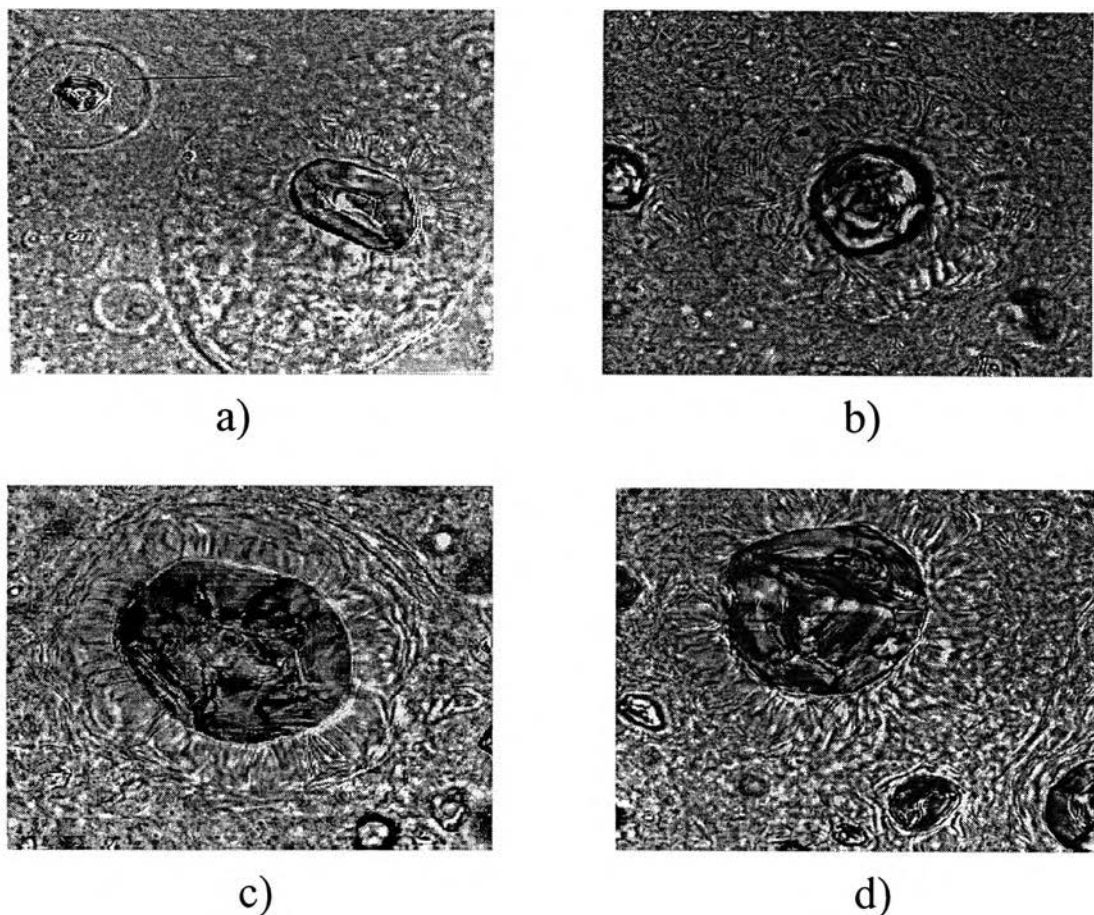


Figure 3.12 Micrograph of BTAC/FA = 0.7/y systems: a) FA = 3.3% at 1 day; b) FA = 3.3% at 7 days; c) FA = 8.0% at 1 day; d) FA = 8.0% at 7 days.

From micrographs of figure 3.12, we can observe that the lamellar phase forms around crystalline FA particles like a sun-flower shape. They are different structure from the CTAC/FA systems due to the different nature of the cationic surfactant. At both low and high FA concentrations, there is some crystalline FA left in the middle of structure. The less favorable interaction and longer time to interact between BTAC and FA lead to crystalline FA even at low FA concentration. The formation of lamellar also increases in size and number with aging time as in the CTAC/FA systems.

### 3.2 Pseudo-Equilibrium Properties of Emulsion Systems

As shown in previous section, emulsions reach equilibrium after 1 week. We define the  $G_N^0$  to be equal to  $G'(\omega)$  at 100 rad/s. It is referred to as the liquidlike entanglement storage modulus and gives a measure of material rigidity or elasticity.  $\eta_0$  is the viscosity at zero shear rate which is estimated from  $\eta$  at a shear rate of  $0.01 \text{ s}^{-1}$ .  $\tau_y$  is the yield stress which is obtained from a plot of the stress versus shear rate as the stress or force require to initiate the flow of the emulsion.

#### 3.2.1 Effect of CTAC and FA Concentration

Systems with two concentrations of CTAC were investigated: 0.7% and 1.05%. The level of FA was increased from 2-8% wt.

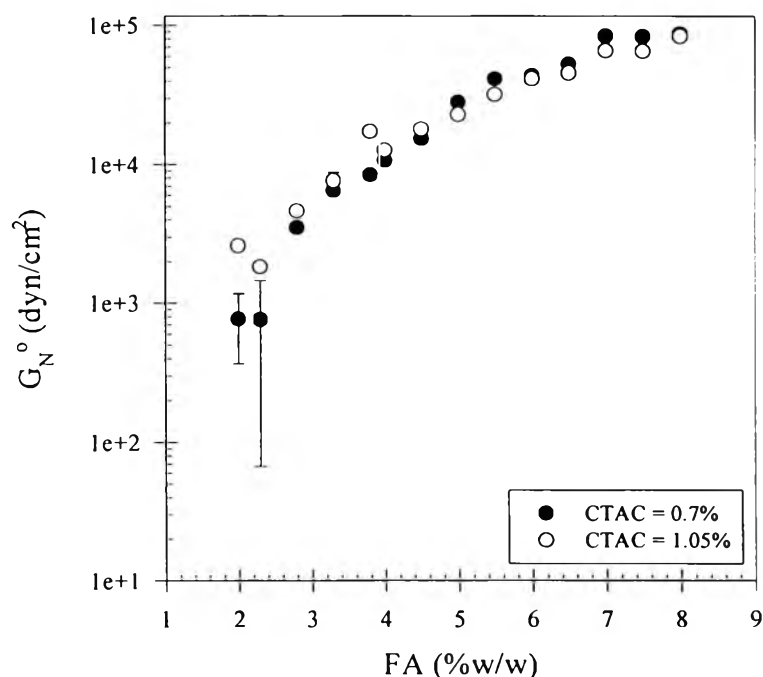


Figure 3.13a Plot of shear entanglement modulus ( $G_N^0$ ) against FA concentration of CTAC/FA systems at equilibrium.

Figures 3.13a and 3.13b show, respectively the plot of the entanglement modulus and  $\tan\theta$  versus FA concentration, respectively. The entanglement modulus increases from  $1.0 \cdot 10^3$  to  $1.0 \cdot 10^5$  dyn/cm<sup>2</sup> and reaches a saturation state as FA content varies from 2 to 8%wt; this is an increase by 2 orders of magnitude. We can not discern any differences in the value of  $G_N^0$  and  $\tan\theta$  between the mixtures using of CTAC 0.7 and 1.05% wt. A decrease in  $\tan\theta$  with FA content suggests that mixtures with larger FA content are relatively more elastic. In studying the rheology of an emulsion containing cetostearyl alcohol by *Talman et al. (1987)*, they found that the rheology can be controlled by adding cetostearyl alcohol. This increases the yield value and the plastic viscosity of the emulsion.

Figures 3.14a and 3.14b show, respectively the zero shear viscosity and the yield stress versus FA concentration. These plots show the same trend as in the shear entanglement modulus. We can observe some differences in the zero shear rate viscosity between the mixtures using CTAC of 0.7 and 1.05%wt. where 1.05% CTAC is higher. *Axon (1990)* reported that the viscosity of oil-in-water emulsions increased with increasing concentration of emulsifying agents or surfactant. An increase in surfactant concentration can produce in most cases an increase in viscosity. The higher zero shear rate viscosity, the higher stress or force required to initiate the flow of emulsion. The existence of a yield stress is very useful in processing of emulsion and in packaging of emulsion product in bottle.

