# CHAPTER V

# RESULTS AND DISCUSSION

## 5.1 Characterization of cellulose nitrate solution at various water content

### 5.1.1. Rheological behavior of cellulose nitrate solution

Viscosity of cellulose nitrate (CN) solution was moderately affected by its water contents such that to lower its viscosity as shown in Fig.5.1. At the shear rate range of 34 $s^{-1}$ to 600 $s^{-1}$, the viscosity of CN solution at the lowest water content i.e. 1% by weight, showed the highest value while the viscosity of CN water content at 10wt% is the lowest. All curves exhibited as a horizontal line of Newtonian plateau or showed negligible shear rate dependency in the range of 34 $s^{-1}$ to 600 $s^{-1}$. The viscosity of these cellulose nitrate solutions is ranging from 156 to 242 mPa.s. The required viscosity of a commercial nail enamel should be in range of 400-1200 mPa.s [30]. While a commercial nail enamel needs to incorporate a resin to promote adhesion, a plasticizer to enhance flexibility, as well as a pigment or other solid contents to obtain a finish nail enamel product. Those solid additions will further raise the nail polish viscosity very often, with more complex flow characteristics. According to Newton's law of viscosity, a plot of shear stress versus shear rate for a given fluid should give a straight line, and the slope of this line is the viscosity of the fluid at a given temperature. As shown in Fig.5.2, every curve of our CN solution showed a straight line, at low shear rate, while each corresponding slope was a viscosity of each solution. The expression of Newton's Law of viscosity is as follow:

$$\eta = \tau / \dot{\gamma}$$

where $\eta$ is a viscosity (Pa.s)

$\tau$ is a shear stress (Pa.)

$\dot{\gamma}$ is a shear rate ($s^{-1}$)

As a consequence, all solutions used exhibited Newtonian behavior in the range of shear rate below 600 $s^{-1}$ which is required for the nail polish application. Figure 5.3, in shear rate range of 600 $s^{-1}$ to 1000 $s^{-1}$, showed shear thinning behavior of nail enamel solution which according to Carreau's equation given $R^2$ = 0.93689 and standard deviation = 0.0015887.

$$\eta = \frac{\eta_0 - \eta_f}{(1 + (\lambda\dot{\gamma})^2)^{(1-n)/2}} + \eta_f$$

where $\eta_0$ = a zero shear rate viscosity

$\eta_f$ = a final shear rate viscosity (its value rarely appear)

$\lambda$ = characteristic (or relaxation) time

n = dimensioless parameter

The slope of $\eta$ versus $\dot{\gamma}$ in the power law region is given by n-1. In the special case of n =1 or $\lambda\dot{\gamma}$ close to zero, this equation simplifies to the Newtonian fluid model. For n < 1, this equation predicts shear thinning behavior. One major goal of our research is to develop a nail polish solution to exhibit a complex non-Newtonian with time-dependency of a thixotropic type. The utilization of a layered clay additive was thus necessary to alter this flow behavior of the resulting enamel to achieve a thixotropic flow. As viscosity measurement, as shown in Figure 5.4, we had confirmed again that increasing water content reduced viscosity of cellulose nitrate solution but not the flow pattern.

### 5.1.2 Drying time of cellulose nitrate solution

The drying time of the obtained cellulose nitrate (CN) solution was found to increase as its water content increased as illustrated in Figure 5.5. At 90±5% relative humidity at room temperature, CN solution with water contents of 1, 2, 3, 4, 6, 8, and 10 wt% took about 6, 7, 7, 7.5, 8, 9 and 9 minutes to fully dry and at 50±5% relative humidity at 23±2 $^0$C which is the standard condition, the CN solution with the same water contents of 1, 2, 3, 4, 6, 8, and 10wt% took about 3, 3, 3, 3.30, 3.30, 5 and 5 minutes to fully dry in the respective order. Our nail polish formula contained

ethyl alcohol, butyl acetate, ethyl acetate, and toluene as major liquid components while the contaminated water was a minor component possessing the highest heat of evaporation or latent heat among those. The latent heat for the phase change at constant temperature may be expressed in terms of the latent heat and the heat capacity of the phase

$$\Delta Q = T_d (S_g - S_l)$$

where $\Delta Q$ is eaporation heat or latent heat (cal/g)

