CHAPTER IV
RESULTS AND DISCUSSION

Rheological and optical behaviors of emulsion systems were investigated for the effect of fatty alcohol concentration, the effect of temperature, the effect of annealing temperature, and the effect of pH. The systems studied were as follow:

Table 4.1 Effect of Fatty Alcohol Concentration

CTAC/FA (%wt/wt)	BTAC/FA (%wt/wt)
1.0/2.0	1.0/2.0
1.0/4.0	1.0/4.0
1.0/5.0	1.0/5.0
1.0/6.0	1.0/6.0

Table 4.2 Effect of Temperature

Temperature (^oC)	CTAC/FA (%wt/wt)	BTAC/FA (%wt/wt)
26	1.0/2.0	1.0/2.0
	1.0/4.0	1.0/4.0
	1.0/6.0	1.0/6.0
35	1.0/2.0	1.0/2.0
	1.0/4.0	1.0/4.0
	1.0/6.0	1.0/6.0
45	1.0/2.0	1.0/2.0
	1.0/4.0	1.0/4.0
	1.0/6.0	1.0/6.0
55	1.0/2.0	1.0/2.0
	1.0/4.0	1.0/4.0
	1.0/6.0	1.0/6.0

Table 4.3 Effect of Annealing Temperature

Annealing Temperature (°C)	CTAC/FA/HEC (%wt/wt/wt)	BTAC/FA/HEC (%wt/wt/wt)
26	1.0/2.0/0.5 1.0/4.0/0.5	1.0/2.0/0.5 1.0/4.0/0.5
40	1.0/2.0/0.5 1.0/4.0/0.5	1.0/2.0/0.5 1.0/4.0/0.5
53	1.0/2.0/0.5 1.0/4.0/0.5	1.0/2.0/0.5 1.0/4.0/0.5
80	1.0/2.0/0.5 1.0/4.0/0.5	1.0/2.0/0.5 1.0/4.0/0.5

Table 4.4 Effect of pH

pH	CTAC/FA (%wt/wt)	BTAC/FA (%wt/wt)
3	1.0/2.0 1.0/4.0 1.0/6.0	1.0/2.0 1.0/4.0 1.0/6.0
5	1.0/2.0 1.0/4.0 1.0/6.0	1.0/2.0 1.0/4.0 1.0/6.0
7	1.0/2.0 1.0/4.0 1.0/6.0	1.0/2.0 1.0/4.0 1.0/6.0
9	1.0/2.0 1.0/4.0 1.0/6.0	1.0/2.0 1.0/4.0 1.0/6.0

4.1 Effect of Fatty Alcohol Concentration

Figure 4.1 shows the plot of G_N^o vs. mole ratio of FA to the surfactants or N_{FA}/N_{CTAC} and N_{FA}/N_{BTAC}. The plots indicate that the values of G_N^o of both emulsions increase with increasing mole ratio of fatty alcohol concentration and there is no significant difference in G_N^o between the CTAC/FA and the BTAC/FA emulsions. Figure 4.2 shows a plot of τ_B vs. mole ratio of FA to CTAC and BTAC. Measured values of τ_B of the CTAC/FA emulsions are higher than those of the BTAC/FA emulsions. This result is consistent with the previous finding of Barameesangpet (1999) who found that the values of G_N^o and τ_B of the two emulsions increased with fatty alcohol content until reaching the saturation values. Figure 4.3 shows the η_o versus mole ratio of FA to CTAC and BTAC. At low fatty alcohol concentration (2 %wt), η_o of the BTAC/FA emulsions are higher than the CTAC/FA emulsions. The η_o of both emulsions increase with fatty alcohol concentration and show nearly the same values at the saturation states.

The morphology of these two emulsion systems are shown in Figures 4.4 and 4.5. Figure 4.4 shows micrographs of the CTAC/FA emulsions and Figure 4.5 shows micrographs of the BTAC/FA emulsions at various fatty alcohol concentrations. For the CTAC/FA emulsions, we can observe a lamellar structure occurring in the emulsions at very low fatty alcohol concentration (1 %wt) and it changed to a the vesicle structure when fatty alcohol was increased (2 %wt). At 4.0 - 5.0 %wt, the emulsions were consisted of lamellar aggregate structures with droplets of fatty alcohol existing inside. The structures appearing in micrographs at very high fatty alcohol concentration (5.0 – 8.0 %wt) suggest a binding between lamellar aggregate structures. For the BTAC/FA emulsions, the vesicle structure was formed even at very low fatty alcohol concentrations (1.0 – 2.0 %wt). At 4.0 %wt, the lamellar structure was formed in the shape of sphere surrounded by the vesicle structure. These structures may occur because of the hydrophobic portions of surfactant molecules at the edge of the lamellar structure did not want to expose to water layers. They could avoid water molecules by forming into a sphere in order to form a more stable structure. We can see a small droplet of fatty alcohol left inside the lamellar structure, in the same manner as the CTAC/FA emulsions. At very high fatty alcohol concentrations (5.0 - 8.0 %wt), the emulsions were consisted of sunflower-like structures or a lamellar structures surrounding large fatty alcohol droplets and there was no network structure.

The results from optical measurement are consistent with the rheological data. As fatty alcohol was increased, there was more fatty alcohol to interact with the surfactants so the lamellar or the vesicle structure became larger leading to increases in viscosity and elasticity of emulsions. However, the values of τ_B and η_o of the CTAC/FA emulsions at high fatty alcohol concentrations were higher than those of the BTAC/FA emulsions due to the formation of the network structure.

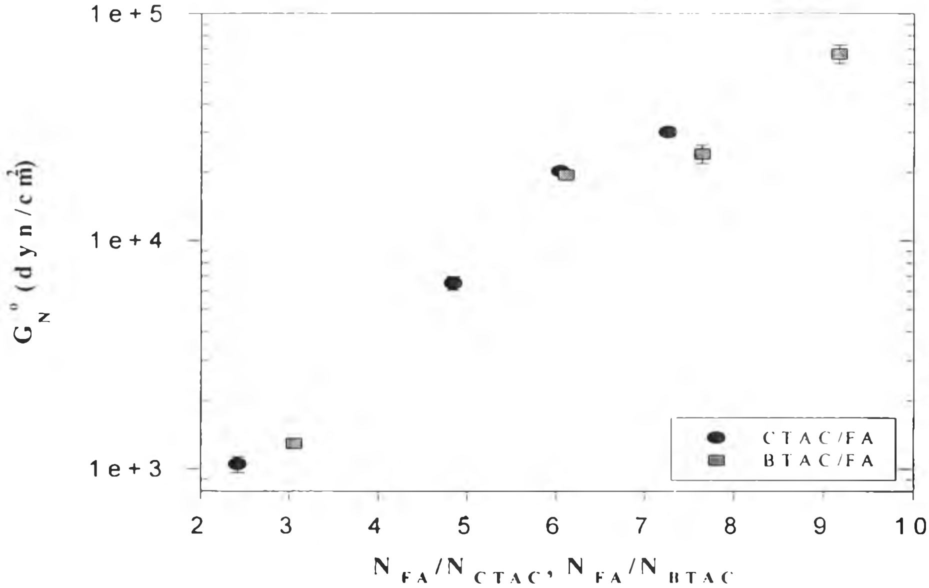


Figure 4.1 G_N^0 vs. fatty alcohol concentration of the CTAC/FA and BTAC/FA emulsions at equilibrium.

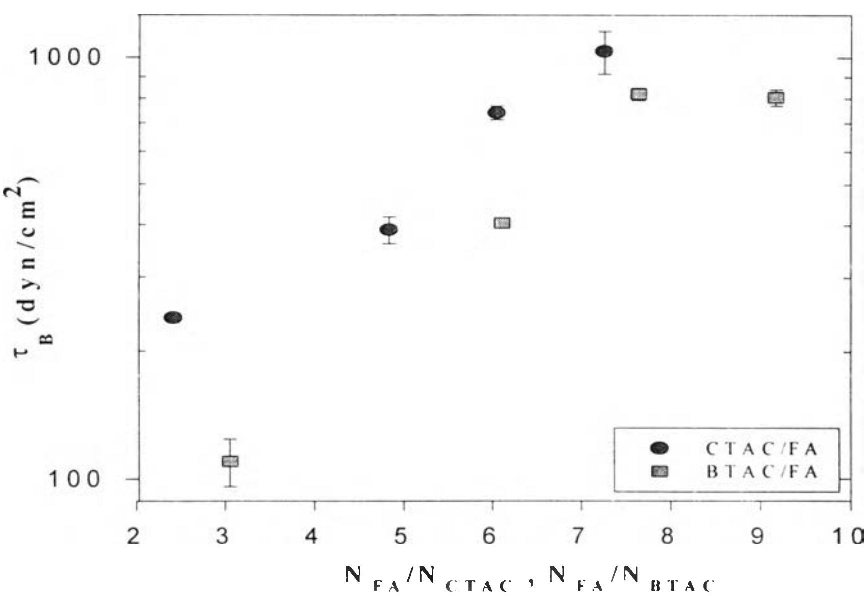


Figure 4.2 τ_B vs. fatty alcohol concentration of the CTAC/FA and BTAC/FA emulsions at equilibrium.

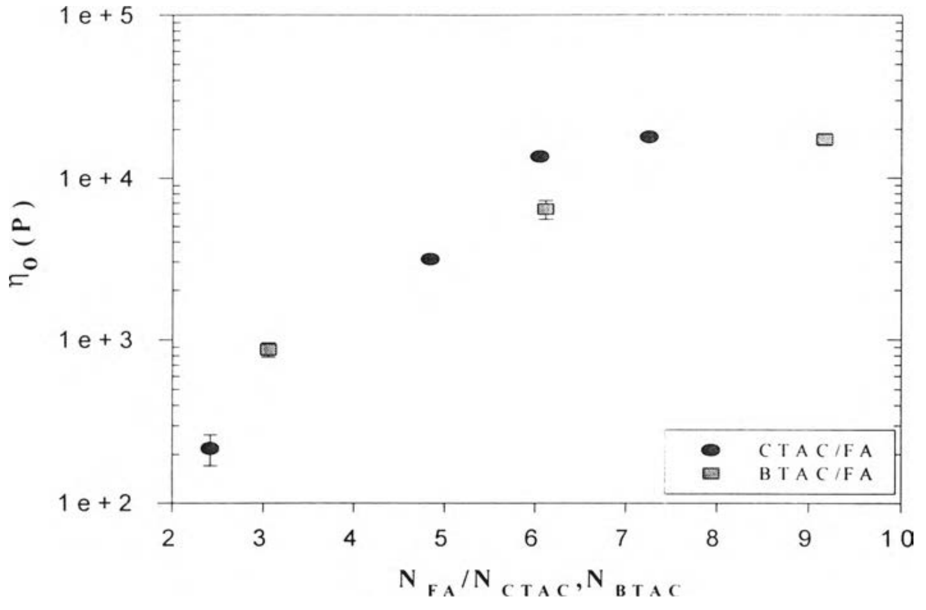


Figure 4.3 η_o vs. fatty alcohol concentration of CTAC/FA and BTAC/FA emulsions at equilibrium.

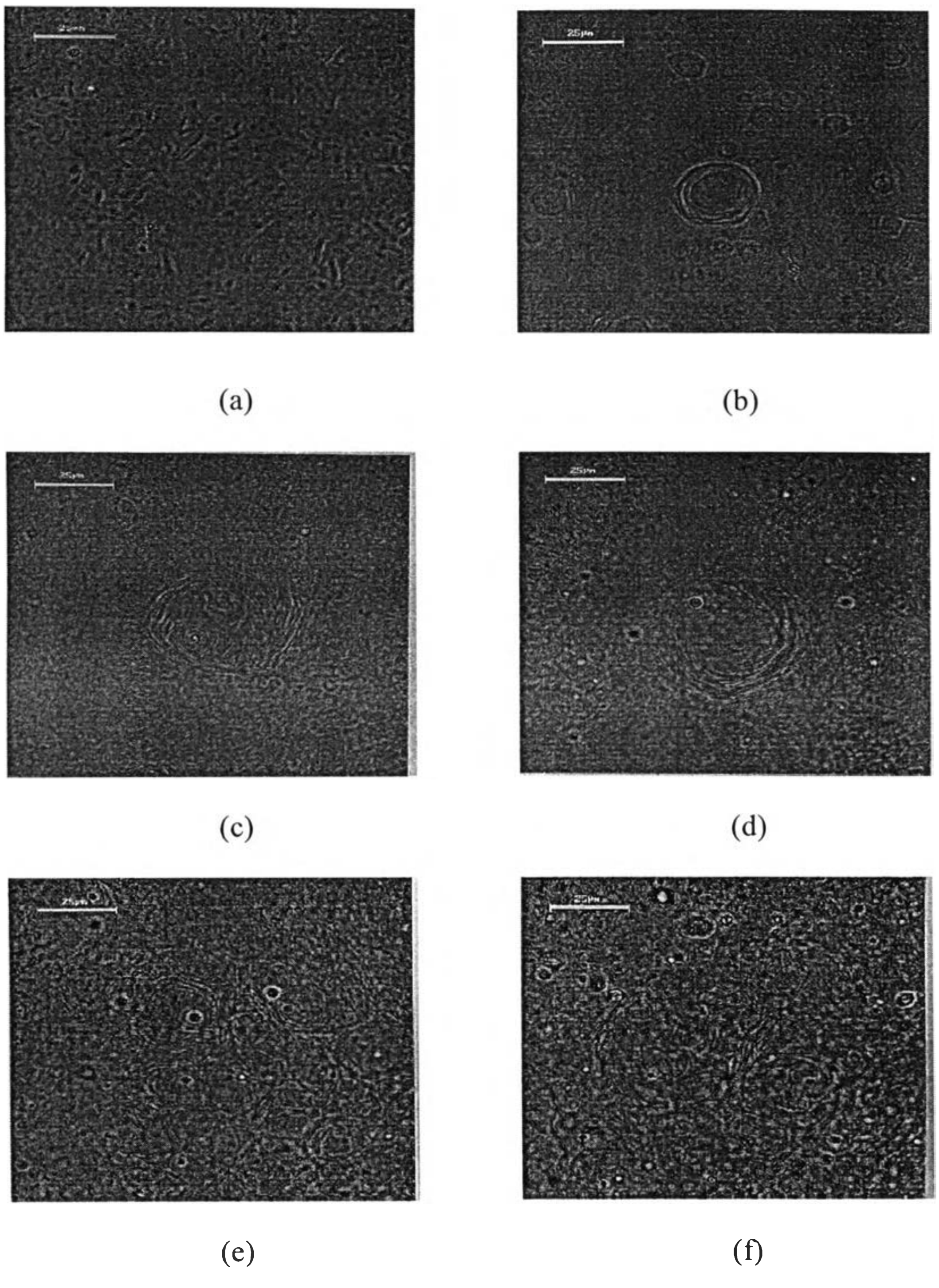
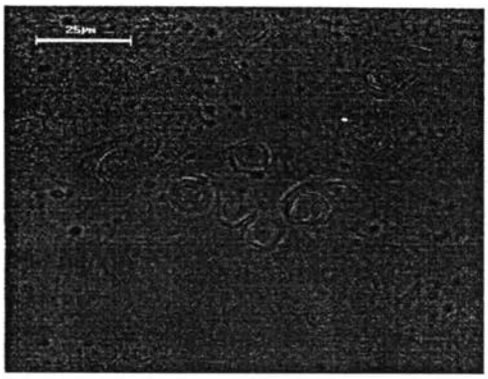
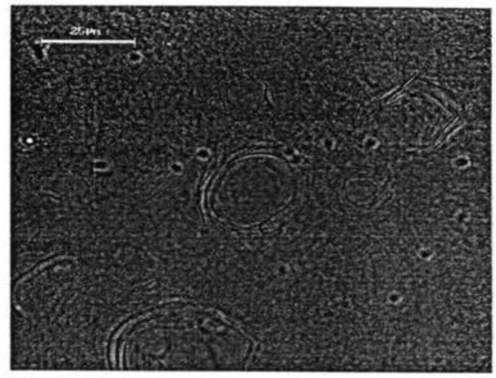


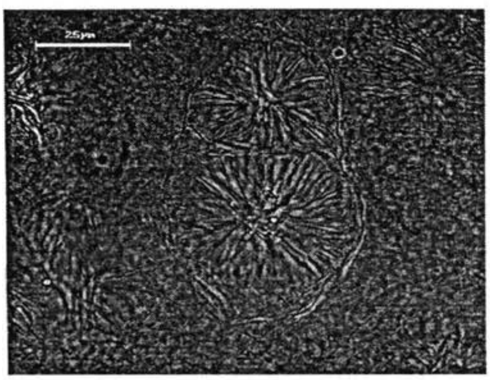
Figure 4.4 Micrographs of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium: (a) CTAC/FA = 1.0/1.0; (b) CTAC/FA = 1.0/2.0; (c) CTAC/FA = 1.0/4.0; (d) CTAC/FA = 1.0/5.0; (e) CTAC/FA = 1.0/6.0; (f) CTAC/FA 1.0/8.0.