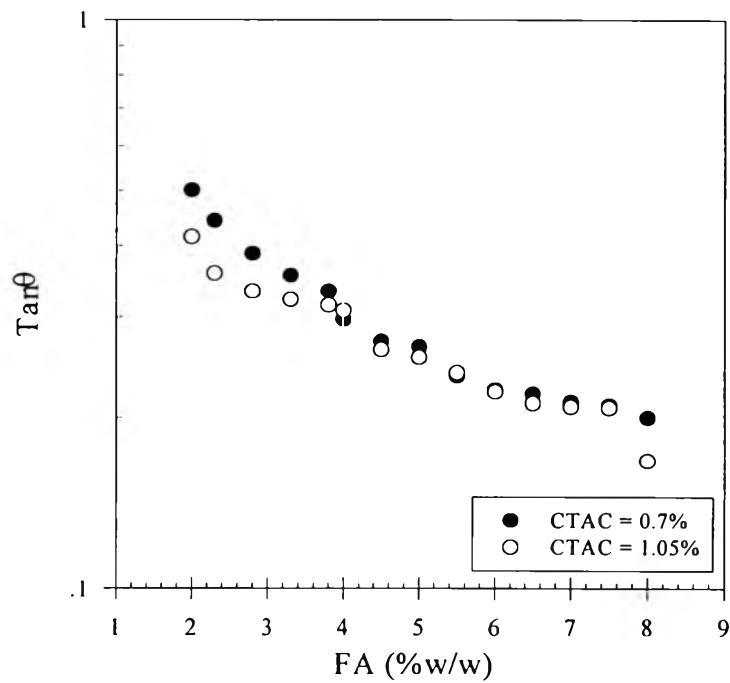


Figure 3.13b Plot of  $\tan\theta$  against FA concentration of CTAC/FA systems at equilibrium.

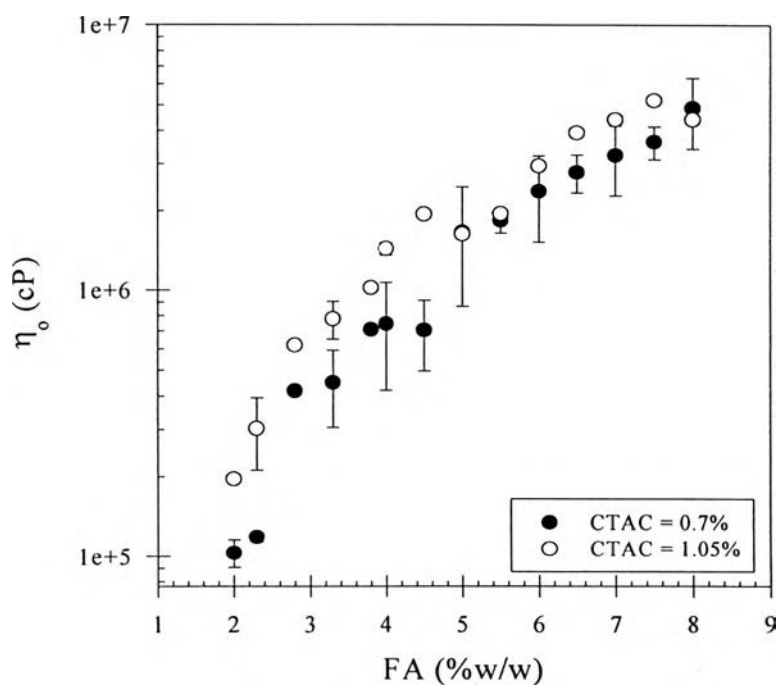


Figure 3.14a Plot of viscosity against FA concentration of CTAC/FA systems at equilibrium.

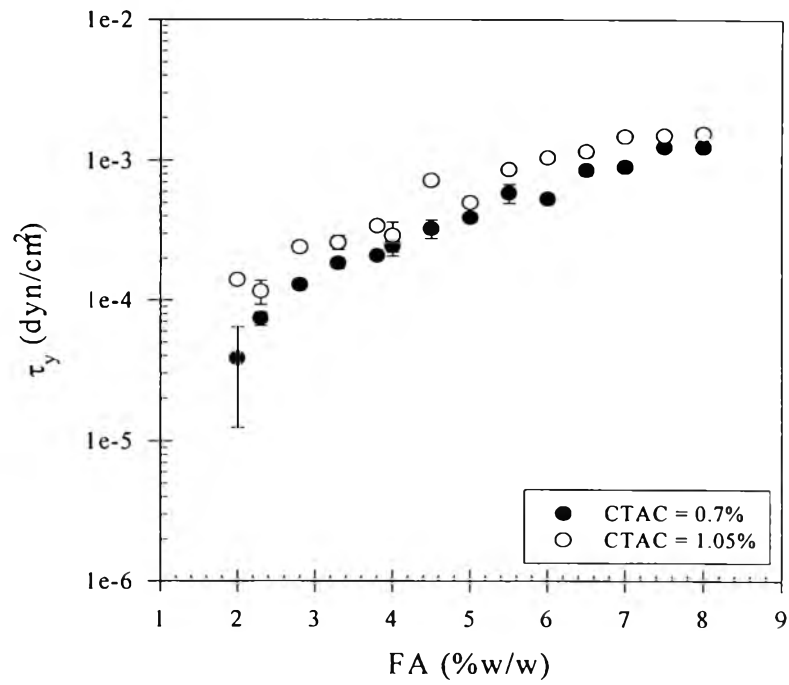


Figure 3.14b Plot of yield stress against FA concentration of CTAC/FA systems at equilibrium.



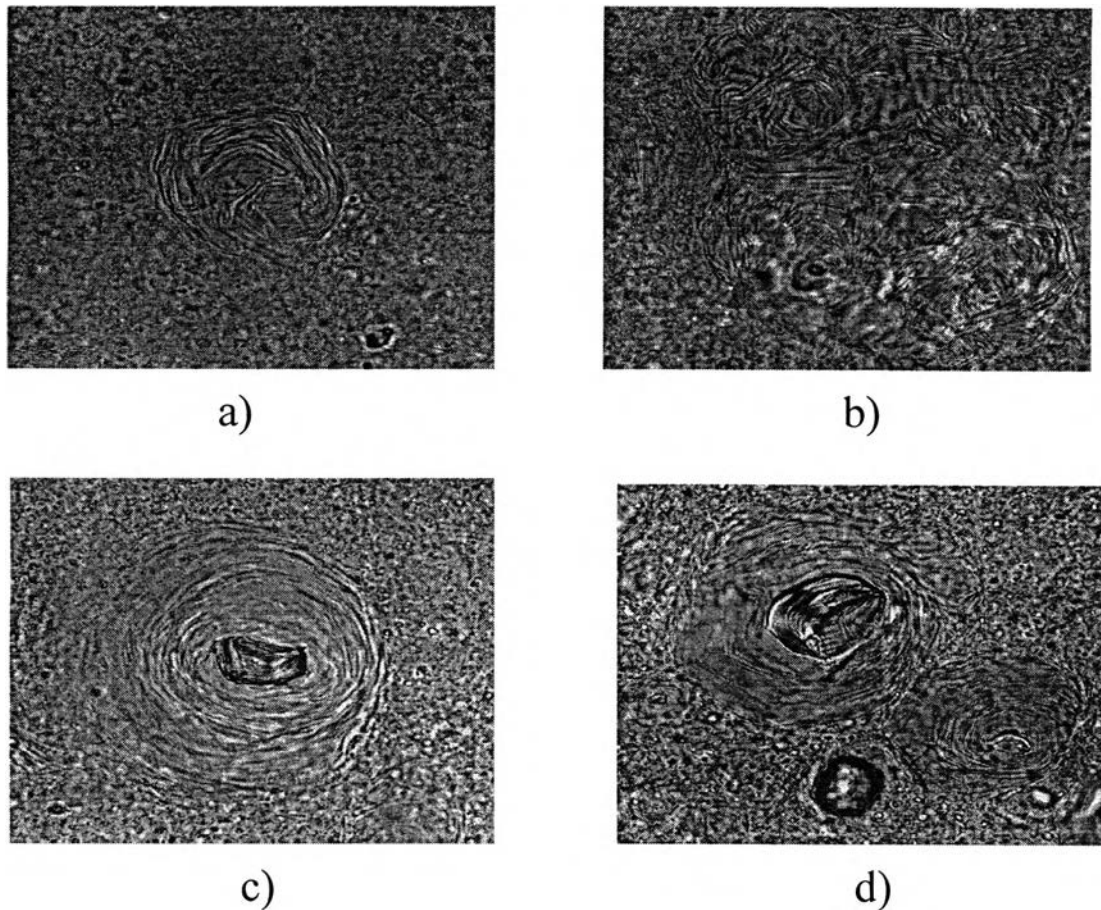


Figure 3.15 Micrograph of CTAC/FA = 0.7/y systems at equilibrium:

a) FA = 2.0%; b) FA = 3.3%; c) FA = 6.0%; d) FA = 8.0%.

From micrographs of CTAC/FA = 0.7/y systems of figure 3.15, we can observe that there is growth of lamellar structure with increasing FA concentration. At 6 and 8% FA, we notice that there are some crystalline FA formed probably due to an excess FA concentration.

Figure 3.16 show micrographs of CTAC/FA = 1.05/y systems, showing that the lamellar phase of this systems has a larger volume than that of CTAC = 0.7%. This is because there is more CTAC concentration in the system to interact with FA to form the lamellar phase. We can further observe that there are no crystalline FA unclusious even at FA = 8.0% due to an excess CTAC.