$T_d$ is evaporation temperature ($^0$C),

$S_g$ is entropy of gas phase

$S_l$ is entropy of liquid phase

The values of heat of evaporation of solvent are as follows: ethyl alcohol = 204.26 cal/g, butyl acetate = 73.82 cal/g, ethyl acetate = 102.01 cal/g, and toluene = 86.8 cal/g. While the latent heat of water is 539 cal/g [14]. The drying time was; therefore, higher at the presence of water and from this experiment could be estimated by a linear relationship with the amount of the water. The increasing drying time was also caused by an effect of ambient humidity. Solvent evaporation was expectedly occurred at a lower rate with increasing the humidity of the environment. The suitably drying time of nail enamel should be 1-4 minutes at 50$\pm$5% relative humidity (25$^0$C) [30]; consequently, the obtained cellulose nitrate solution meets the application standard event at the present of some water i.e. less than 6wt%. In the case of a more slowly drying time at high humidity condition, the solvent content needed to be adjusted in order to optimize the heat of evaporation of solvents.

### 5.1.3 Hardness of cellulose nitrate film

The values of CN film hardness were in the range of 14-17 of vicker scale as shown in Figure 5.6 implying water content had no significant effect to CN films. After solvent evaporation, the water ingredient of each thin film could also evaporate so all of the films were of similar hardness value. From those hardness results, it is essential that CN films are to be modified to improve their flexibility, typically by adding plasticizer such as dibutyl phthalate.

### 5.1.4 Gloss of cellulose nitrate film

All of CN films were measured by a gloss meter which had been calibrated by a standard black glass as calibration. Gloss of a standard black glass at 20°, 60°, and 85° are 112.8, 129.7, and 99 G.U, respectively. Whereas gloss of CN films at 20°, 60°, and 85° are 101.97-103.41, 122.42-124, and 97.99-99.14 G.U, respectively as depicted in Figure 5.7. The results indicated that CN films possed high gloss values close to a standard black glass. This property is required for the good appearance of nail enamel films.

### 5.1.5 Surface texture of cellulose nitrate film

The micrograph in Figure 5.8 depicts CN surface of 1 and 10wt% water contents. These films disclosed smooth morphology of the casted film surface which explained the good optical properties such as gloss of the enamel film.

## 5.2 Effect of adhesion promoter on CN film

In this study, four types of resins were investigated in order to improve adhesion of CN film. Table 5.1 shows that silicone, maleic resin (ER-912), epoxy (Epon 828) and benzoxazine are useful for improved adhesion of CN film compared with a relatively high-end commercial nail enamel i.e. Red Earth™. Since silicone and benzoxazine gave unpleasant appearance and color to the resulting films so these resins were not suitable for utilization as nail enamel composition. The effect of adhesion of mixture of maleic and epoxy resin was also studied and showed an optimal in adhesive as shown in Table 5.2 and hardness properties. The obviously effect of these mixture was in the film hardness as shown in Figure 5.9. The increasing in maleic resin content increased hardness of films while epoxy resin acted like plasticizer which decreased the hardness of the CN films as well as maintaining the good adhesion. As the composition of maleic resin in the nail enamel is about 10wt%, the hardness of the nail enamel film is about 4.8 in vicker scale. The optical microscope depicted deformation of film after loading of 100 $g_f$ for 15 seconds, that its shape was sharp while that of filled epoxy resin of 10wt% showed plastic deformed shape and its hardness value is only about 0.6 vicker which lower than that

of the neat CN i.e. 2.8 in vicker scale. From this experiment, we can adjust requirement hardness value by selecting the content of maleic-epoxy mixture. For nail enamel application, the CN film needed to be relatively hard but not too hard to avoid brittle fracture. The composition of 5wt% maleic resin and 5wt% of epoxy resin was found to be preferable in nail enamel ingredient with appropriate adhesion and hardness. The hardness of CN films of mixed maleic resin and epoxy resin contents was shown in Figure 5.10.

## 5.3 Clay suspension preparation

### 5.3.1 Mechanical stirring

In Figure 5.11, mixing time of clay suspension was studied by mechanical stirring at a constant shear rate 650 rpm for 4, 8, 14, 24, and 48 hr. The result revealed that all suspensions were shear thinning fluid. Viscosity of clay suspension at the mixing time of 4, 8, and 14 hr were in the range of 10-13600 mPa.s while the mixing time up to 24, and 48 hr rendered viscosity in a range of 31.6-24800 mPa.s. These results indicated that mixing time expectedly affected clay delamination. The clay layers were sheared by Teflon paddle for long mixing time, the layers were more delaminated and formed the strong three dimension network that obtained high viscosity. The hysteresis loop of the suspension was shown in Figure 5.12 with the wide loop implied greater thixotropic behavior. The mixing time of 4, 8, and 14 hr showed unclear thixotropic loop which is required for nail enamel rheological behavior. Whereas, the mixing time of 24, and 48 hr. were preferable suspension preparation for the nail enamel application.