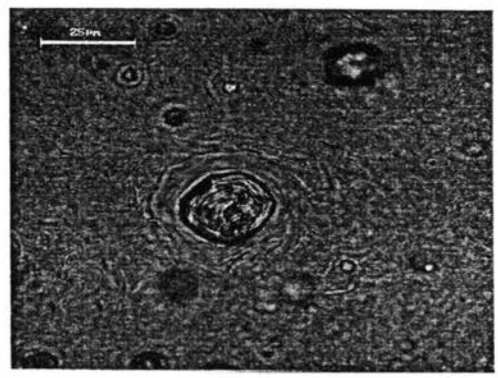
(a)



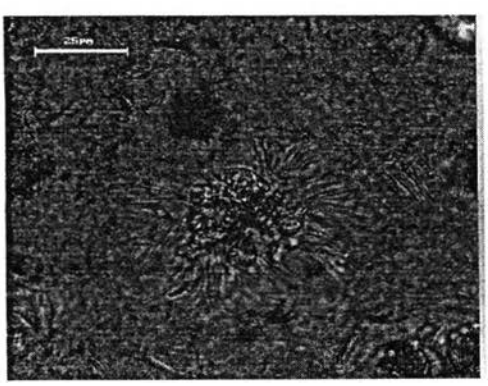
(b)



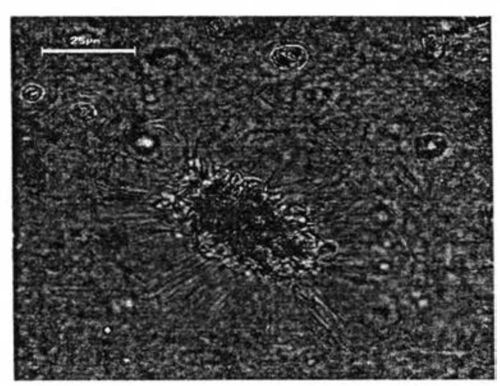
(c)



(d)



(e)



(f)

Figure 4.5 Micrographs of the BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium: (a) BTAC/FA = 1.0/1.0; (b) BTAC/FA = 1.0/2.0; (c) BTAC/FA = 1.0/4.0; (d) BTAC/FA = 1.0/5.0; (e) BTAC/FA = 1.0/6.0; (f) BTAC/FA 1.0/8.0.

4.2 Effect of Temperature

Figures 4.6 and 4.7 show G_N^o versus temperature of CTAC/FA and BTAC/FA emulsions at various fatty alcohol concentrations. At 2 %wt of fatty alcohol concentration, G_N^o decreases with increasing temperature but the temperature has no influence on G_N^o for the emulsions with 4 and 6 %wt of fatty alcohol concentrations. The plots of τ_B versus temperature of CTAC/FA and BTAC/FA emulsions with various fatty alcohol concentrations are shown in Figures 4.8 and 4.9. We can notice that τ_B of both emulsions do not vary with temperature at high fatty alcohol concentration (4-6 % wt) but τ_B shows a slight decrease with temperature at low fatty alcohol concentration especially for the CTAC/FA emulsion. Figures 4.10 and 4.11 show η_o versus temperature as a function of fatty alcohol concentration. The values of η_o of both emulsions at all fatty alcohol concentrations do not change markedly with temperature. When temperature was increased it caused a reduction in the hydration of the hydrophilic group of surfactant, leading to the disruption between the water molecules and the polar group of surfactants. Because there was more amount of water at low fatty alcohol concentration than at high fatty alcohol concentration, we can observe the decrease in G_N^o at low fatty alcohol concentration. We can summarize that the hydration force is more pronounced only at low fatty alcohol concentration. This suggests that the elasticity and viscosity of both CTAC/FA and BTAC/FA emulsions especially at high fatty alcohol concentration (4 - 6 %wt) are independent of temperature.

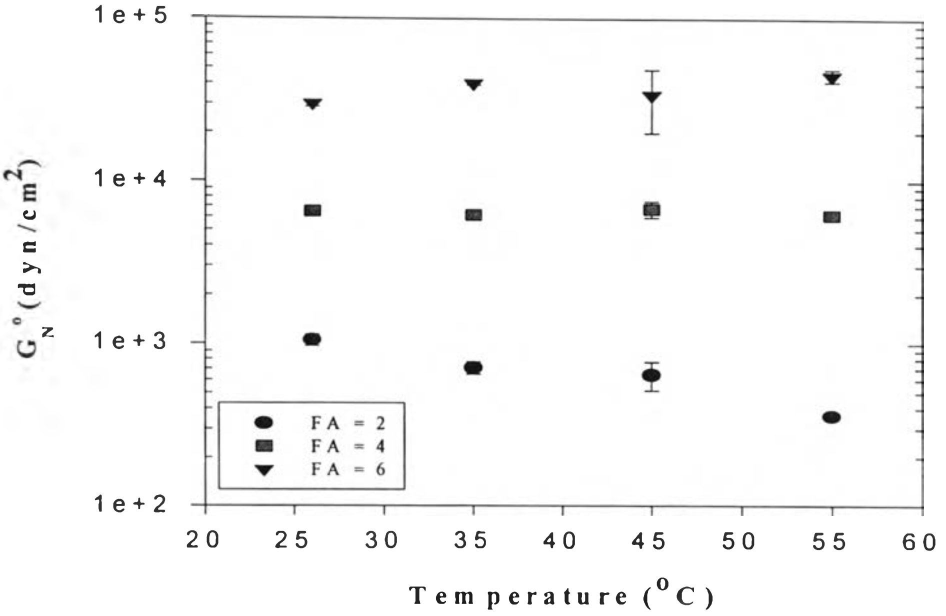


Figure 4.6 G_N^o vs. temperature of CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

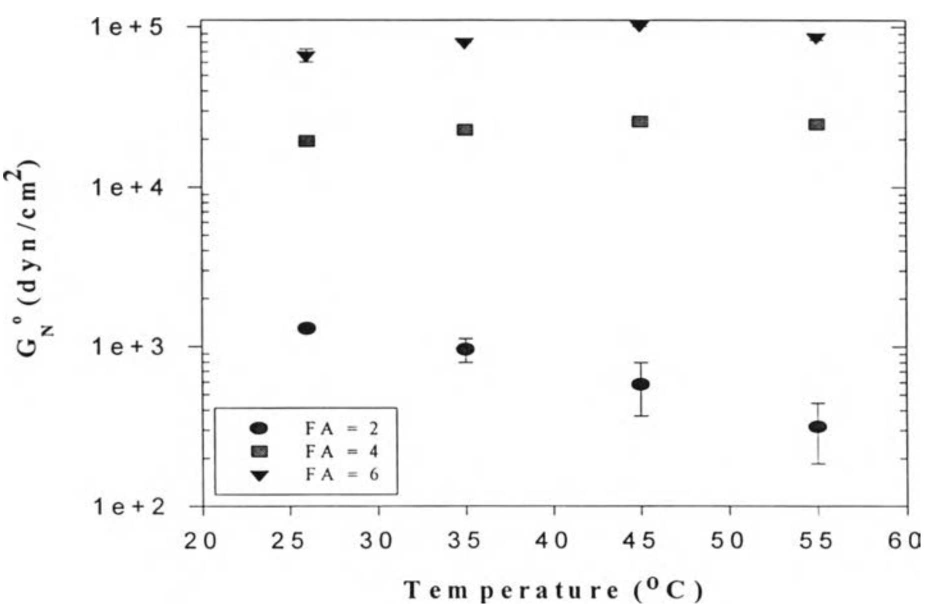


Figure 4.7 G_N^o vs. temperature of BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

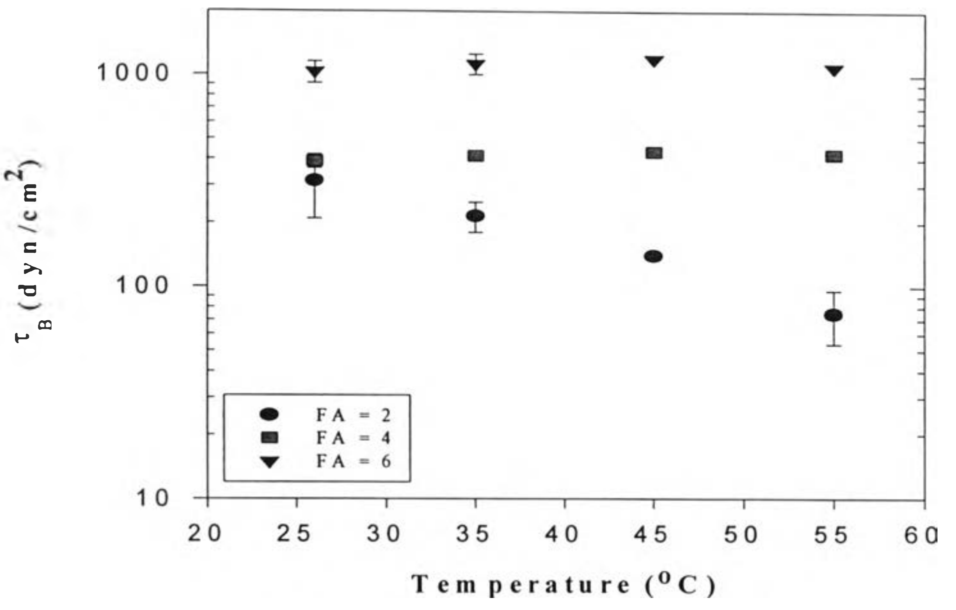


Figure 4.8 τ_B vs. temperature of CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

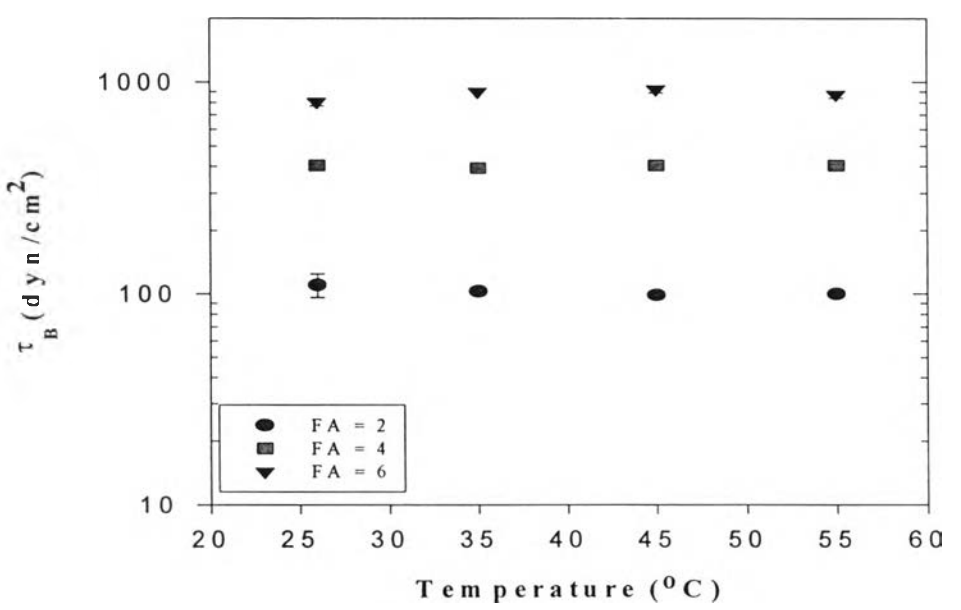


Figure 4.9 τ_B vs. temperature of BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

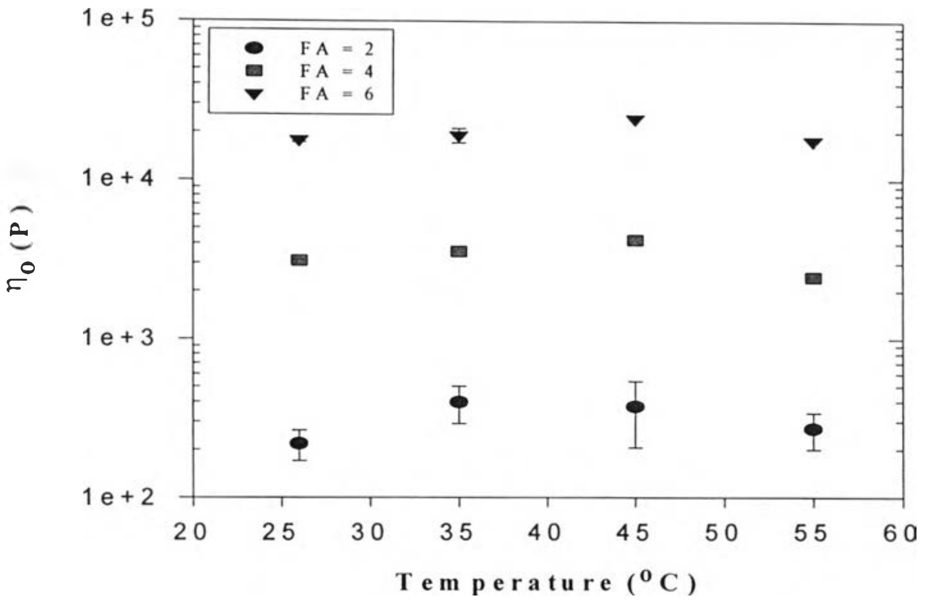


Figure 4.10 η_o vs. temperature of CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

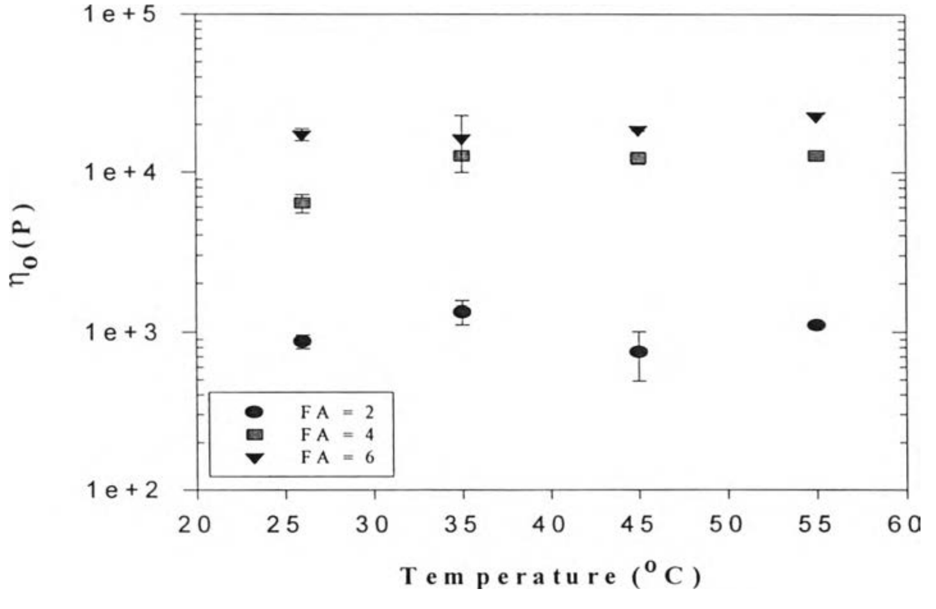


Figure 4.11 η_o vs. temperature of BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

4.3 Effect of Annealing Temperature

The effect of annealing was studied after the emulsions were annealed at 40, 53 and 80 °C respectively. Then the emulsions were cooled down naturally toward room temperature. After cooling, we investigated the rheological and optical properties of the emulsion systems as a function of aging time. G_N^o, τ_B and η_o were used to describe the changes in the emulsion properties.