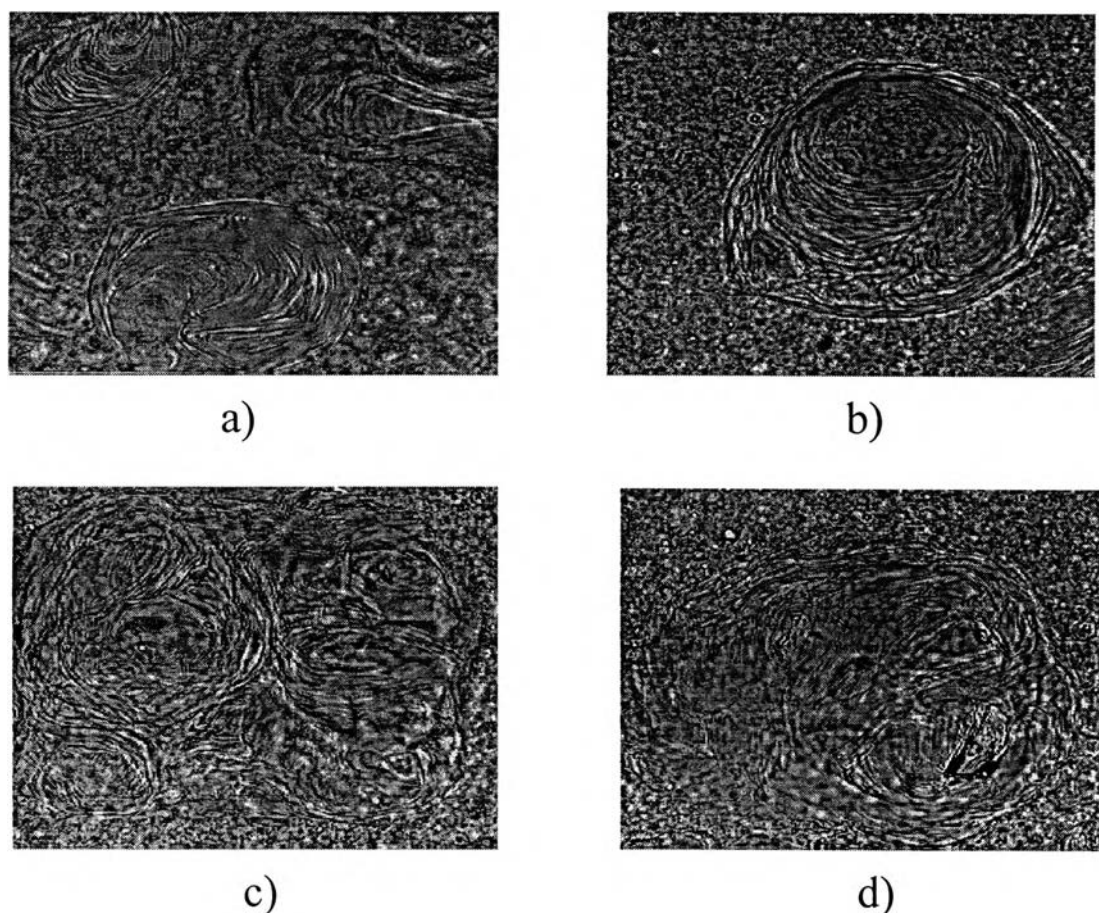


Figure 3.16 Micrograph of CTAC/FA = 1.05/y systems at equilibrium:

a) FA = 2.0%; b) FA = 3.3%; c) FA = 6.0%; d) FA = 8.0%.

The proposed model based on the micrographs of CTAC/FA = 0.7/y will be more illustrative which is shown in figure 3.17a. At low FA concentration, CTAC and FA interact with each other to form lamellar and there is some excess CTAC left in the system due to excess CTAC. At higher FA concentration, there is more FA in the system to interact with CTAC, so there is more lamellar formation or growth of lamellar phase than at low FA concentration. At the highest FA concentration, there is not enough CTAC to interact with FA, so there is some crystalline FA left.

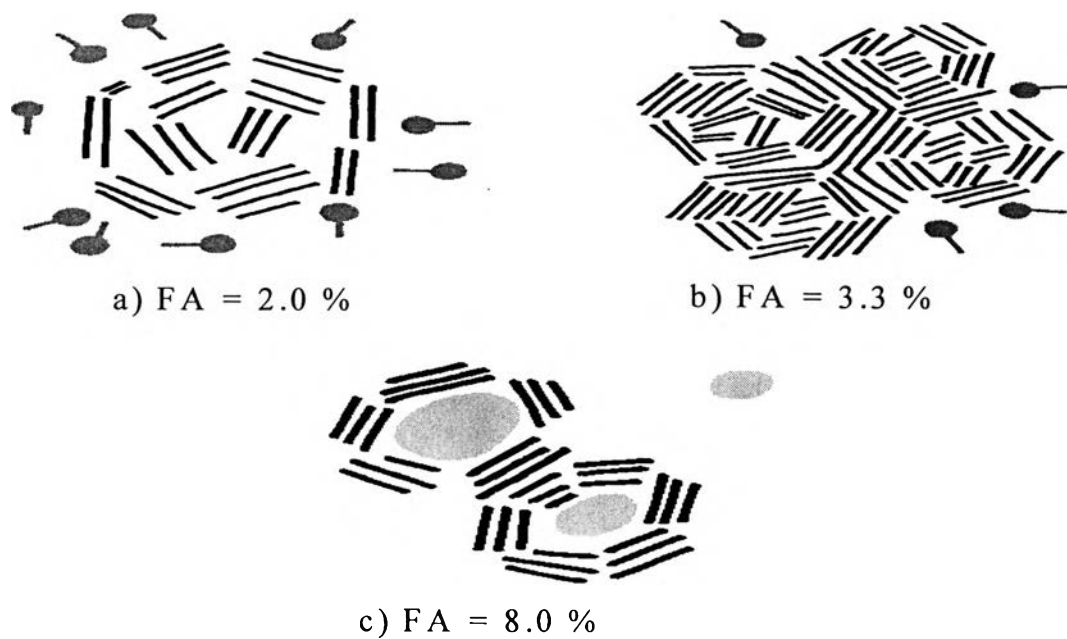


Figure 3.17a Proposed model of CTAC/FA = 0.7/y systems at equilibrium:

a) FA = 2.0%; b) FA = 3.3%; c) FA = 8.0%.

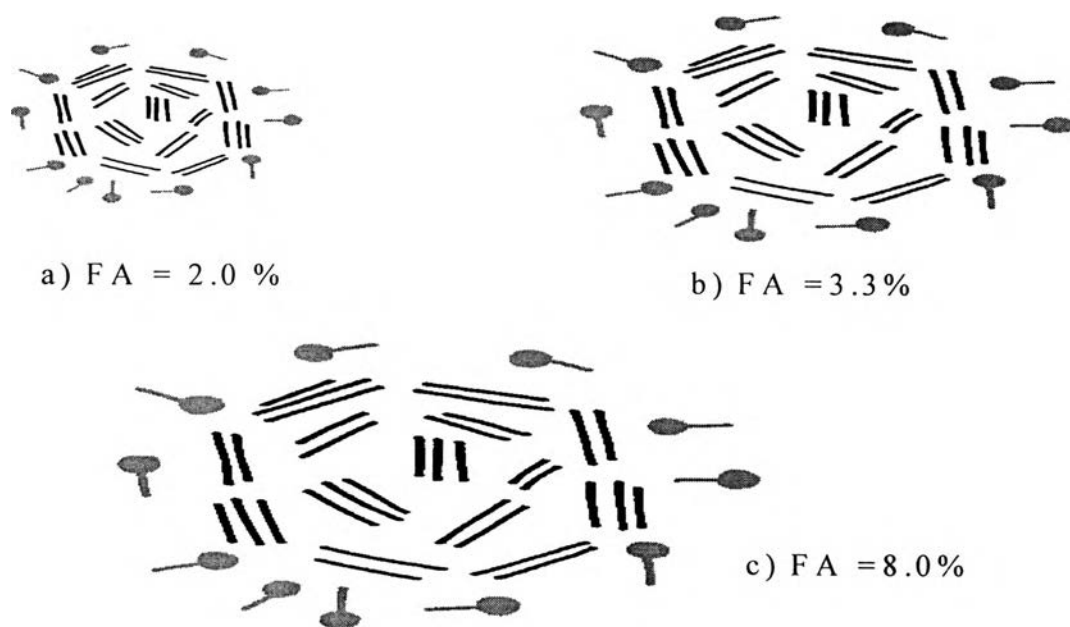


Figure 3.17b Proposed model of CTAC/FA = 1.05/y systems at equilibrium:

a) FA = 2.0%; b) FA = 3.3%; c) FA = 8.0%.

Figure 3.17b show the corresponding model from micrographs of the CTAC/FA = 1.05/y system. At low FA concentration, CTAC and FA interact each other to form lamellar phase and there is CTAC left in the system because of excess of CTAC. When added higher and higher FA, there is more and more FA to interact with CTAC. So there is more lamellar formation. The growth of lamellar phase increases with increasing FA concentration.