### 5.3.2 Homogenizing

Bentone38 at 8wt% in toluene was also prepared and tested using a homogenizer at various shear rates of 6500, 9500, 13500, 21500, and 24000 rpm for 5 minutes as shown in Figure 5.12. At the shear rate of 6500 rpm, the relatively low viscosity in range of 37.7-3240 mPa.s was obtained while all other shear rates provided viscosity in range of 97.7-17800 mPa.s showing strong three dimension

network. It was observed that the viscosity at higher shear rates from 9500-24000 rpm was similar in value. Therefore, the moderate shear rate of 9500 rpm is chosen for the clay suspension preparation for good gel and for energy saving and for safety purpose. Figure 5.14 also showed hysteresis loop of various high shear rate, the graphs depicted all of high shear rate are thixotropic behavior.

The clay suspension preparation was compared motor stirring with homogenizing, we found that motor stirring provided gelation over than 24 hours while homogenizing contributed good gel network in 5 minutes. Therefore, the homogenizing is high efficiency and suitable for suspension preparation.

## 5.4 X-ray diffraction patterns of organoclays in CN nail enamel films

### 5.4.1 Bentone 38

CN films incorporated various loading of the organoclay were investigated for the d-spacing of the clay layer by XRD as shown in Figure 5.15. Bentone 38 powder showed a peak at 2θ of 3.39 and d-spacing of 26 angstroms. The CN films with 1, 3, and 5wt% bentone38 depicted a XRD peak with the 2θ of 2.26, 2.39, and 2.55 respectively. This implied that the layers of montmorillonite were intercalated by the polymer chains and the particle structure still maintained its order. The CN films at 0.35wt% of bentone38 showed no diffraction of the clay powder as shown in the XRD pattern. This means two cases, first is that the micro particles were exfoliated into nanocomposites by high shear mixing. As a consequence, the low concentration of montmorillonite in CN films (<0.35wt%) tended to provide the exfoliation-typed nanocomposites while the high concentration above 0.35wt% of the montmorillonite contributed the intercalated nanocomposites. We can confirm this case by using Transmission Electron Microscope (TEM) to observe the polymer-clay nanocomposite. Second case is that the clay concentration in films is too low to absorb x-ray intensity therefore no showing peak of clay d-spacing.

### 5.4.2 Bentone 27

In Figure 5.16, bentone 27 powder exhibited a x-ray diffraction peak at 2θ of 4.96 with a d-spacing of 18 angstroms. CN films incorporated with 3, and 5wt% bentone27 possessed a XRD peak of the 2θ at 2.35, and 2.45 respectively, This result means that the layer of montmorillonite clay was intercalated by the polymer chains and the particles structure can still maintain their ordered morphology. CN films of 0.35, and 1wt% bentone27 show no peak of diffraction as illustrated in the pattern. That means two cases, first is that the micro-particles of the clay particles were exfoliated by high shear rate when the clay composition was low enough. Therefore, the suspension of 0.35 and 1 wt% of bentone 27 was capable of forming exfoliated nanocomposite whereas 3, and 5wt% of bentone 27 were intercalated in nature. We can confirm this case by using Transmission Electron Microscope (TEM) to observe the polymer-clay nanocomposite. Second case is that the clay concentration in films is too low to absorb x-ray intensity therefore no showing peak of clay d-spacing.

### 5.4.3 Bentone 34

The XRD results of the nanocomposites of various bentone34 contents in CN films were shown in Figure 5.17, the sign of intercalated nanocomposites was disclosed at the contents above 1wt% of bentone34. The intercalation of bentone34 content of 1, 3, and 5 wt% exhibited a sharp diffraction peak of their ordered structure at 2θ equal to 2.45, 2.48, and 2.55, respectively. No diffraction peak; however, was not observed at lower clay content i.e. 0.35 wt% in our case. This means two cases, first is that some fraction of the clay thixotrope seems to be able to be fully exfoliated whereas must of the clay particles were intercalted during the preparation process. We can confirm this case by using Transmission Electron Microscope (TEM) to observe the polymer-clay nanocomposite. Second case is that the clay concentration in films is too low to absorb x-ray intensity therefore no showing peak of clay d-spacing.