4.3.1 <u>CTAC/FA/HEC Emulsions</u>

Figures 4.12 and 4.13 show the G_N^o versus aging time at various annealing temperatures for the CTAC/FA emulsions at 1.0/2.0 %wt and 1.0/4.0 %wt respectively. Initially, G_N^O at high fatty alcohol concentrations are higher than G_N^o at low fatty alcohol concentrations at about one order of magnitude. After the emulsions were annealed to 40 and 53 °C, the values of G_N^o of both two systems recovered the initial values within 1 day whereas the emulsion annealed at 80 °C cannot recover. Figures 4.14 and 4.15 show τ_B versus aging time of the CTAC/FA/HEC = 1.0/2.0/0.5 %wt emulsion compared with the 1.0/4.0/0.5 %wt emulsion. It can be seen that τ_B of both systems do not change with annealing temperatures. For the plots of η_o versus aging time at low fatty alcohol concentration (CTAC/FA/HEC = 1.0/2.0/0.5) as shown in Figures 4.16, we found that η_o do not change with annealing temperature. On the contrary, at high fatty alcohol concentration (CTAC/FA/HEC = 1.0/4.0/0.5), the values of η_o annealed at 80 °C cannot recover their initial values as shown in Figure 4.17.

Micrographs in Figures 4.18 - 4.23 show the liquid crystalline structure in the form of lamellar aggregate structures at low and high fatty alcohol concentrations. Larger structures appeared at high fatty alcohol concentration. G_N^o of both systems did not vary significantly with annealing temperature except at 80 °C. At this temperature, G_N^o shows a drastic decrease and they cannot return to their initial values. The micrographs in Figures 4.20 and 4.23 can be used to describe these occurrences. There are no liquid crystalline phases in the emulsions annealed at 80 °C, instead we observed isotropic dispersed phases. For the annealing temperature higher than the melting point of fatty alcohol, 53 °C, there was a reduction in the viscosity of the disperse phase and the corresponding change in emulsion rheological properties. So G_N^o at 80 °C are different than those annealed at other temperatures or unannealed.

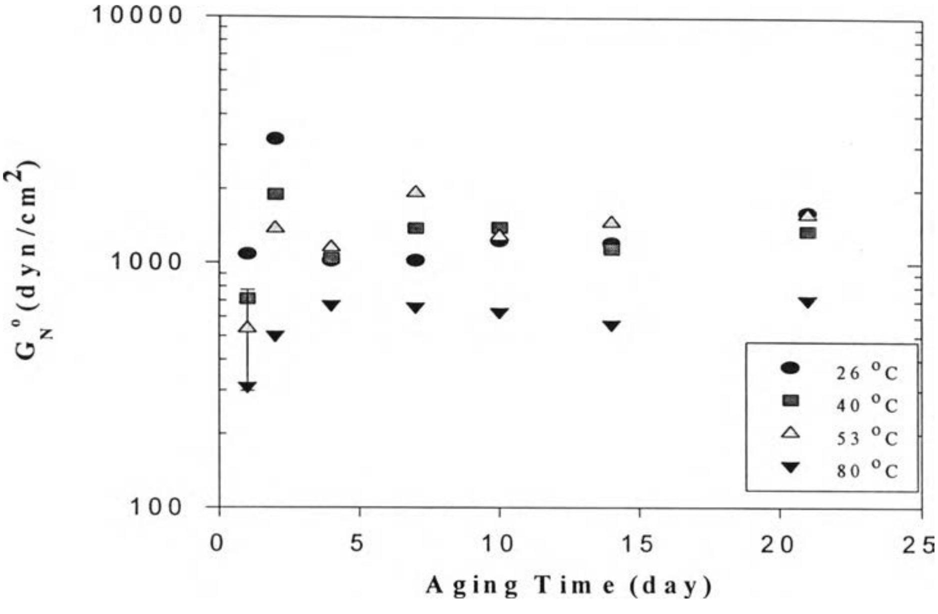


Figure 4.12 G_N^o vs. aging time of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.

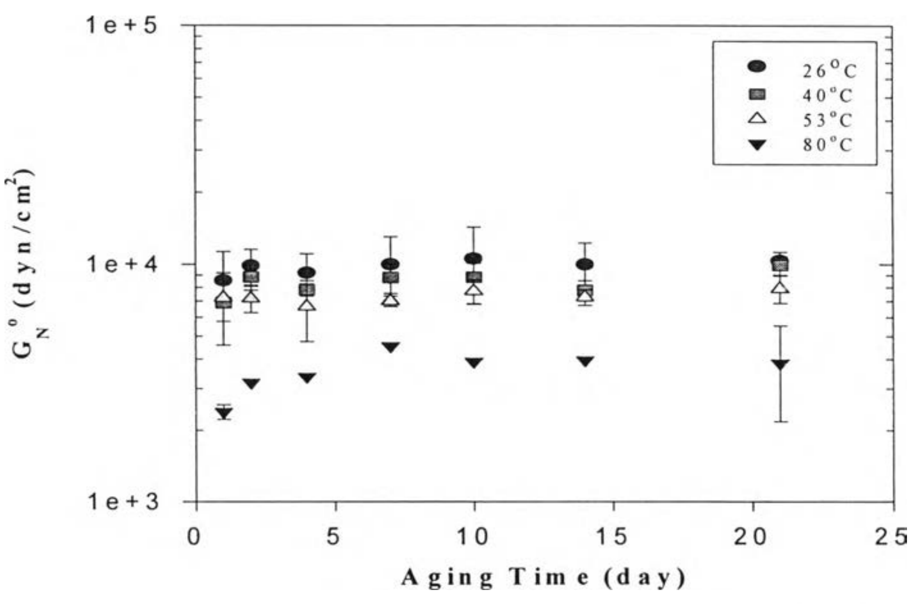


Figure 4.13 G_N^o vs. aging time of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.

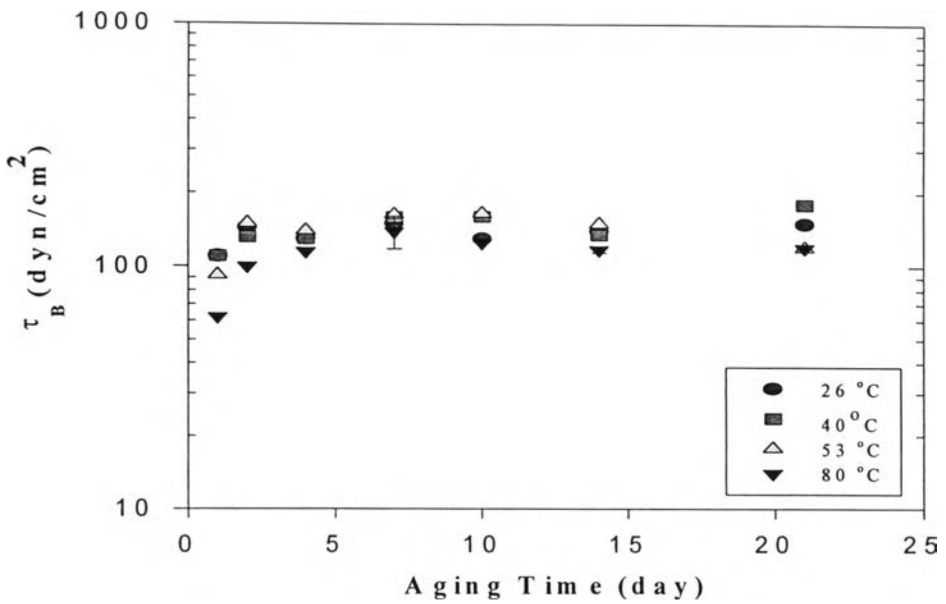


Figure 4.14 τ_B vs. aging time of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures

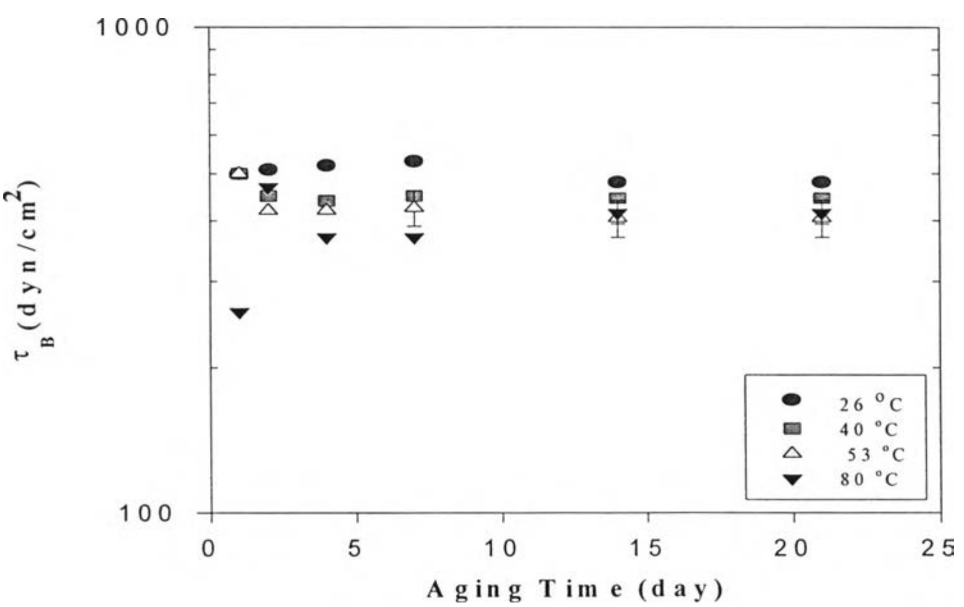


Figure 4.15 τ_B vs. aging time of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.

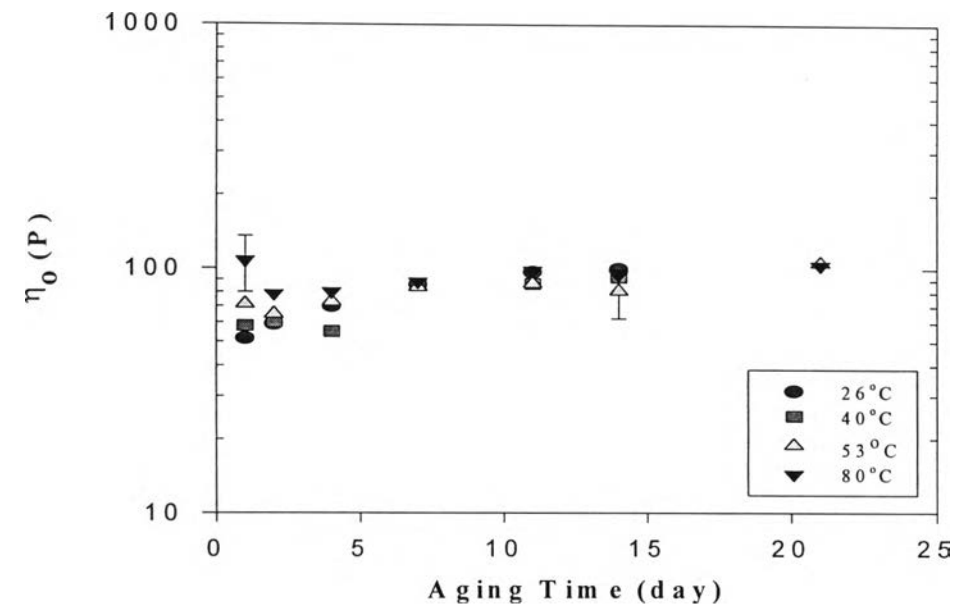


Figure 4.16 η_o vs. aging time of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.

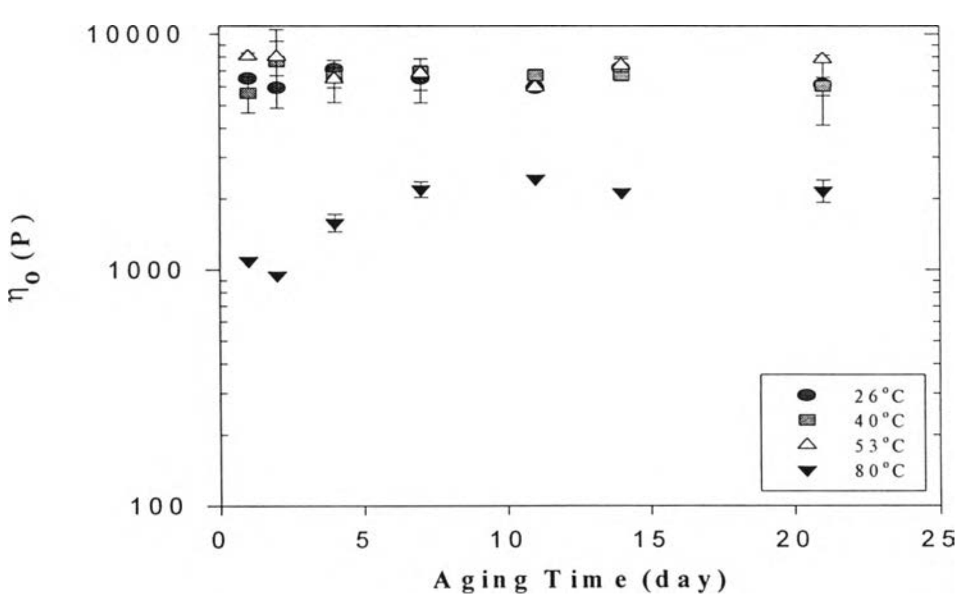
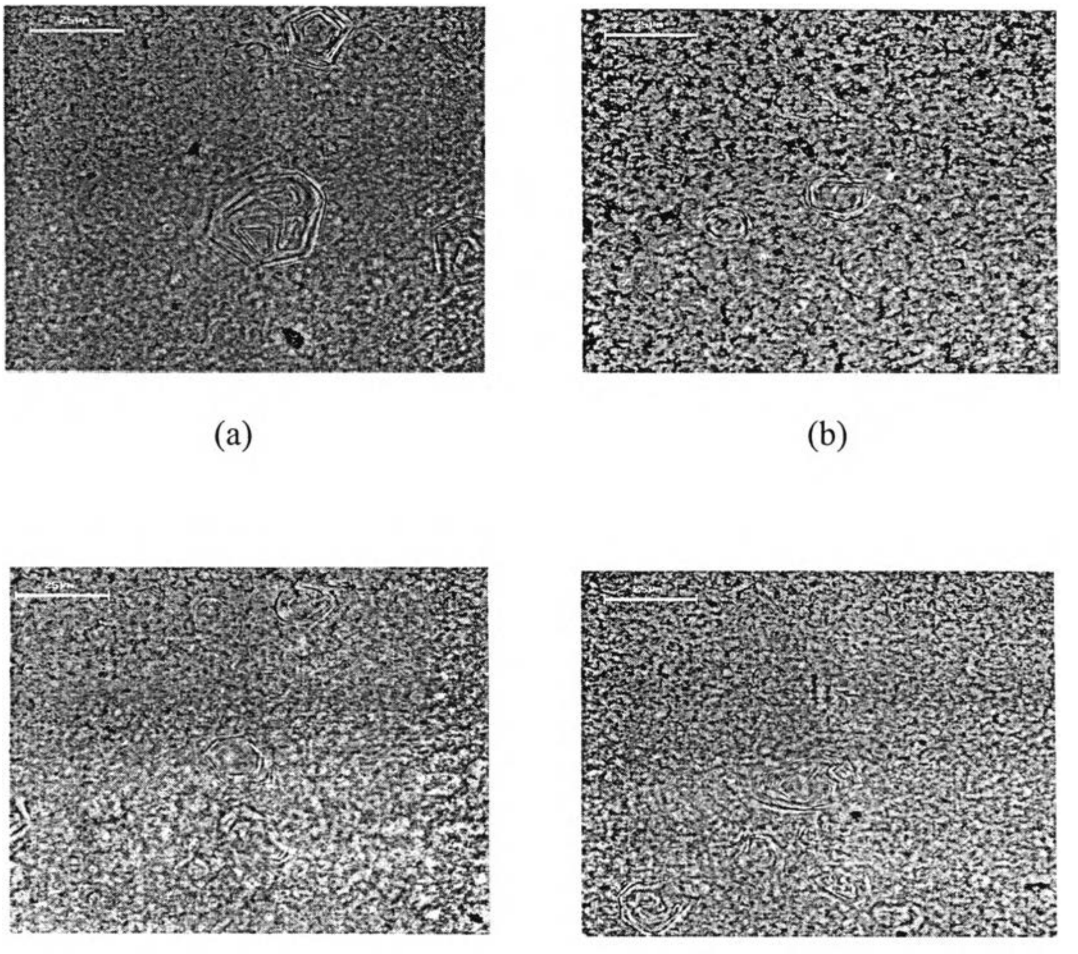