### 3.2.2 Effect of HEC and modified HEC Concentration

We investigated the effect of two polymers, one is hydroxyethyl cellulose (HEC) and the other is modified hydroxyethyl cellulose (modified HEC). We fixed the concentration of CTAC and FA equal to 0.7 and 3.3%, respectively and varied the concentration of HEC and modified HEC.

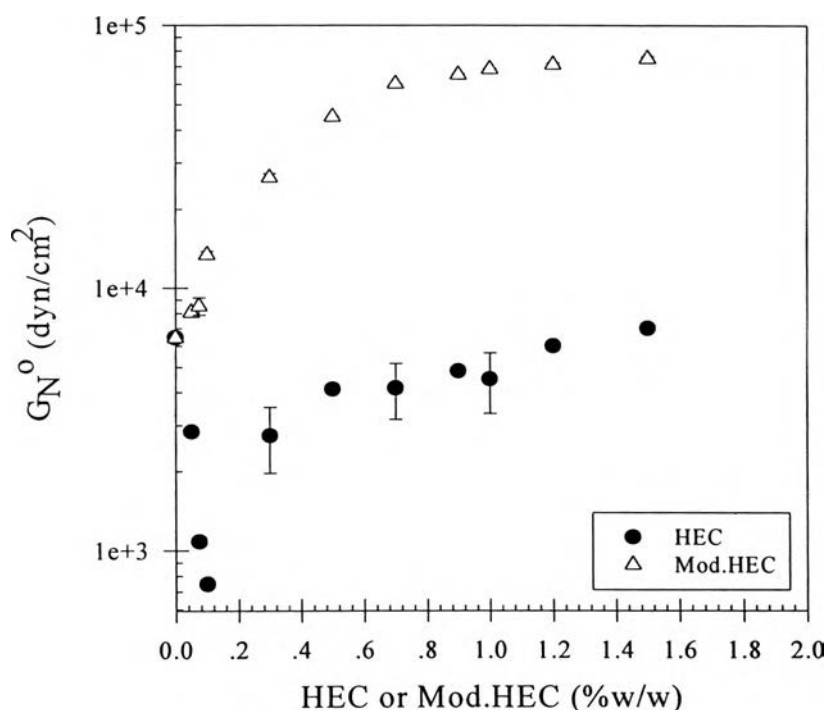


Figure 3.18a Plot of shear entanglement modulus against HEC or modified HEC concentration of CTAC/FA/HEC and CTAC/FA/modified HEC = 0.7/3.3/z at equilibrium.

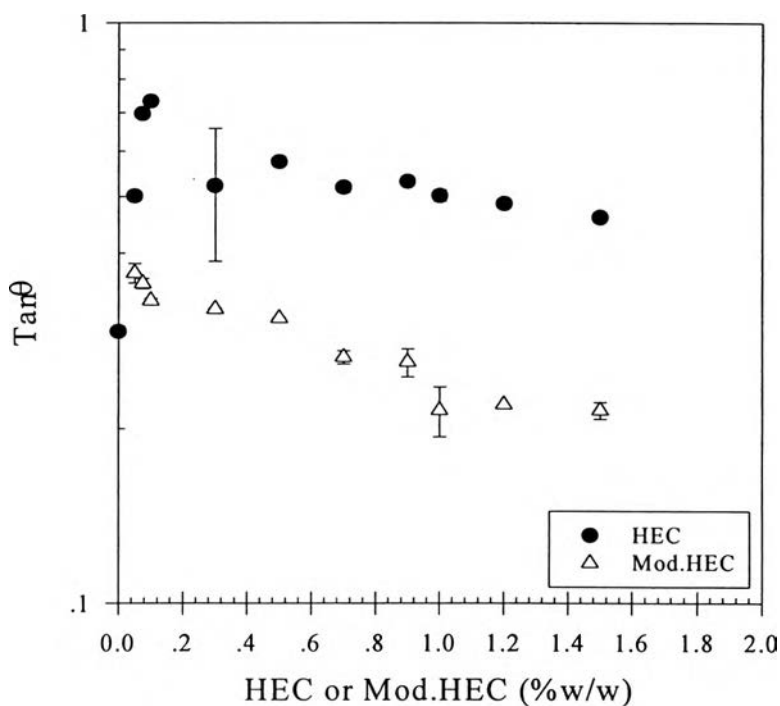


Figure 3.18b Plot of  $\tan\theta$  against HEC or modified HEC concentration of CTAC/FA/HEC and CTAC/FA/modified HEC = 0.7/3.3/z at equilibrium.

Figure 3.18a shows the shear entanglement modulus as a function of HEC and modified HEC concentration. For the HEC system, the results can be divided into 2 regimes. In the first regime, the shear entanglement modulus sharply decreases at small amounts of HEC concentration. The concentration of HEC equal to 0.1% make the minimum shear entanglement modulus. This occurs because the polymer chains of HEC act as a steric hindrance and can disrupt the formation of lamellar structure. The interaction between HEC and CTAC induces a chain expansion. Moreover, HEC has a large hydrodynamic volume, it will absorb a substantial amount of water which will not be available to stabilize the lamellar structure.

In the second regime, the shear entanglement modulus slightly increases until reaching the saturation value. The elasticity of the emulsion increases again possibly due to the rigidity of the polymer structure that consists of cellulose rings only. These results are supported by the micrographs from laser scanning microscope.

In modified HEC systems, the shear entanglement modulus increases with increasing modified HEC concentration monotonically. Modified HEC is the HEC that has cetyl groups in the molecule. These cetyl chains can cause a hydrophobic interaction with the hydrophobic part of both CTAC and FA. This leads to the formation of an interconnected lamellar structure between cetyl chains. Thus the shear entanglement modulus increases with modified HEC concentration. *Goldszal (1991)* reported that the thermal behavior of two non-ionic cellulose, ethyl(hydroxyethyl) cellulose or EHEC and methyl cellulose or MC in dilute aqueous solutions. They found that two polymers behave in a very different way: micellization followed by a collapse was observed for EHEC which reduced the aggregation; while only a fraction of the MC sample was sensitive to CTAB.

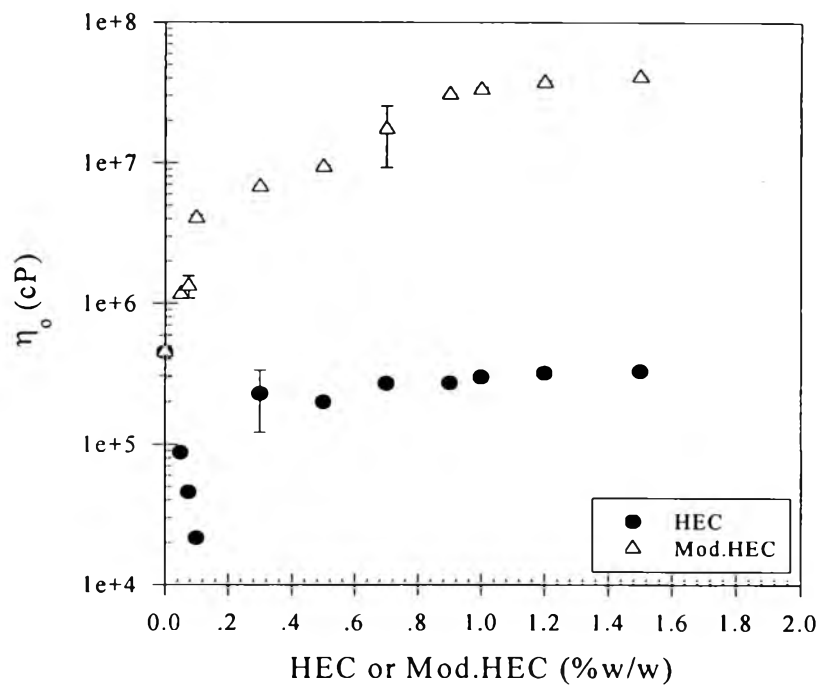


Figure 3.19 Plot of viscosity against HEC or modified HEC concentration of CTAC/FA/HEC and CTAC/FA/modified HEC = 0.7/3.3/z at equilibrium.

Figures 3.18b and 3.19 show  $\tan\theta$  and zero shear rate viscosity versus HEC and Modified HEC concentration of the same system, respectively. They also show the same trend as the shear entanglement modulus and can be explained by the same reasoning.