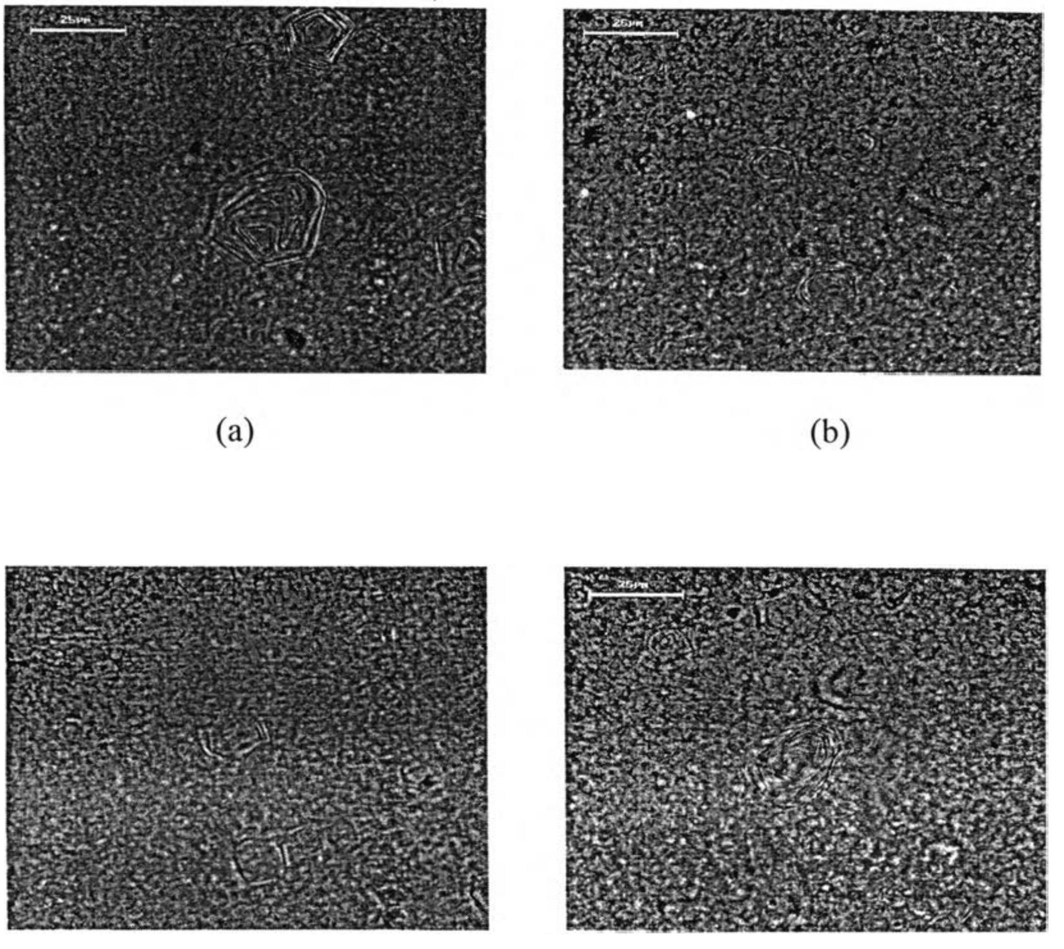
Figure 4.17 η_o vs. aging time of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.



(a) (b)

(c) (d)

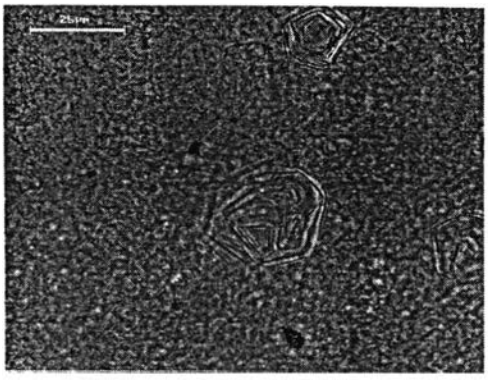
Figure 4.18 Micrographs of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 40°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.



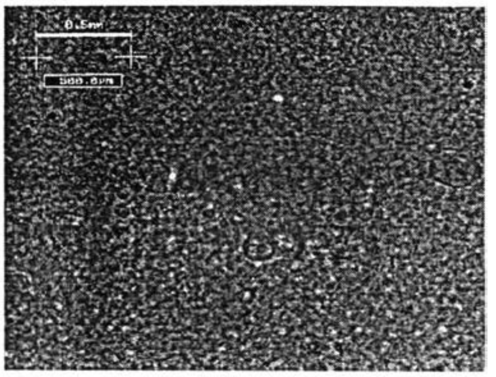
(a) (b)

(c) (d)

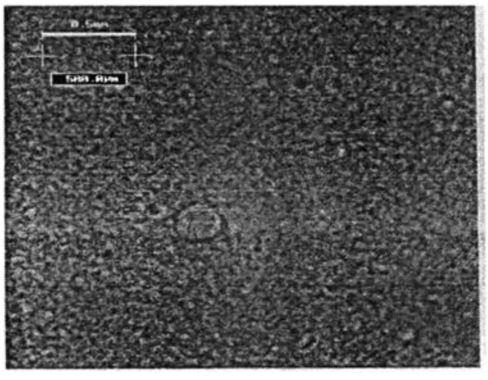
Figure 4.19 Micrographs of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 53°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.



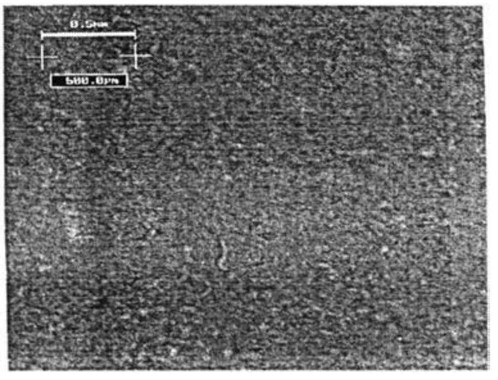
(a)



(b)



(c)



(d)

Figure 4.20 Micrographs of the CTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 80°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.

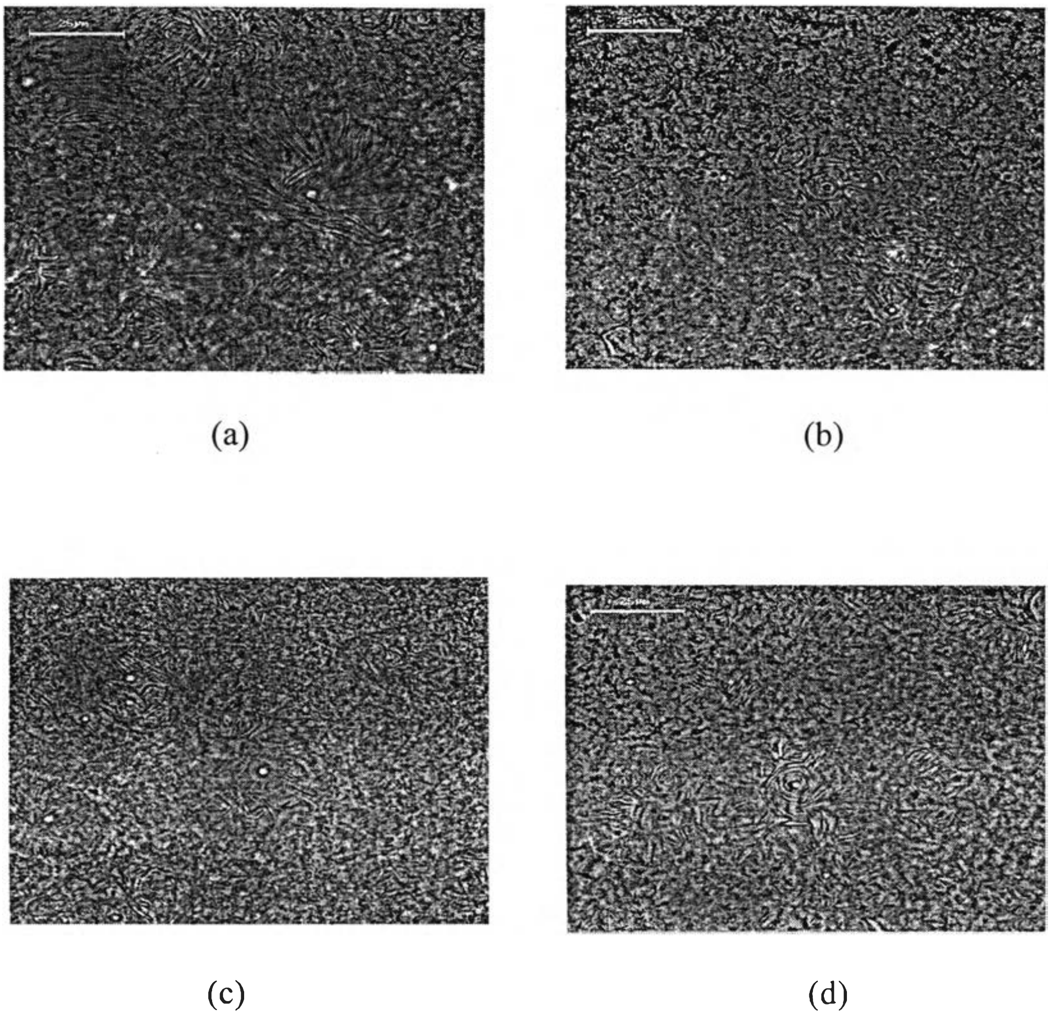
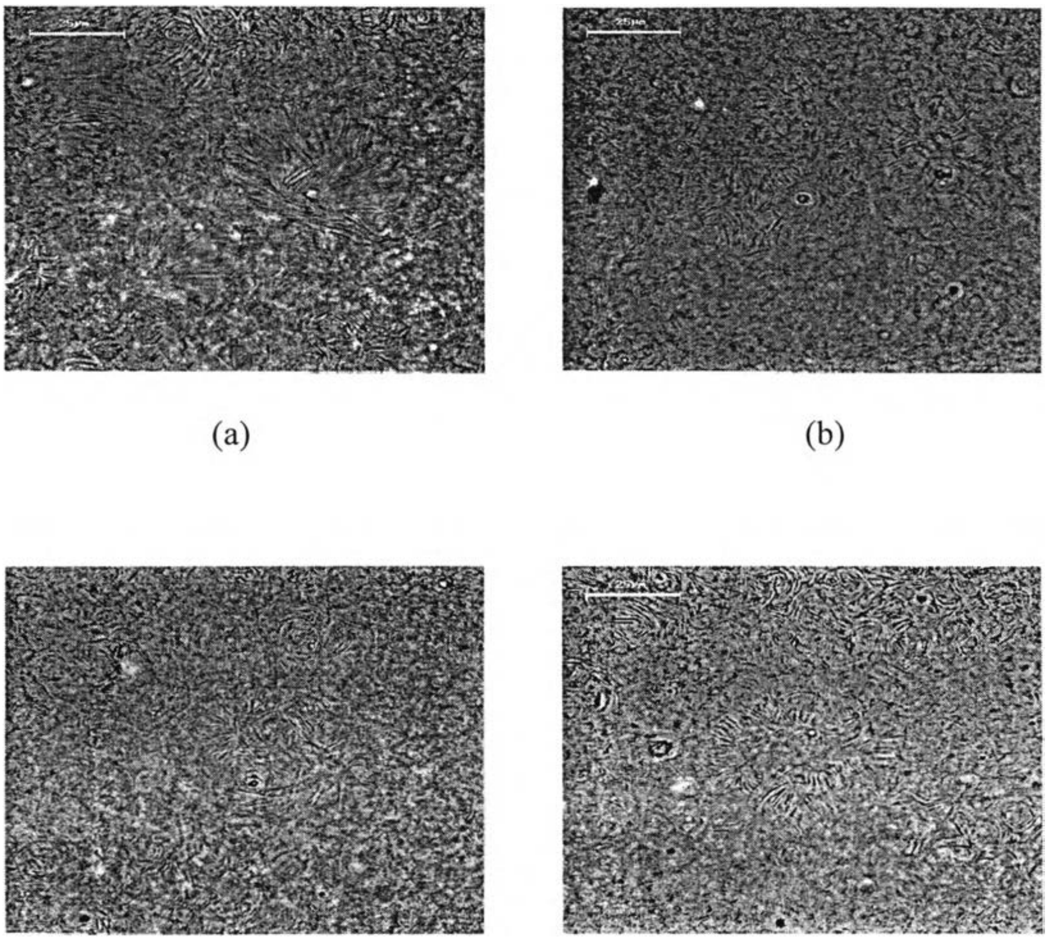


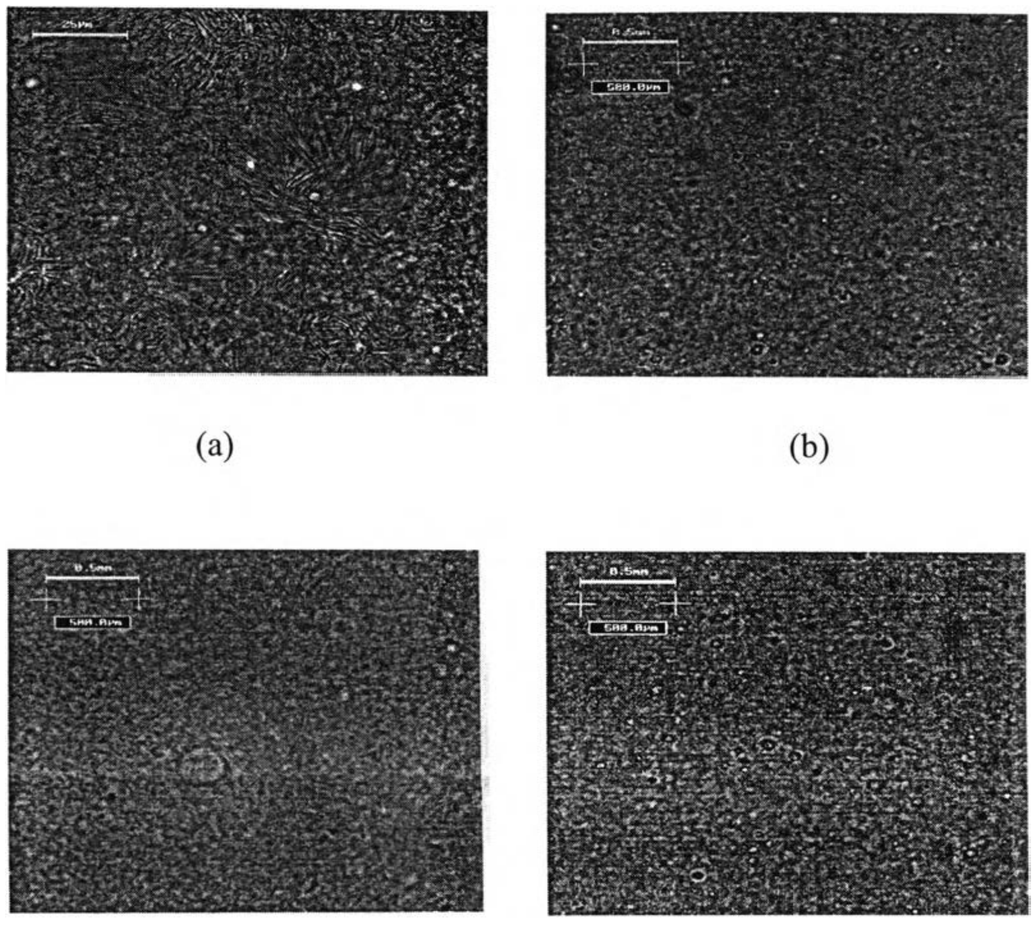
Figure 4.21 Micrographs of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 40°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days and (d) aging 14 days.



(a) (b)

(c) (d)

Figure 4.22 Micrographs of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 53°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.



(a) (b) (c) (d)

Figure 4.23 Micrographs of the CTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 80 °C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.

4.3.2 BTAC/FA/HEC Emulsions

The G_N^o versus aging time of the BTAC/FA/HEC = 1.0/2.0/0.5 %wt and 1.0/4.0/0.5 %wt emulsions at various annealing temperatures are shown in Figures 4.24 and 4.25. The values of G_N^o at high fatty alcohol concentrations are much greater than those at low fatty alcohol concentrations. It can be seen that for the emulsions annealed at 80 °C, G_N^o did not return to the initial values whereas the emulsions at other temperatures did. G_N^o recovered to the original values after aging around 1 days. Figures 4.26 and 4.27 show τ_B versus aging time of BTAC/FA/HEC = 1.0/2.0/0.5 %wt and 1.0/4.0/0.5 %wt emulsions. It can be clearly seen that there is no significant change in τ_B with annealing temperature. Figures 4.28 and 4.29 show η_o versus aging time of the same emulsions. At low fatty alcohol concentration, η_o at the annealing temperature of 80 °C seems to be lower than those at other annealing temperatures. But at the high fatty alcohol concentration (BTAC/FA/HEC = 1.0/4.0/0.5 %wt), the annealing temperature has no affect on η_o. These results can be explained by using the same arguments as those of the CTAC/FA/HEC emulsions.

The micrographs of BTAC/FA/HEC = 1.0/2.0/0.5 %wt and 1.0/4.0/0.5 %wt emulsions are shown in Figures 4.30 - 4.35. The sizes of the lamellar aggregate structure became larger at high fatty alcohol concentration. In addition, the structures of the emulsion systems at the annealing temperatures of 40 and 53 °C were significantly different from the emulsion without annealing (26 °C). Only at the annealing temperature of 80 °C, as shown in Figures 4.32 and 4.35, we can observe there was no lamellar structure in the emulsion systems. These results are consistent with the rheological measurement data. In the BTAC/FA/HEC = 1.0/4.0/0.5 %wt emulsion, we observed that the fatty alcohol droplets existed in the emulsion system. This was because of BTAC has a longer hydrophobic chain than CTAC and interacted with a lesser degree with fatty alcohol, thus we can observe fatty alcohol left in the BTAC emulsions more than the CTAC emulsions.

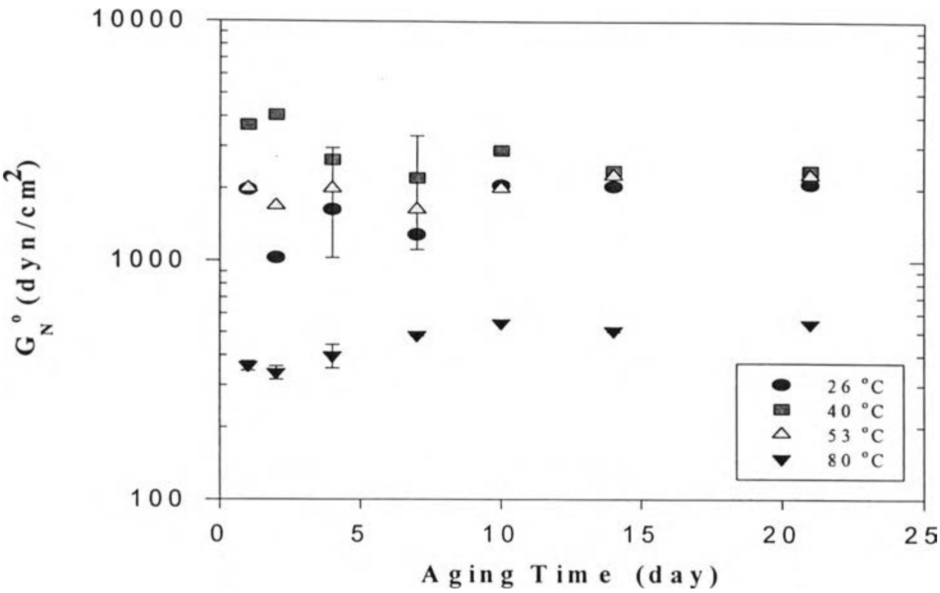


Figure 4.24 G_N^o vs. aging time of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.

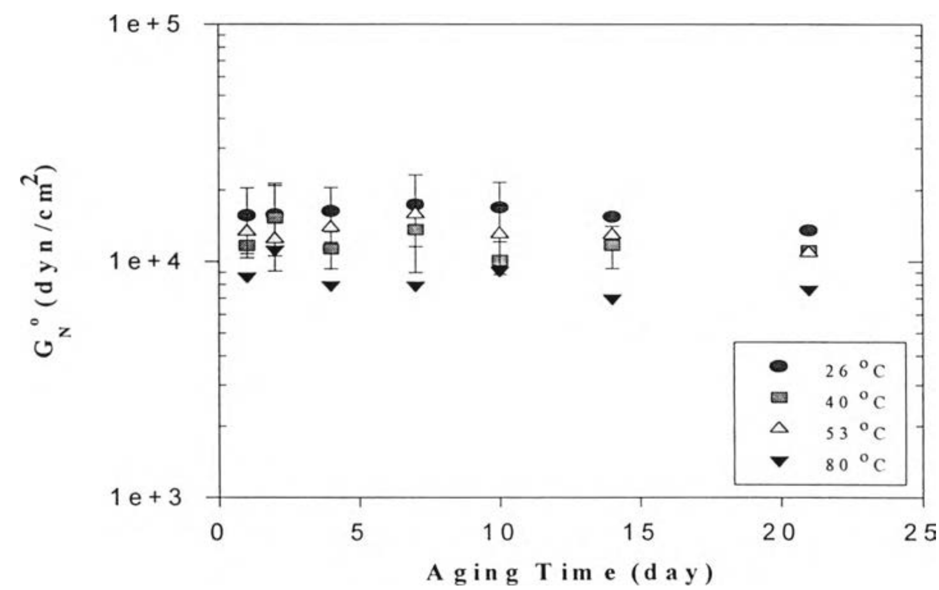


Figure 4.25 G_N^o vs. aging time of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.

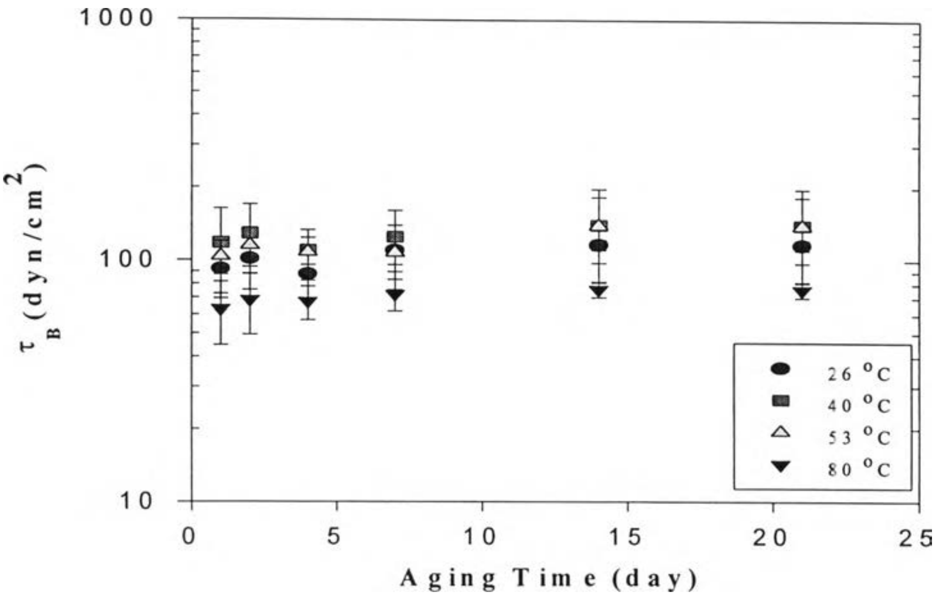


Figure 4.26 τ_B vs. aging time of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures

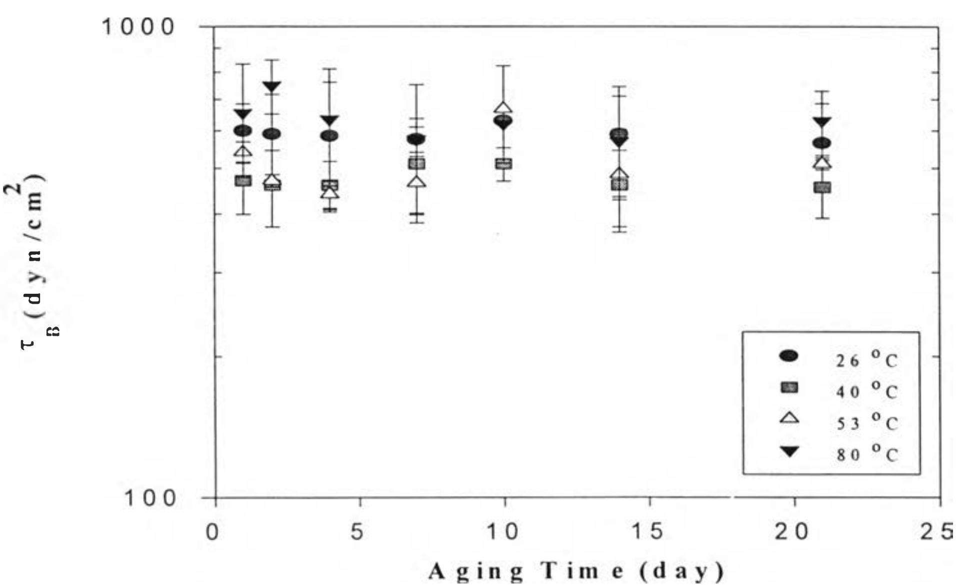


Figure 4.27 τ_B vs. aging time of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.

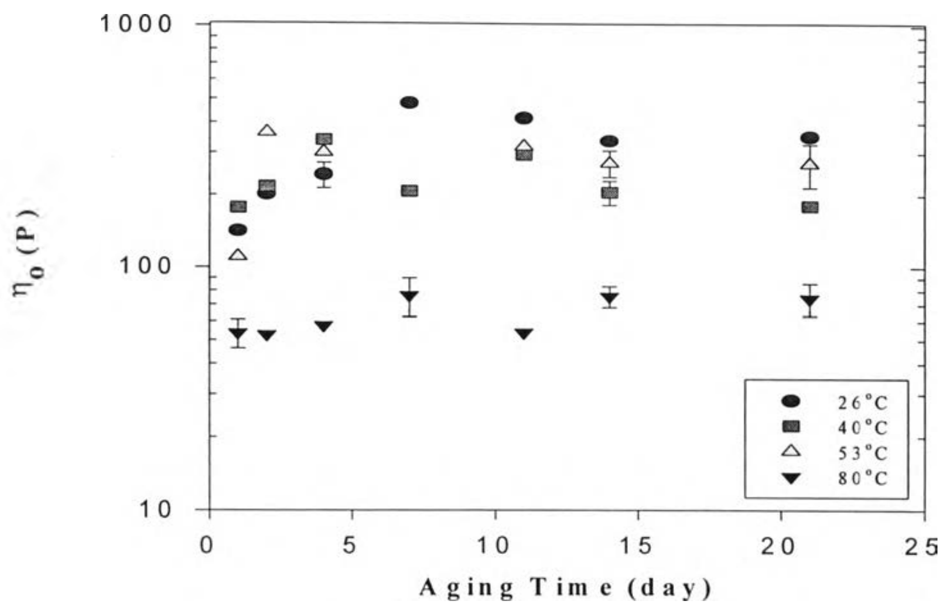


Figure 4.28 η_o vs. aging time of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at various annealing temperatures.

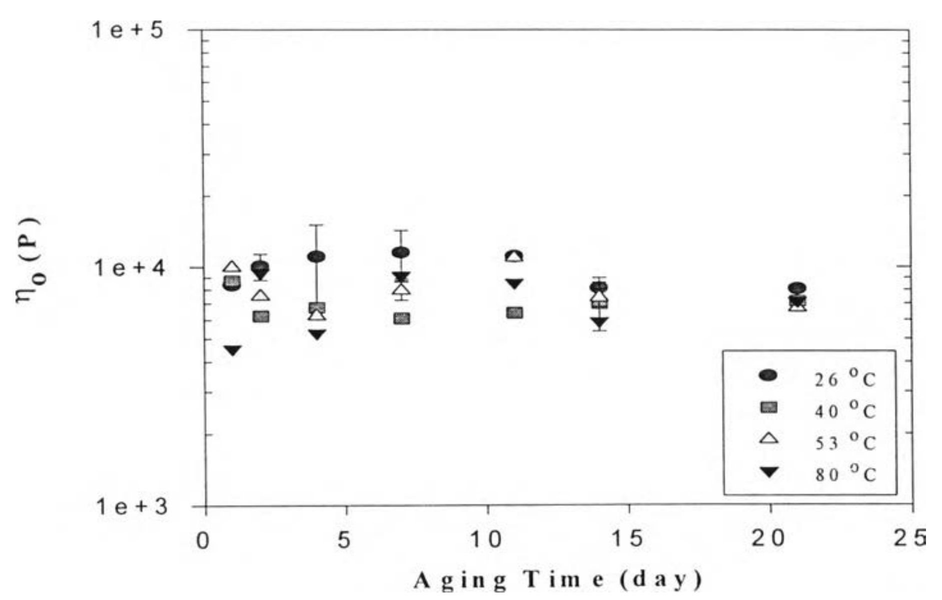
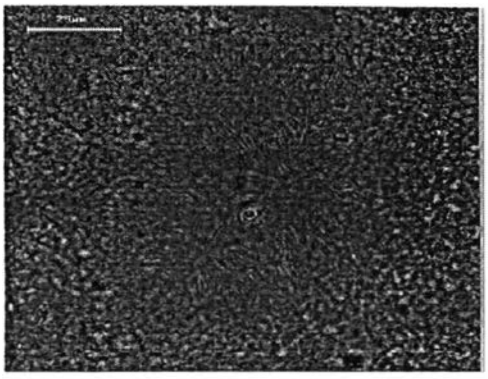
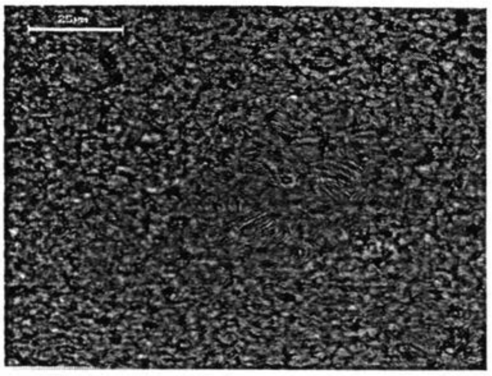


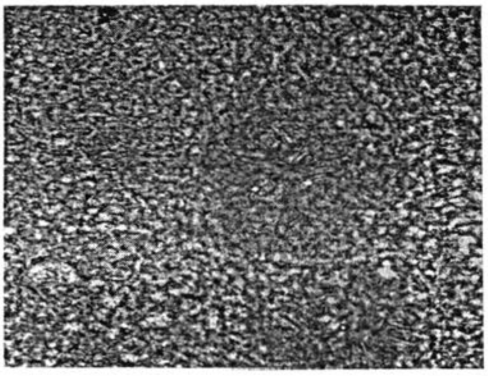
Figure 4.29 η_o vs. aging time of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at various annealing temperatures.