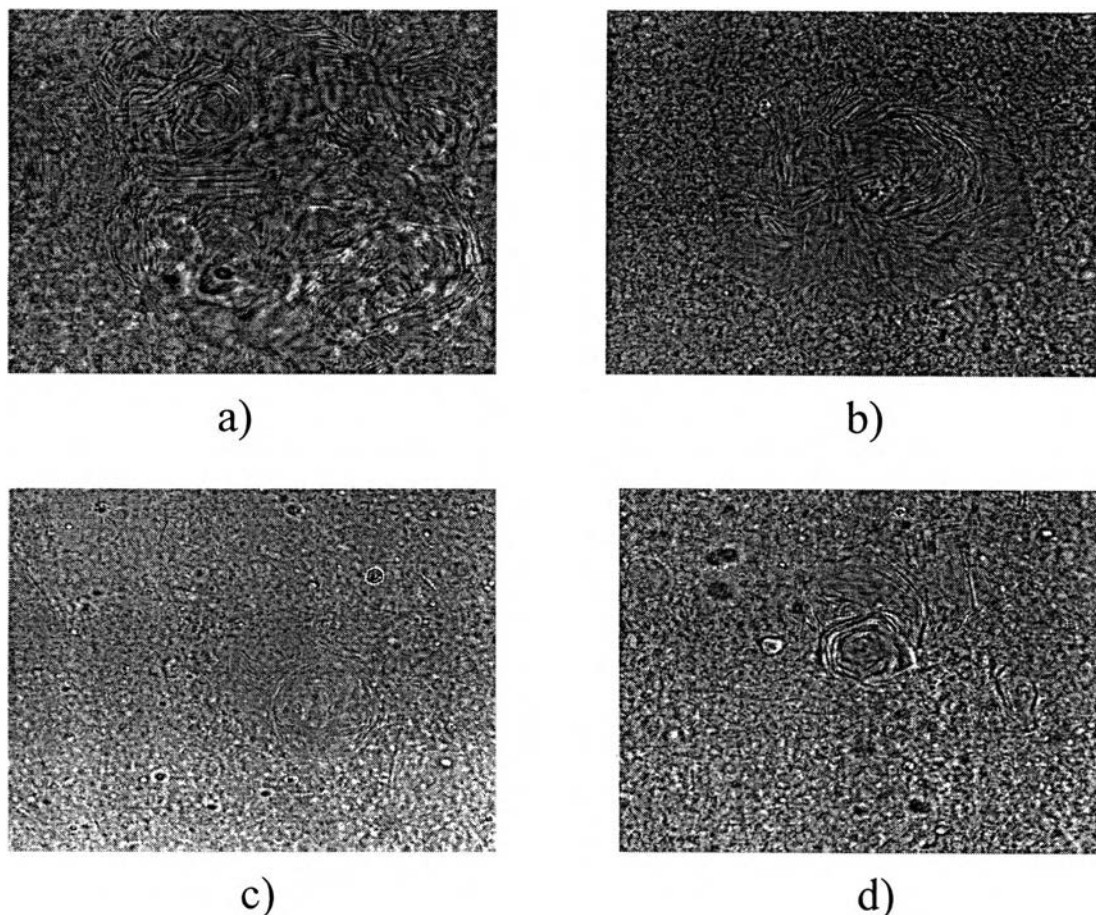


Figure 3.20 Micrograph of CTAC/FA/HEC = 0.7/3.3/z systems at equilibrium: a) HEC = 0%; b) HEC = 0.075%; c) HEC = 0.1%; d) HEC = 1.0%.

From micrographs of HEC systems in figure 3.20, it can be seen that the system without polymer has a large volume of lamellar structure. With polymer added into the system, the volume of lamellar phase decreases due to the interaction between HEC and CTAC. This leads to chain expansion, so the chance of CTAC and FA to interact with each other is reduced. This probably induces the reduction in elasticity which is observed in the rheological measurements. The rheological properties which increase again at higher HEC concentration due to the rigidity and entanglement interaction of the cellulose chain.



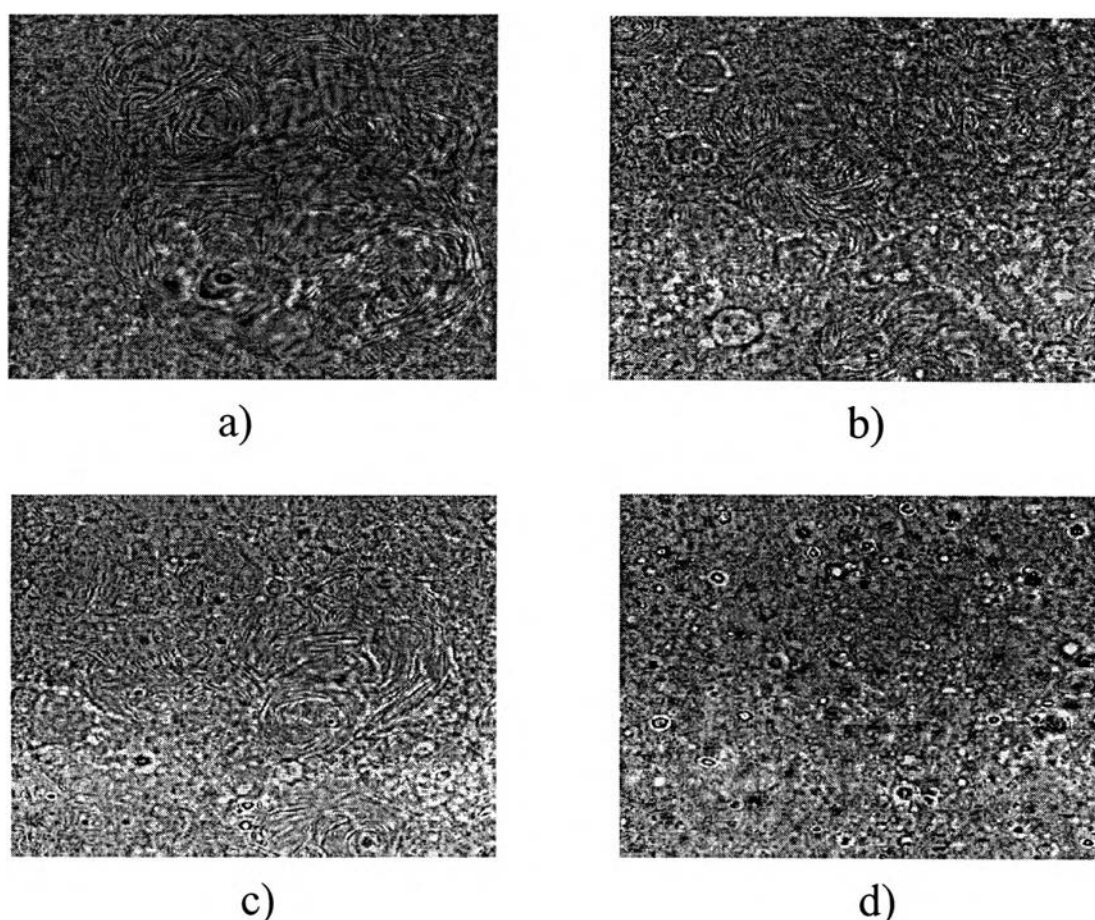


Figure 3.21 Micrograph of CTAC/FA/modified HEC = 0.7/3.3/z systems at equilibrium: a) modified HEC = 0%; b) modified HEC = 0.075%; c) modified HEC = 0.1%; d) modified HEC = 1.0%.

Figure 3.21 show micrographs of modified HEC systems, when added modified HEC until 0.1%, the mixtures exhibit an interconnected of lamellar network. This is because modified HEC is the HEC that has the branch chain or cetyl groups attached to the molecule. This cetyl chains can form network by the hydrophobic interaction with hydrophobic domain of both CTAC and FA. This leads to the formation of a lamellar structure and interconnected lamellar network between cetyl chains. With modified HEC added more than 0.1%, the polymer chain will disrupt the formation of

lamellar phase, so it is difficult to observe the lamellar phase at higher than 0.1% modified HEC.

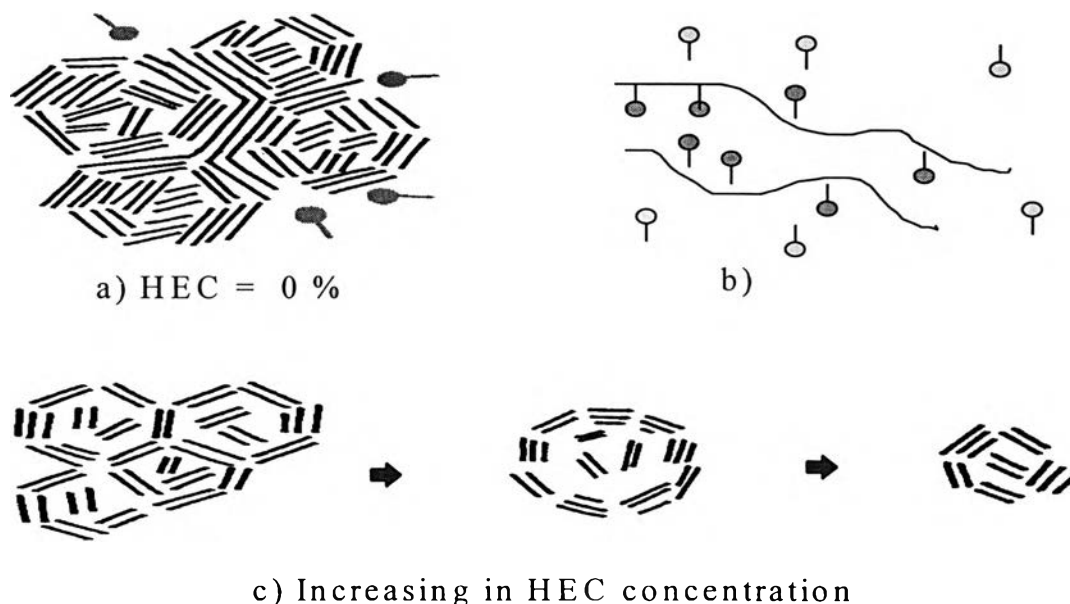


Figure 3.22 Proposed model of CTAC/FA/HEC = 0.7/3.3/z systems at equilibrium: a) HEC = 0%; b) the model of chain expansion; c) Increasing in HEC concentration.