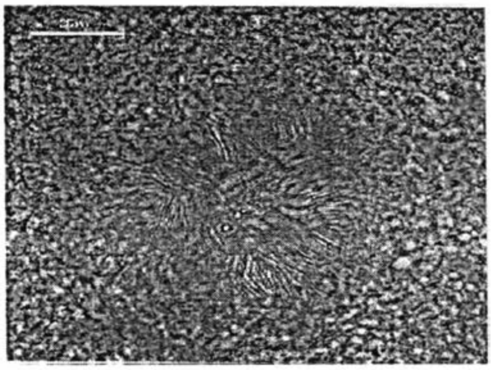
(a)



(b)

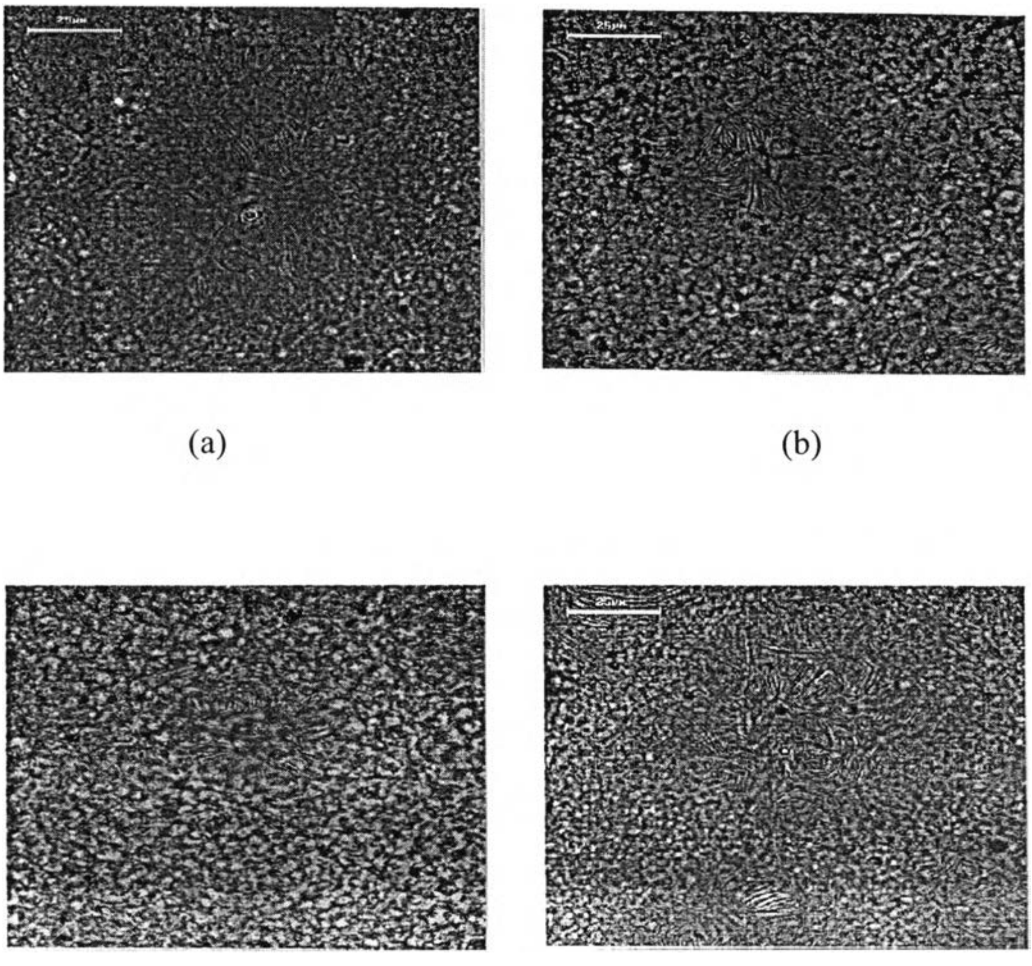


(c)



(d)

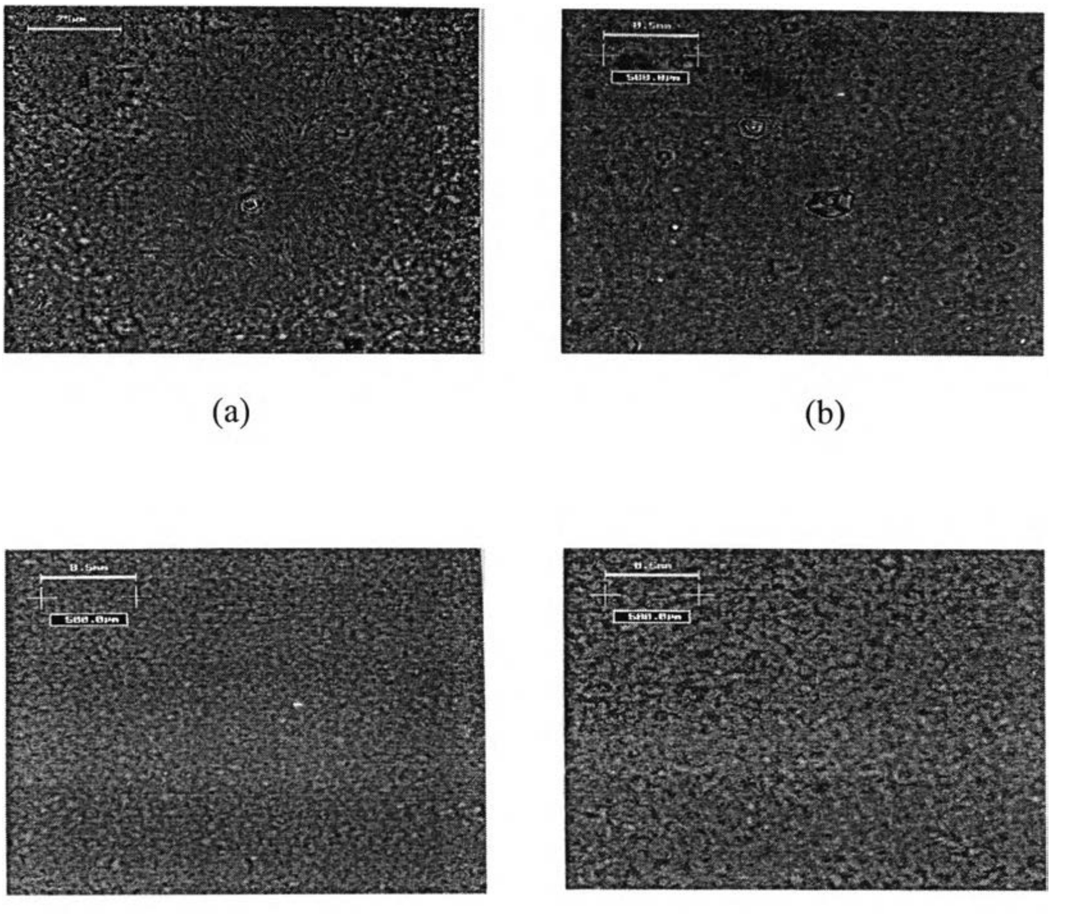
Figure 4.30 Micrographs of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 40°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.



(a) (b)

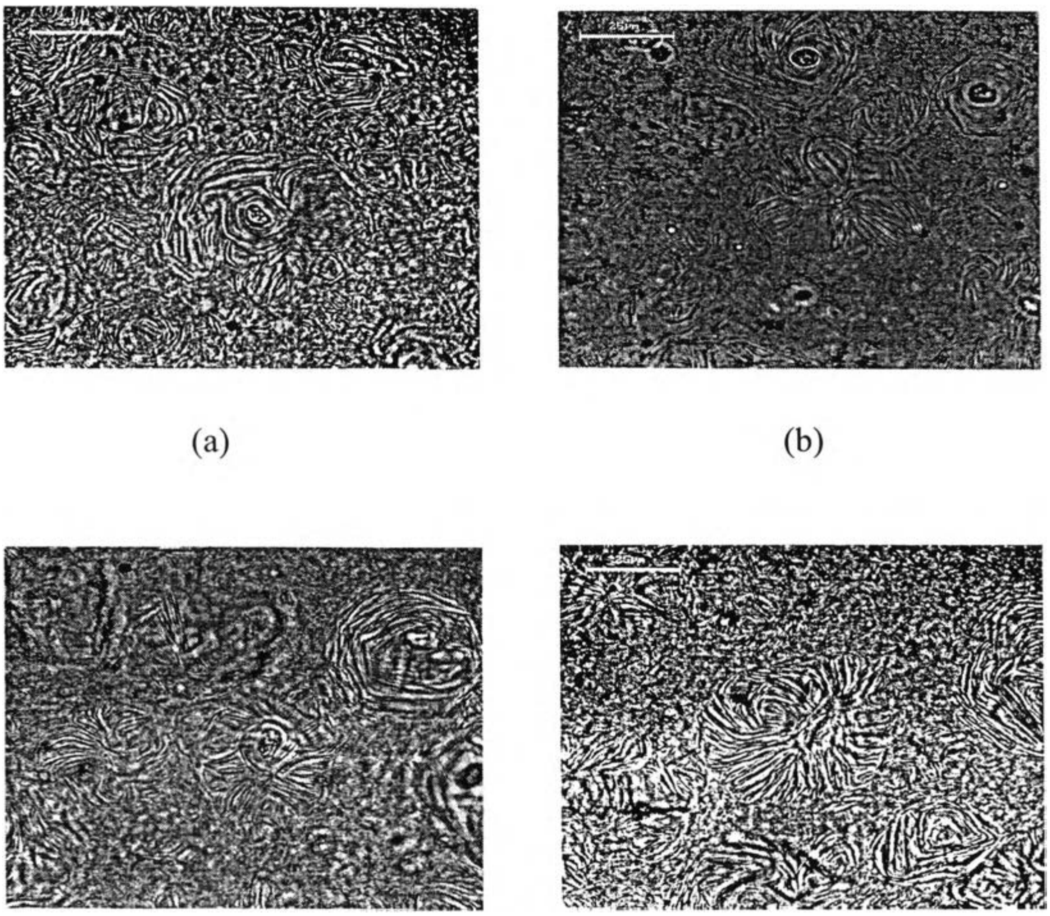
(c) (d)

Figure 4.31 Micrographs of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 53°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.



(a) (b) (c) (d)

Figure 4.32 Micrographs of the BTAC/FA/HEC = 1.0/2.0/0.5 emulsions at the annealing temperature of 80°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.



(a) (b)

(c) (d)

Figure 4.33 Micrographs of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 40°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.

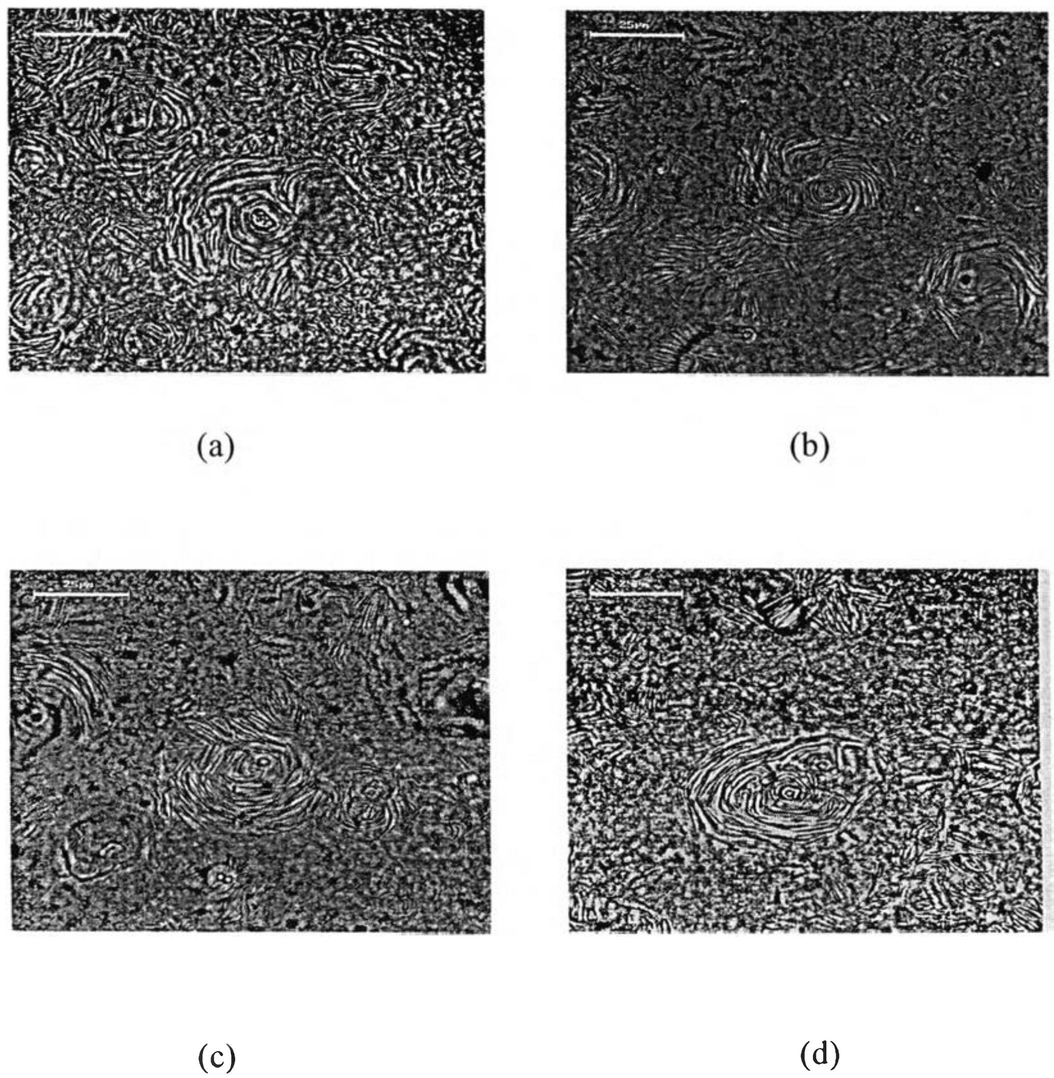


Figure 4.34 Micrographs of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 53°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.

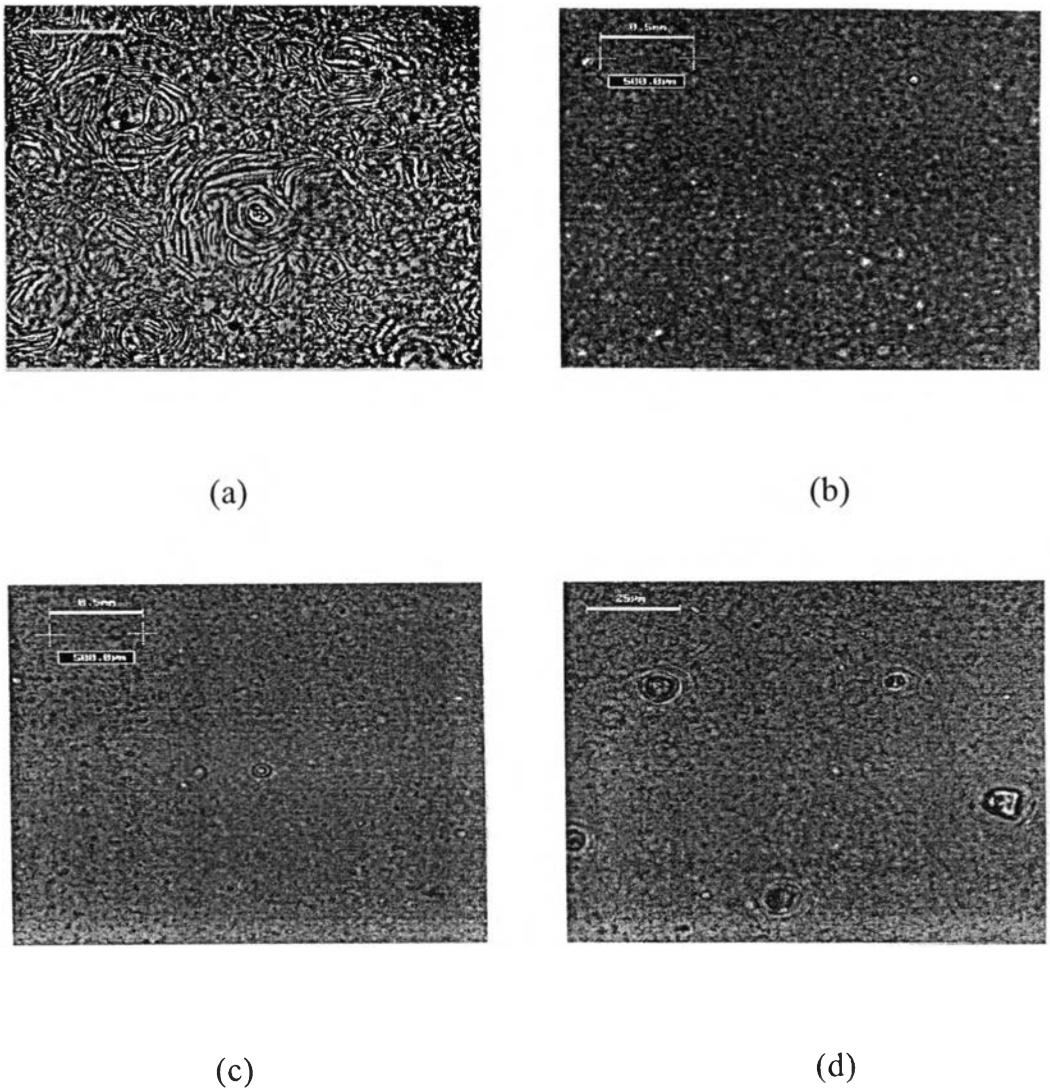


Figure 4.35 Micrographs of the BTAC/FA/HEC = 1.0/4.0/0.5 emulsions at the annealing temperature of 80°C at various aging times: (a) without annealing; (b) aging 1 day; (c) aging 7 days; (d) aging 14 days.

4.4 Effect of pH

The rheological and optical properties of the effect of pH were studied after the emulsion pH values were adjusted to 3,5,7 and 9 and were allowed to equilibrate for 14 days.

Figures 4.36 and 4.37 show G_N^o versus pH of the CTAC/FA and BTAC/FA emulsions at various fatty alcohol concentrations. At any fatty alcohol concentrations of both emulsions, G_N^o appears to be independent on pH. This observation is also true for τ_B and η_o versus pH as shown in Figures 4.38 - 4.41. Micrographs of these two emulsions at various fatty alcohol concentrations are illustrated in Figures 4.42 – 4.47. All systems generally exhibit unchanged microstructures with pH. These results are consistent with the rheological data. It can be summarized that the pH of the emulsion system, which contained the cationic surfactants, has no influence on the elasticity and viscosity of the product. This was because CTAC and BTAC are cationic surfactants in the form of quaternary ammonium salts. They compose of 4 carbons, which are bonded to a positive N atom. This N atom displays sp3 bonding so this means that the cationic molecules lack both acidic protons and nonbonding electron pairs; therefore they are neutral in water. The positive charges of this type of surfactant can remain in acidic, neutral or alkaline media and therefore they are unaffected by pH changes.

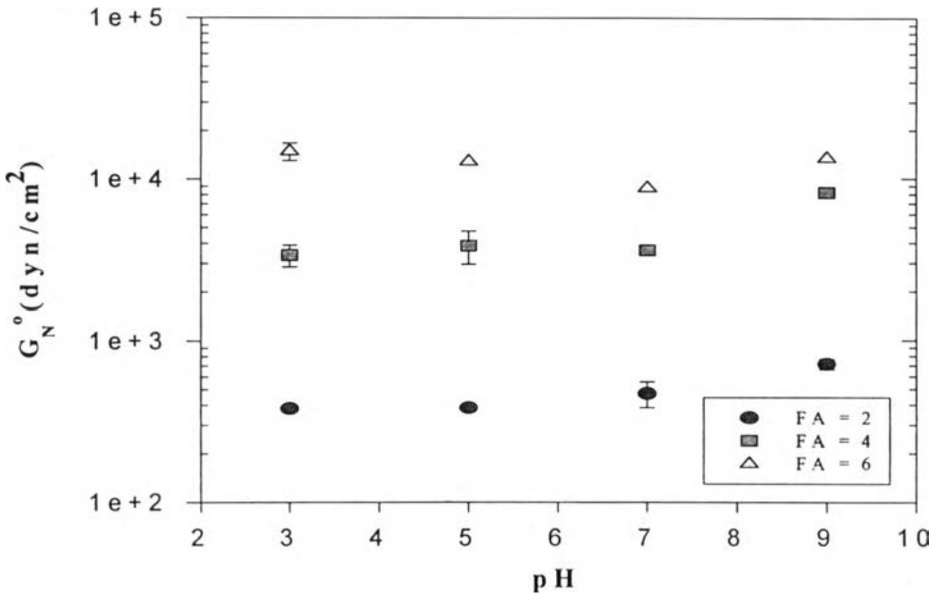


Figure 4.36 G_N^o vs. pH of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

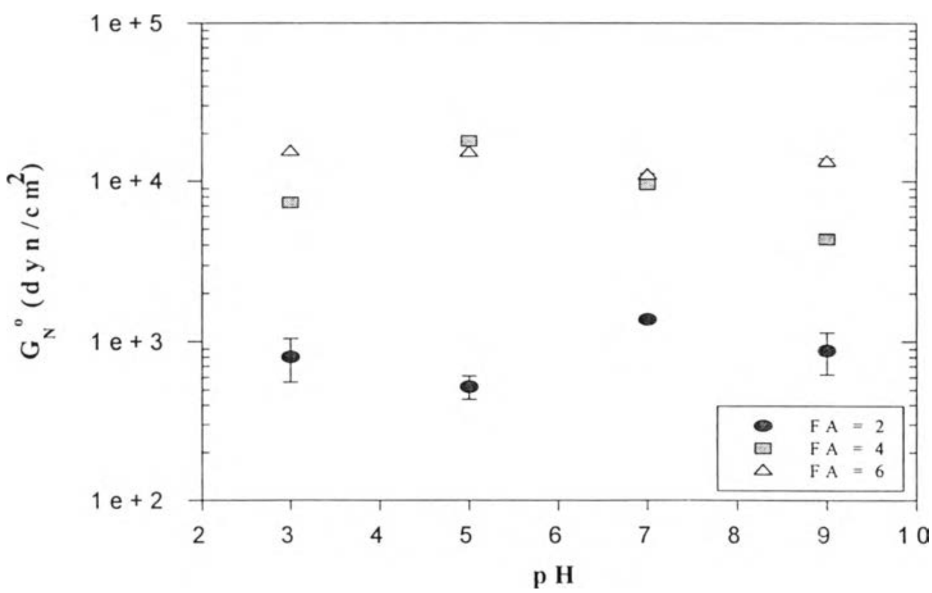


Figure 4.37 G_N^o vs. pH of the BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

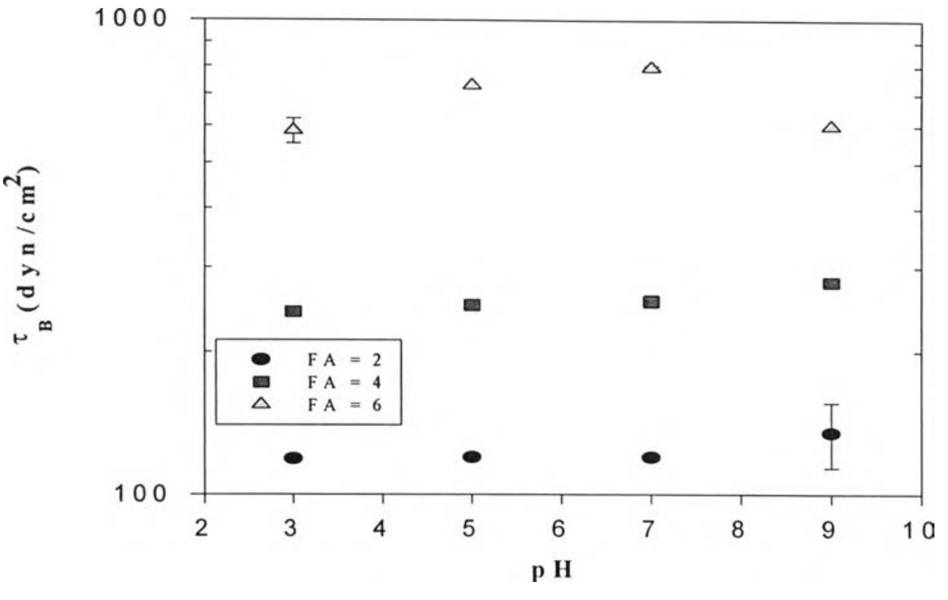


Figure 4.38 τ_B vs. pH of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

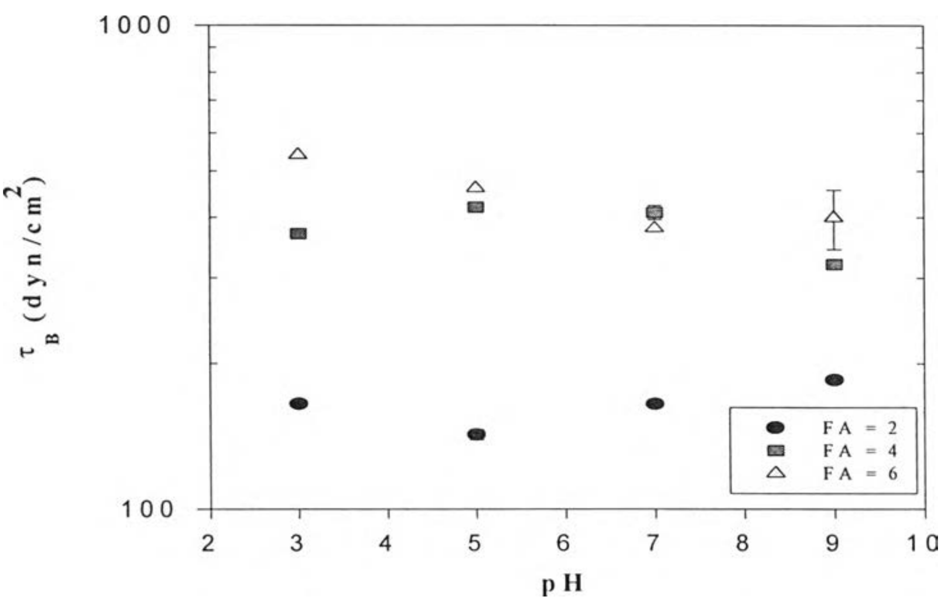


Figure 4.39 τ_B vs. pH of the BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

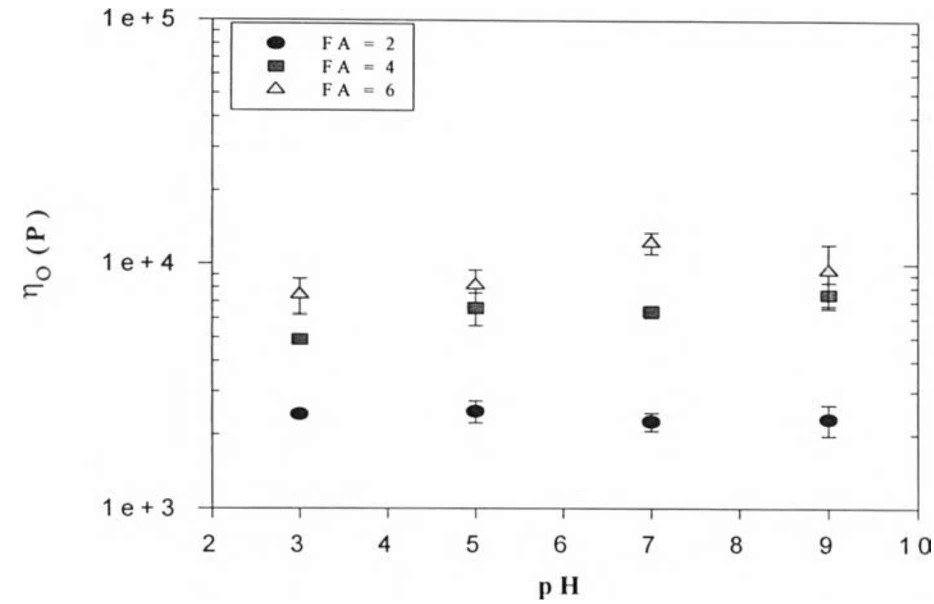


Figure 4.40 η_o vs. pH of the CTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

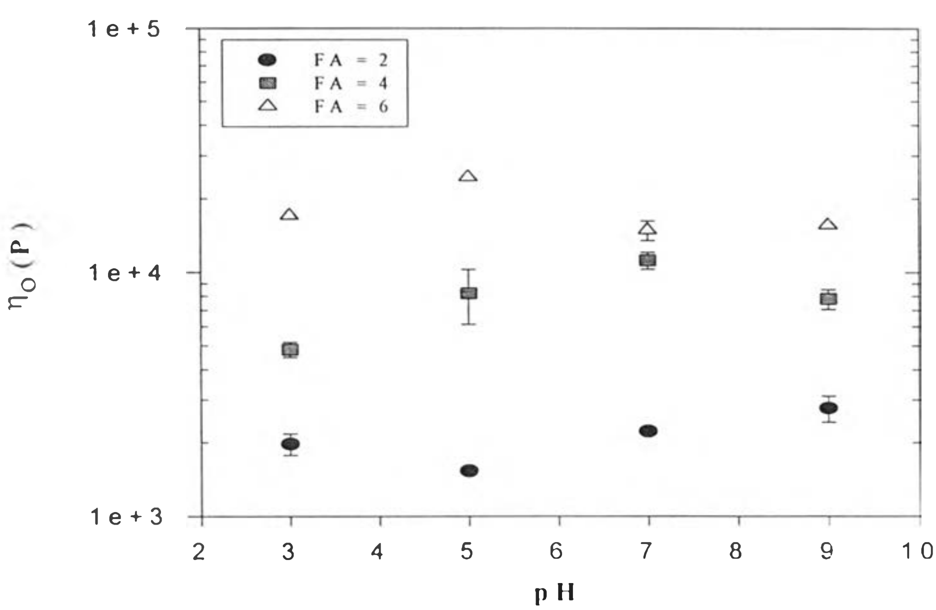


Figure 4.41 η_o vs. pH of the BTAC/FA emulsions at various fatty alcohol concentrations at equilibrium.

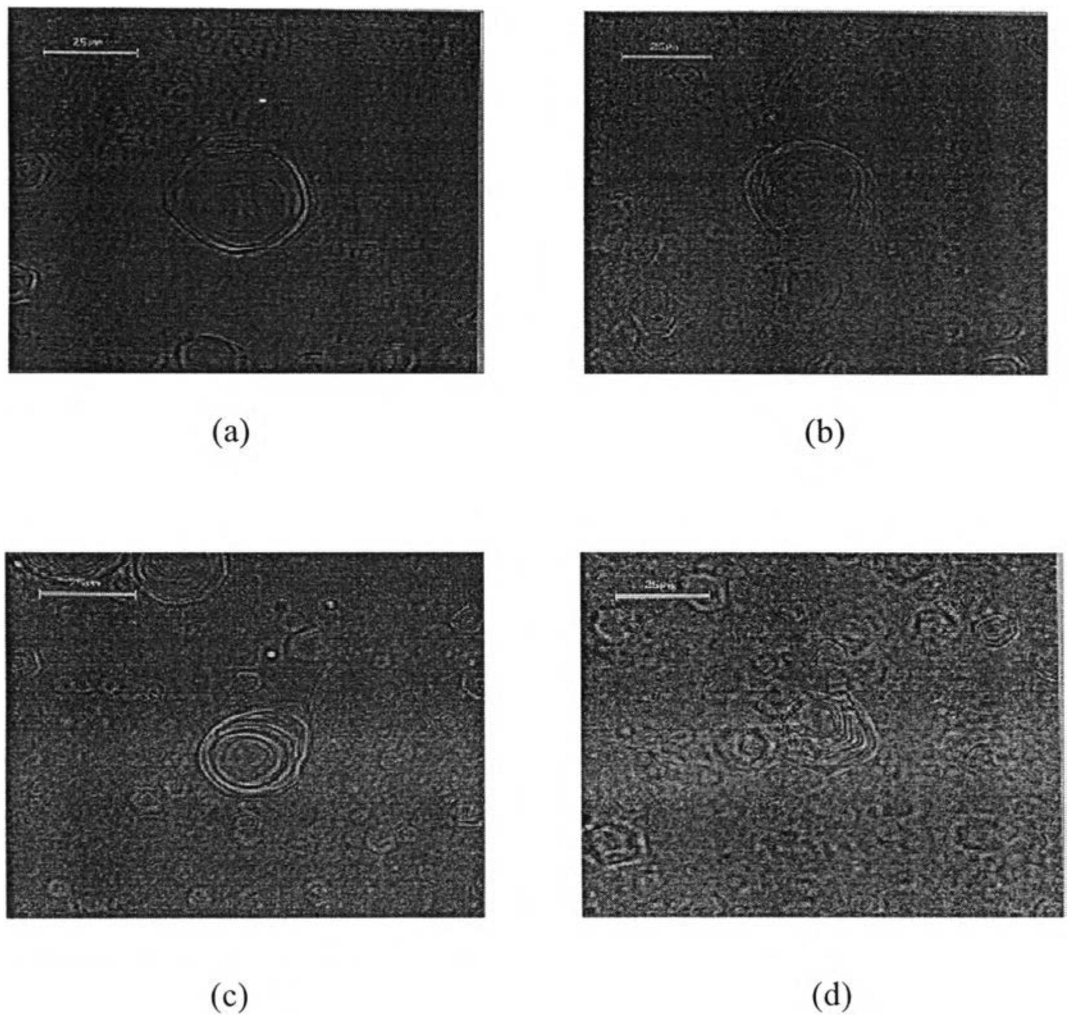
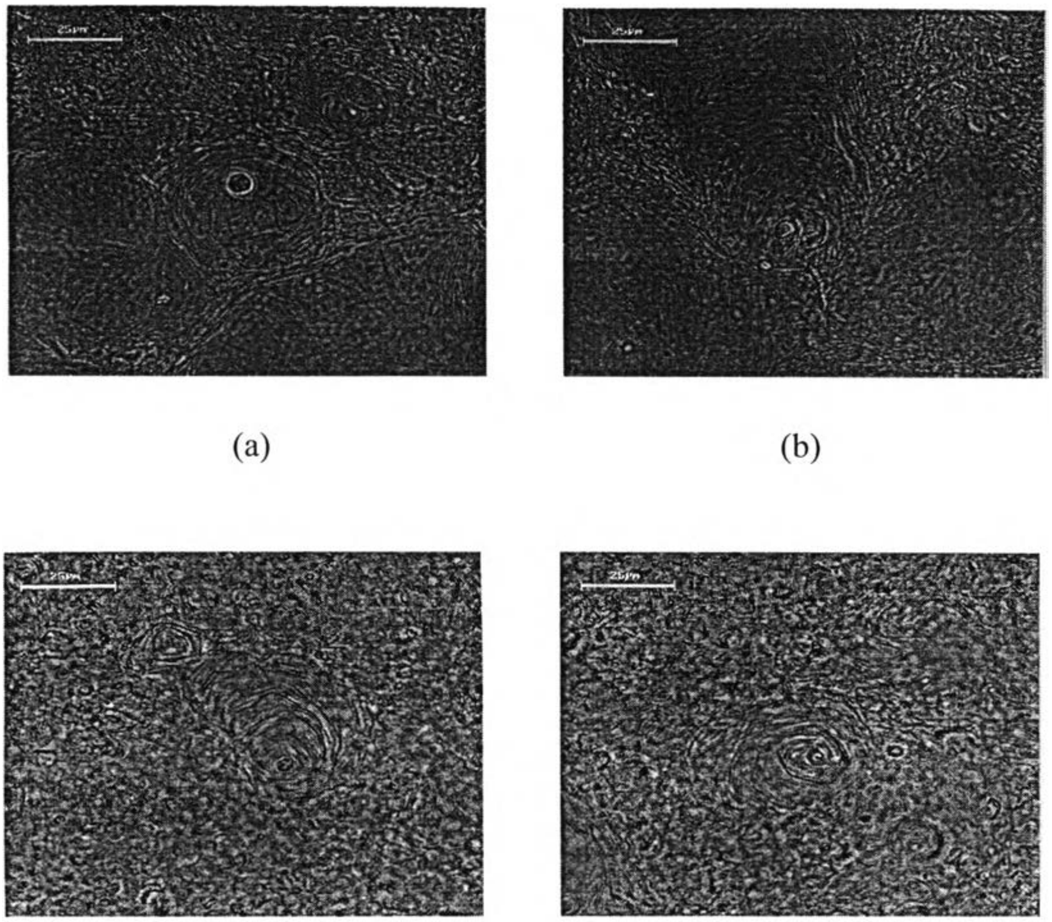