The model in figure 3.22 illustrates the effect of HEC in CTAC and FA system. Figure 3.22a represents the system without polymer, in which there is a large volume of lamellar structure. With added polymer in the system, HEC and CTAC can interact with each other and induce chain expansion as shown in figure 3.22b. Figure 3.22c shows the effect of HEC; the lamellar phase decreases in size with increasing HEC concentration.

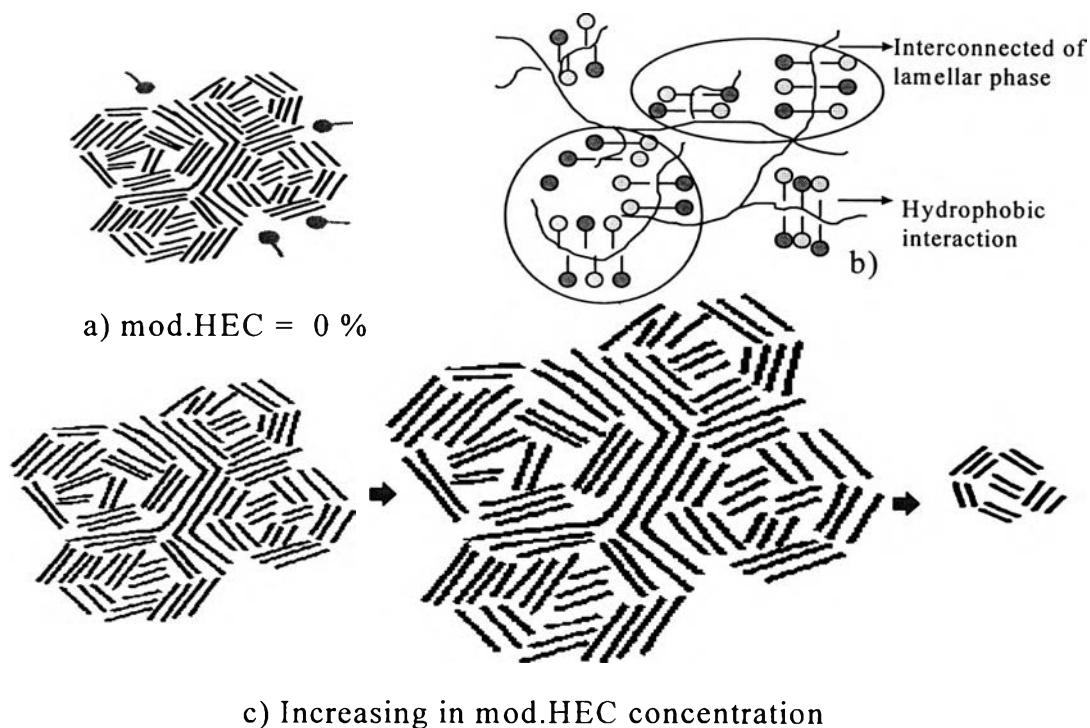


Figure 3.23 Proposed model of CTAC/FA/modified HEC = 0.7/3.3/z systems at equilibrium: a) modified HEC = 0%; b) the model of interconnected of lamellar phase; c) Increasing in modified HEC concentration.

Figure 3.23, this model shows the effect of modified HEC in CTAC and FA system. Figure 3.23a shows the system without polymer, there is a large volume of lamellar structure. With added modified HEC in the system, the hydrophobic chain of modified HEC can interact with hydrophobic part of both CTAC and FA. This leads to the formation of interconnected of lamellar phase that is illustrated in figure 3.23b. Figure 3.23c shows the effect of modified HEC, the lamellar phase increases in size with increasing modified HEC concentration until 0.1%. Above concentration of 0.1% of modified HEC, the lamellar phase will decrease in size due to the disruption via polymer chain.

### 3.2.3 Effect of BTAC and FA Concentration

Systems contain two concentrations of BTAC were investigated: 0.7% and 1.05%. For this system, the entanglement modulus,  $G_N^0$ ,  $\tan\theta$ , zero-shear viscosity,  $\eta_0$ , and yield stress  $\tau_y$  were measured as a function of FA concentrations.

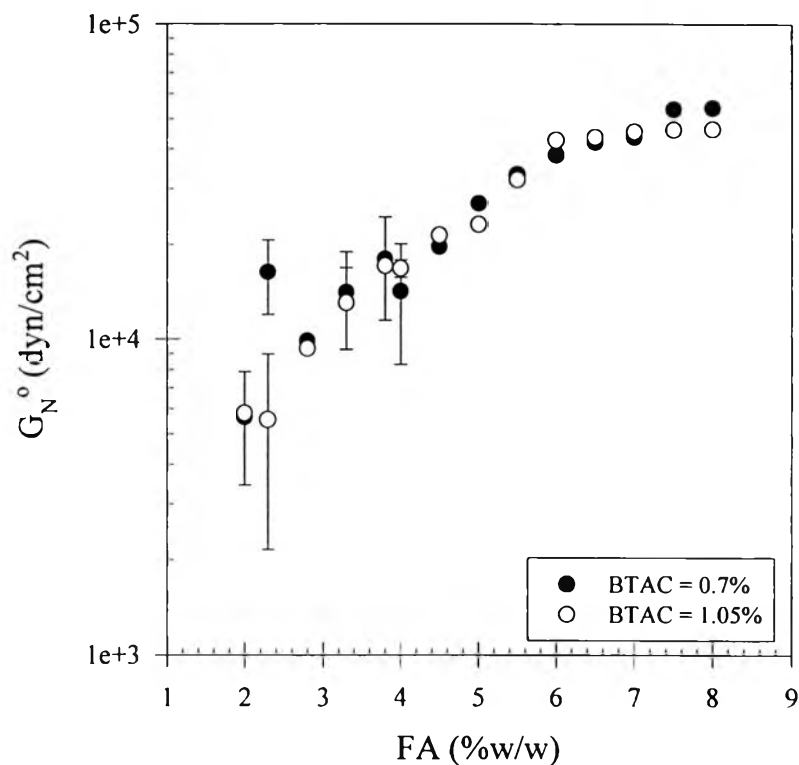


Figure 3.24a Plot of shear entanglement modulus against FA concentration of BTAC/FA systems at equilibrium.

Figures 3.24a and 3.24b show the plot of the shear entanglement modulus and  $\tan\theta$  versus FA concentration, respectively. The shear entanglement increases with FA concentration and reaches the saturation value whereas  $\tan\theta$  decreases with increased FA. This means that the elasticity of emulsion increases with FA concentration.

Figures 3.25a and 3.25b show the zero shear viscosity and the yield stress plotted against FA concentration. These plots also show the same trend as the shear entanglement modulus. The higher the zero shear viscosity, the higher the stress or force required to initiate flow of emulsion.

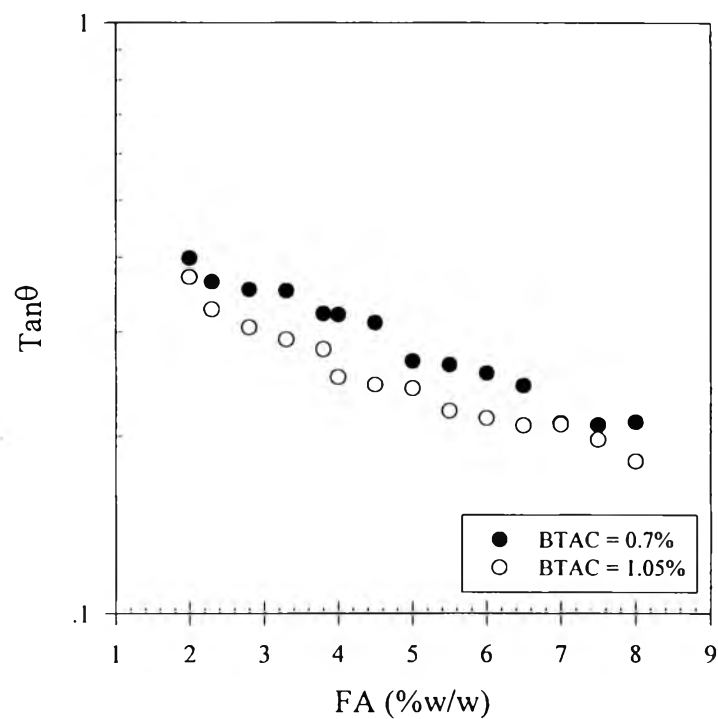


Figure 3.24b Plot of  $\tan\theta$  against FA concentration BTAC/FA systems at equilibrium.