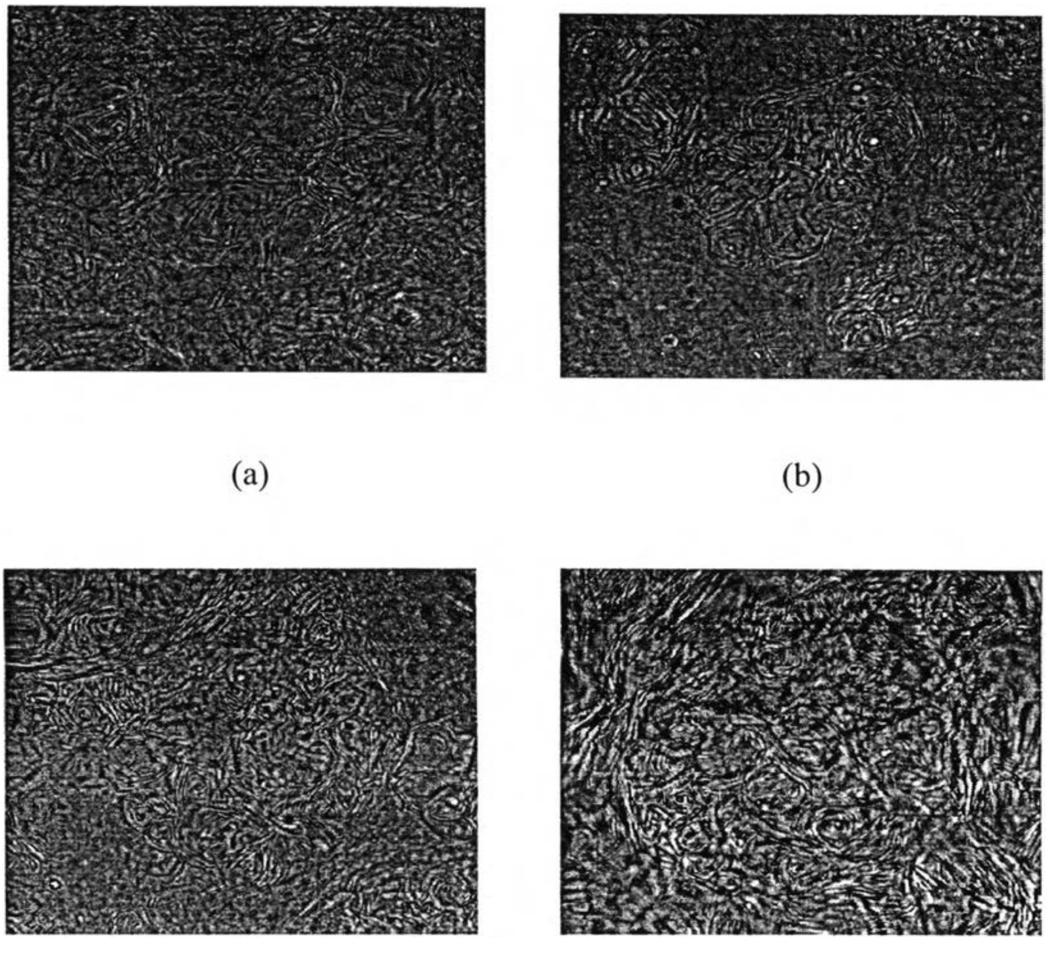
Figure 4.42 Micrographs of the CTAC/FA = 1.0/2.0 emulsions at various pH: (a) pH 3; (b) pH 5; (c) pH 7 and (d) pH 9.



(a) (b)

(c) (d)

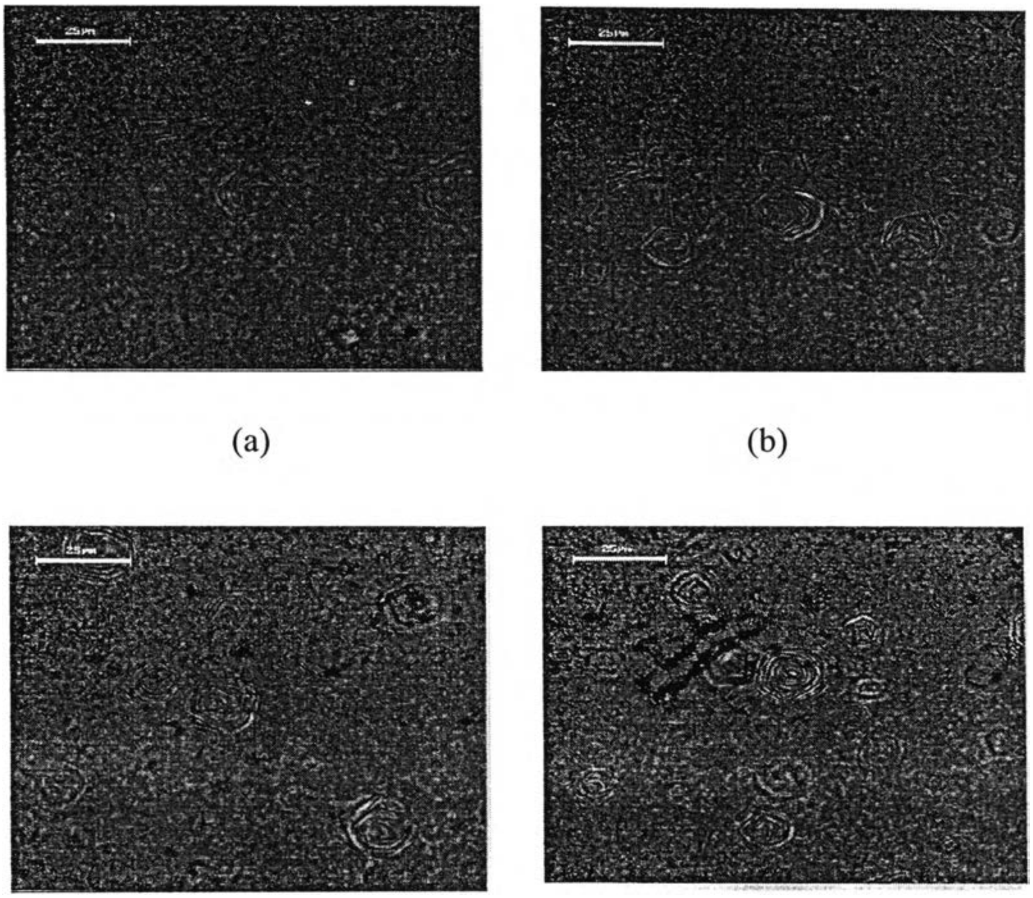
Figure 4.43 Micrographs of the CTAC/FA = 1.0/4.0 emulsions at various pH: (a) pH 3; (b) pH 5; (c) pH 7 and (d) pH 9.



(a) (b)

(c) (d)

Figure 4.44 Micrographs of the CTAC/FA = 1.0/6.0 emulsions at various pH: (a) pH 3; (b) pH 5; (c) pH 7 and (d) pH 9.



(a) (b) (c) (d)

Figure 4.45 Micrographs of the BTAC/FA = 1.0/2.0 emulsions at various pH: (a) pH 3; (b) pH 5; (c) pH 7 and (d) pH 9.

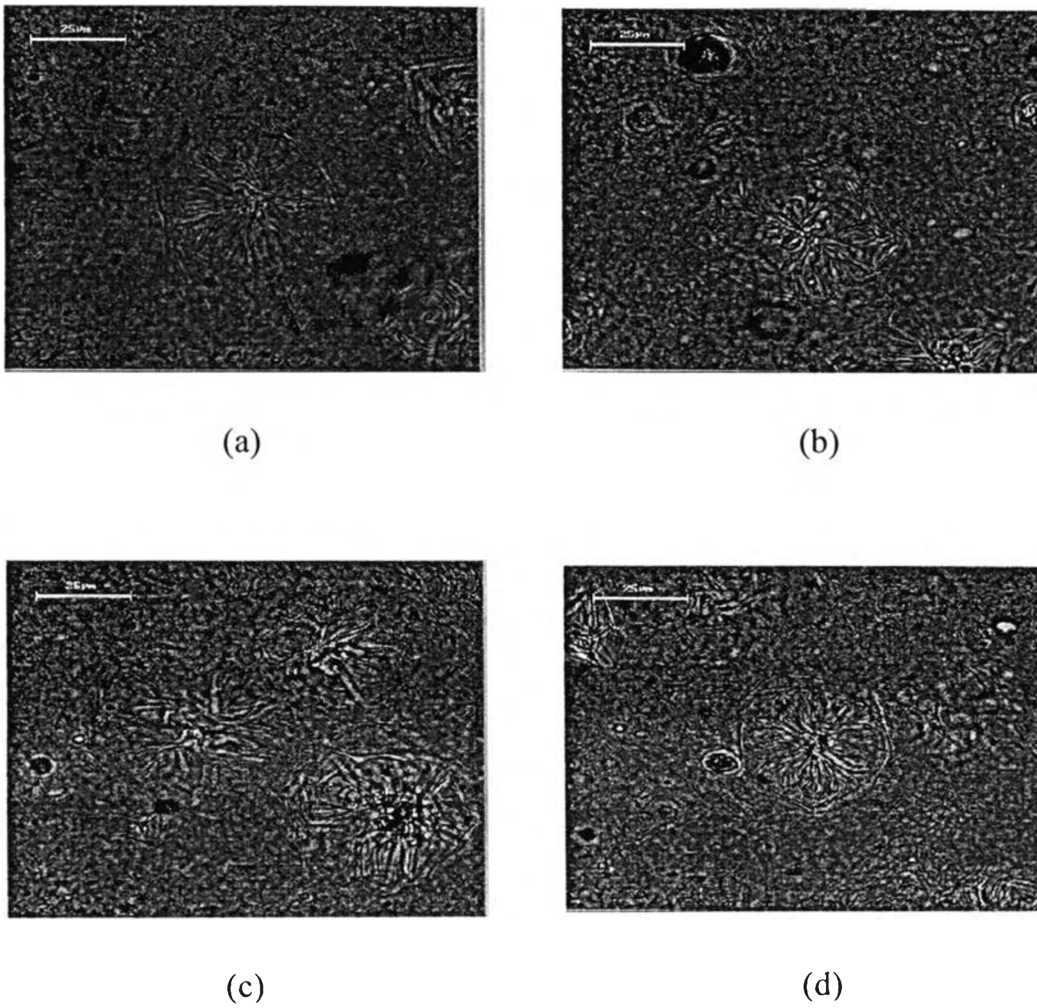
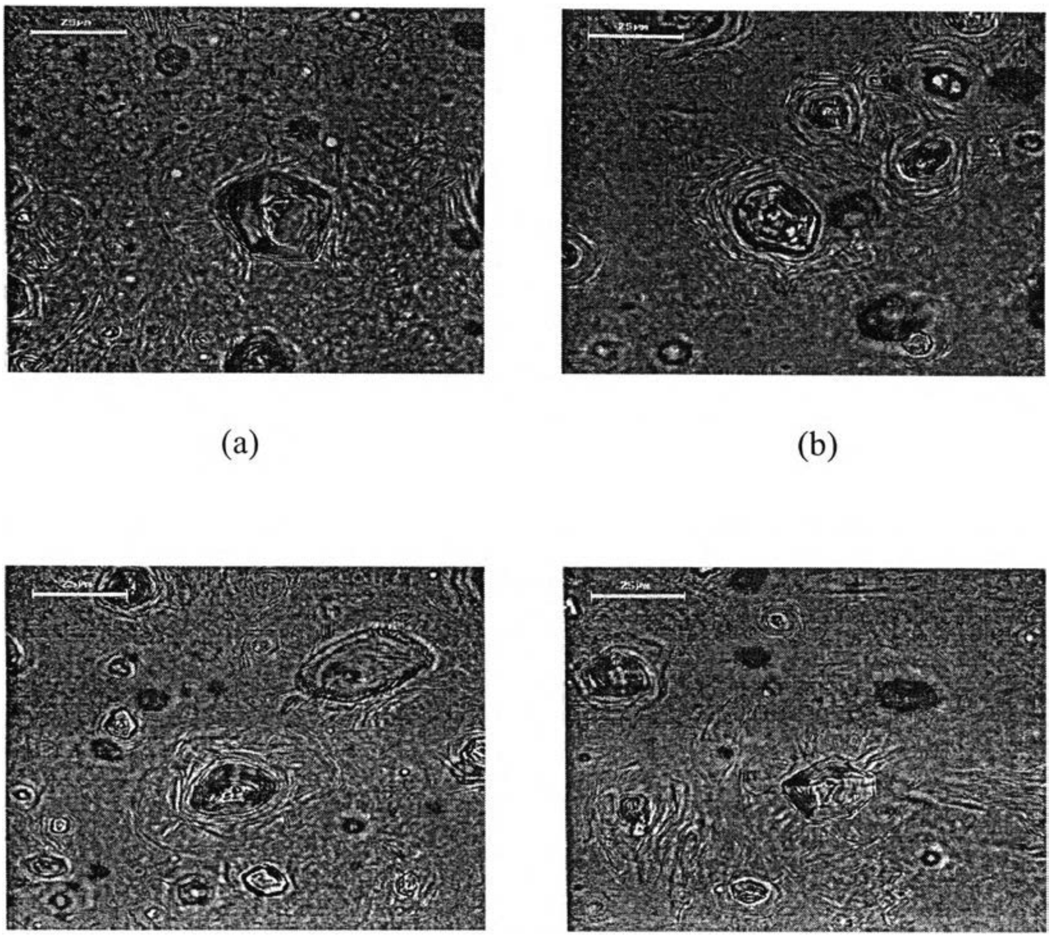


Figure 4.46 Micrographs of the BTAC/FA = 1.0/4.0 emulsions at various pH: (a) pH 3; (b) pH 5; (c) pH 7 and (d) pH 9.



(a) (b)

(c) (d)

Figure 4.47 Micrographs of the BTAC/FA = 1.0/6.0 emulsions at various pH: (a) pH 3; (b) pH 5; (c) pH 7 and (d) pH 9.