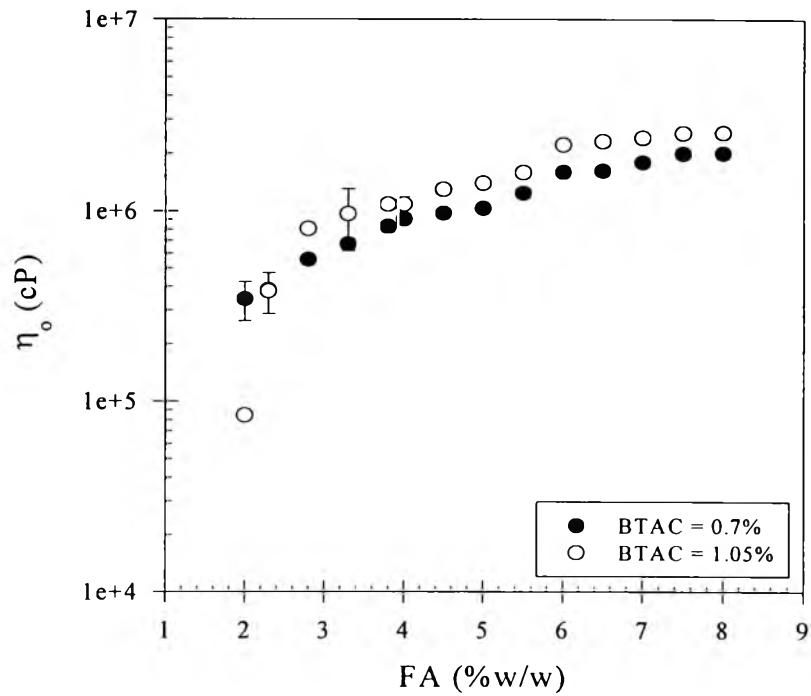


Figure 3.25a Plot of viscosity against FA concentration BTAC/FA systems at equilibrium.

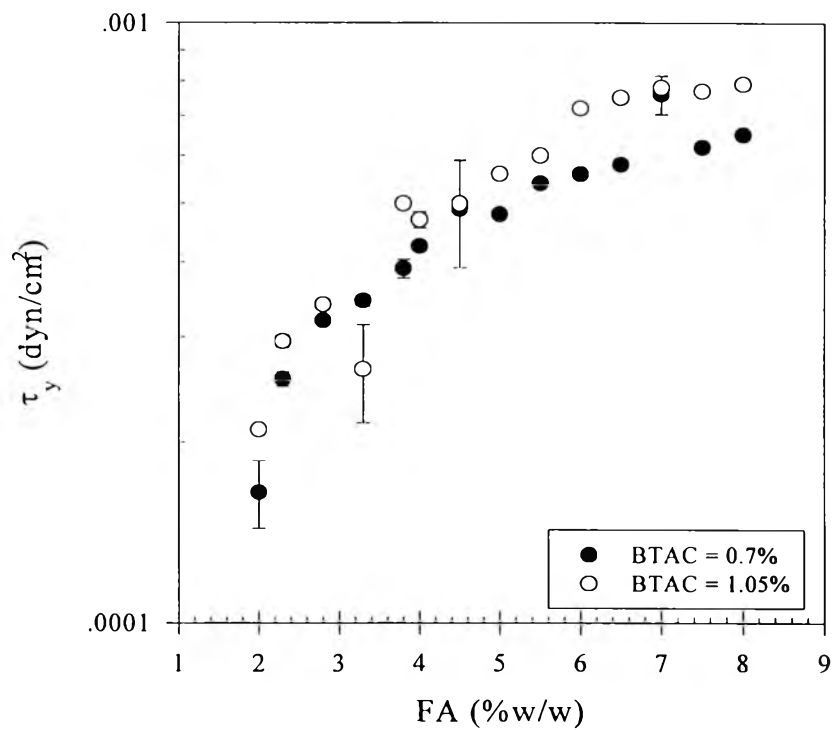


Figure 3.25b Plot of yield stress against FA concentration BTAC/FA systems at equilibrium.

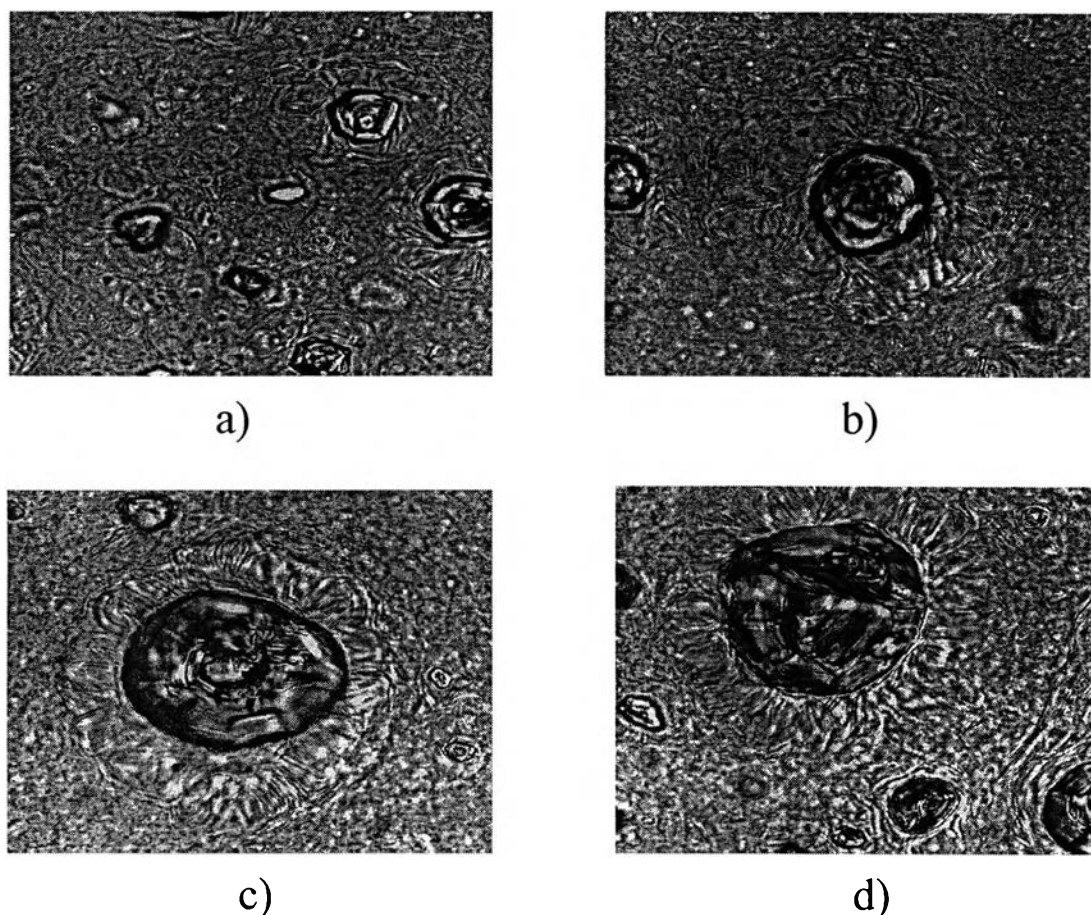


Figure 3.26 Micrograph of BTAC/FA = 0.7/y systems at equilibrium:

a) FA = 2.0%; b) FA = 3.3%; c) FA = 6.0%; d) FA = 8.0%.

From micrographs of BTAC/FA = 0.7/y systems shown in figure 3.26, we can observe that there are some growth of sunflower-like structure with increasing FA concentration in terms of size and number. We noticed that some crystalline FA domains are left at both low and high FA concentrations. This occurs because BTAC has more bulky groups than CTAC. So the interaction time of BTAC system is longer than CTAC. Moreover, BTAC consists of C-22 while CTAC consists of C-16 which is the same carbon number as the FA. This leads to more preferable interaction between CTAC and FA. So we can observe the crystalline FA even at low FA concentration.

Figure 3.27 shows micrographs of BTAC/FA = 1.05/y systems, it can be seen that there is no crystalline FA left at low FA concentration due to excess of BTAC. There is more BTAC concentration in the system to interact with FA to form sunflower-like structure. At high BTAC concentration, we observe that some crystalline FA is left in the middle.

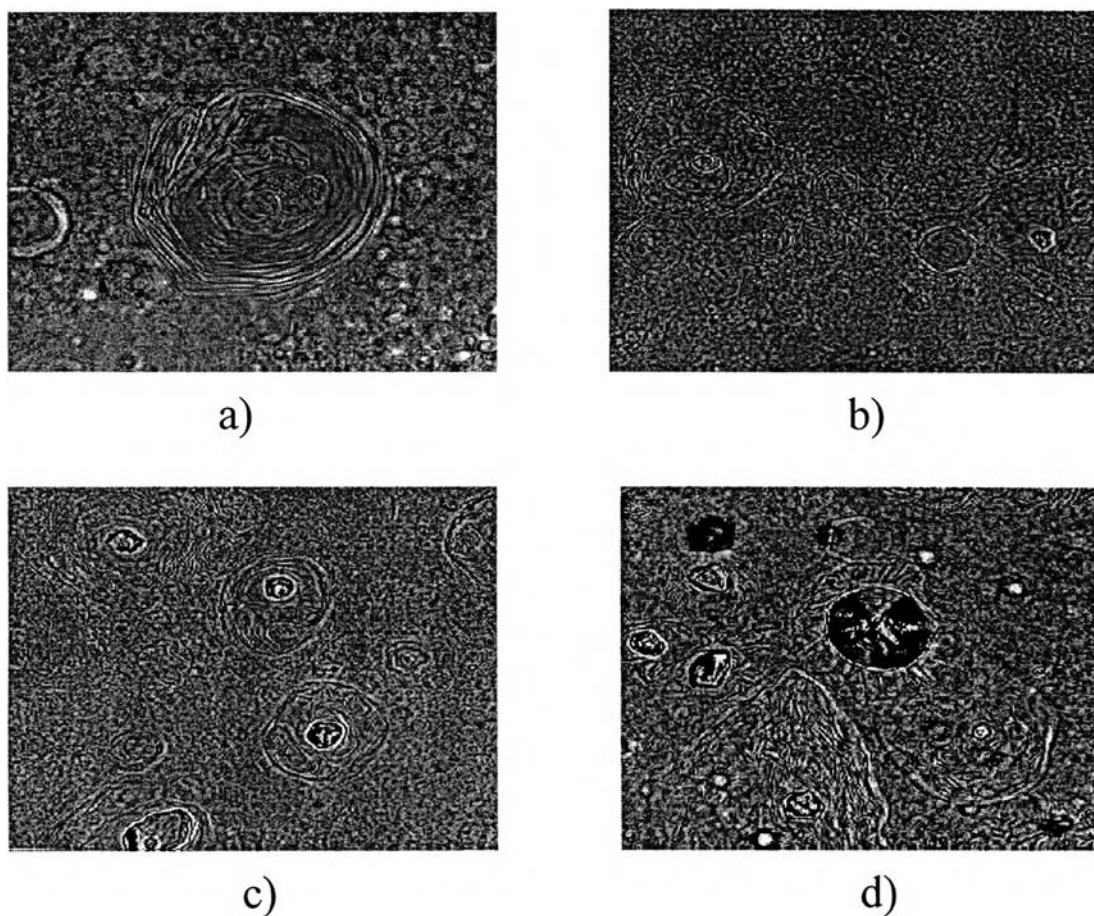


Figure3.27 Micrograph of BTAC/FA = 1.05/y systems at equilibrium:

a) FA = 2.0%; b) FA = 3.3%; c) FA = 6.0%; d) FA = 8.0%.



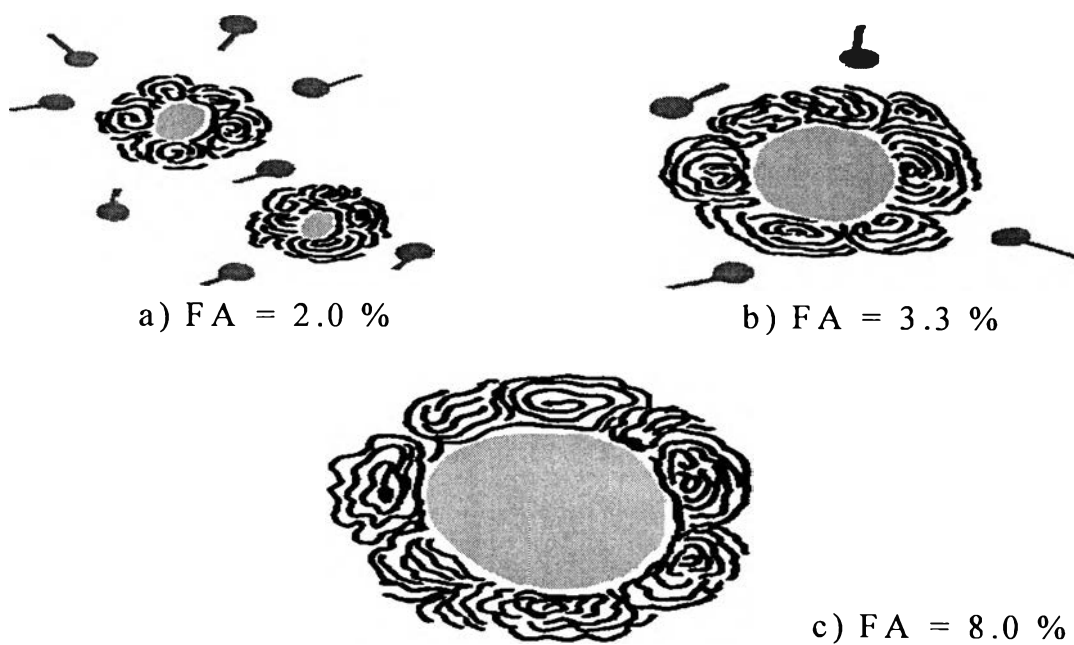


Figure 3.28a Proposed model of BTAC/FA = 0.7/y systems at equilibrium:

a) FA = 2.0%; b) FA = 3.3%; c) FA = 8.0%.

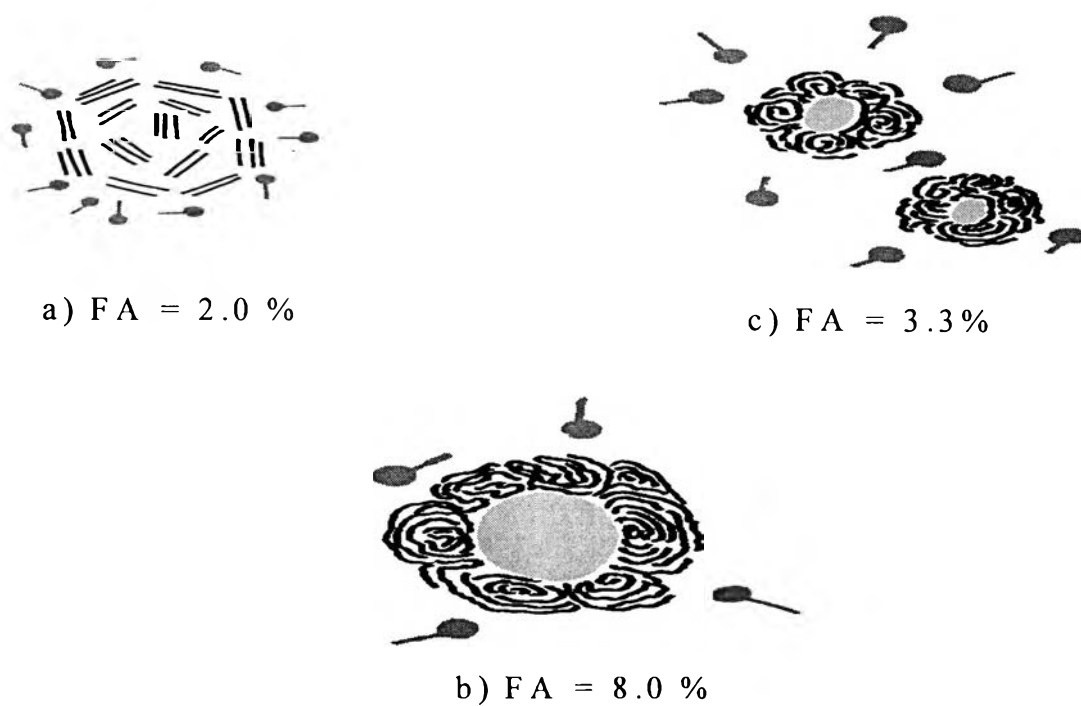


Figure 3.28b Proposed model of BTAC/FA = 1.05/y systems at equilibrium

a) FA = 2.0% b) FA = 3.3% c) FA = 8.0%

The proposed model from micrographs of  $\text{BTAC/FA} = 0.7/y$  is illustrated in figure 3.28a. At low FA concentration, BTAC and FA interact with each other to form sunflower-like structure and there are some BTAC left in the system due to excess BTAC. There also is some crystalline FA left due to longer reaction time and less preferable of interaction. With higher FA concentration, there is more FA in the system to interact with BTAC. There is greater sunflower-like formation or growth of this structure than at low FA concentration. At the highest FA concentration, there is not enough BTAC to interact with FA, so crystalline FA unclusious remain where the system reaches the saturation state.

Figure 3.28b shows the model from micrographs of  $\text{BTAC/FA} = 1.05/y$  system, at low FA concentration, BTAC and FA interact with each other to form sunflower-like structure and there is no crystalline FA left in the system because of an excess amount of BTAC. With higher and higher FA, we can observe the crystalline FA domain left in the middle of the sunflower structure.