In Table 5.3, Δd-spacing of clays were calculated by d-spacing of clay powder as reference. At clay content of 5wt%, we found that bentone27 provided

broad clay Δd-spacing that means the great of polymer chain crawled into interlayer presented intercalated nanocomposite and occured gel forming ability.

### 5.5 Nail enamel film characterization

The micrographs in Figure 5.18 depicted plate-like structure of titanium dioxide coated on mica pigment which was used to incorporate into a CN-clay suspension. The particle size distribution of the pigment platelet was found to vary in a range of 5-25 micrometers. The micrographs also showed the structure and particle size are similar to pigment of commercial nail enamel. Figure 5.19a discloses rough morphology of the film surface which its pigmented suspension was obtained using a mechanical stirrer. This relatively low shear rate preparation technique provided a low degree of deagglomeration of the pigment; therefore, resulting in a rougher film surface. Figure 5.19b shows a SEM micrograph of the smoother film which its suspension was prepared using a homogenizer. The much higher shear rate of the apparatus effectively caused a deagglomeration of the pigment particles thus resulting in a smoother film. These characteristics resulted in a difference in the optical properties such as gloss of the enamel film as mentioned in the previous section. Gloss of these two bentone38 nail enamel films prepared by a motor stirrer, and a homogenizer were 11.8, and 54.1 G.U, respectively. The use of high shear rate apparatus thus provided a film showing gloss value closer to the commercial product required gloss value from 70-95 G.U.

### 5.6 Rheology of resulted nail enamels

The fully formulated nail enamel and commercial one were compared in Figure 5.20 which disclosed again the shear thinning behavior. The viscosity range of the resulting nail enamel were 266-1082 mPa.s at the shear rate of 13.9-400 1/s. while that of the commercial grade were requirement for the 153.9-310.7 mPa.s at the same shear rate above. The industrial viscosity of nail enamel should be in the range of 400-1200 mPa.s. From the rheological testing, the viscosity of the commercial nail enamel was slightly lower than the standard while our systems achieved that requirement. Furthermore, the hysteresis thixotropic flow of our research nail enamels was

illustrated in Figure 5.21 indicating that all of the suspensions were thixotropic or time-dependent flow. The recovery time of the thixotropic nail enamel was depicted in Figure 5.22 at the third interval of the test while the first and second test intervals provided the thixotropic indices. The thixotropic indices of nail enamels using bentone 38, bentone 27, bentone 34, and commercial nail polish were about 1.4, 1.4, 1.4, and 1.5, respectively as shown in Table 5.4. These indices indicated that the obtained nail enamel as these of a commercial one showed similar time-dependent flow behaviors. The lapse of time of the tested samples using bentone 38, bentone 27, bentone 34, and a commercial specimen were approximately 56.6, 8.13, 19.3, and 18.8, respectively as shown in Table 5.5. The bentone38 formulated nail enamels might require long somewhat recovery time of its viscosity which tended to cause the dripping flow from the nail during the application. The brushed mark might expose on the bentone27 formulated nail because of its concise viscosity recovery time. However, the nail enamel based on bentone 34 was capable of building up its viscosity in the same time as the commercial nail enamel.

**5.7 Drying time of resulted nail enamels**

The drying time of resulted nail enamels was discovered as illustrated in Table 5.6 present that the different typed organoclays show no effect to drying time of nail enamel because drying time rely on solvent evaporation. The sort of used solvents in nail enamel system is the same substance group therefore the formulated nail enamel and commercial one presented adjacent drying time where the suitably drying time of nail enamel is about 1-4 minutes.

**5.8 Gloss of resulted nail enamels**

In Table 5.7 indicated that organoclays such as bentone38, bentone27, and bentone34 reduced gloss of clear nail enamel from 122.5 to be 56.8, 29.8, 76.7, and 74.2 G.U, respectively. The different typed of organoclay and surfactant is significant object of resulted film gloss. Bentone38 and bentone34 are the same group of clay as well as the same surfactant nevertheless bentone38 is of lithium rich whereas bentone34 is of aluminium rich. Metal in clay structure might effect to light reflection

providing different gloss value. Bentone38 and bentone27 are the same of lithium rich but they are different surfactant which provide different gloss value.

## 5.9 Sedimentation of various clay-suspended nail enamels

### 5.9.1 Bentone 38

After 10 days, the formulated nail enamel using bentone 38 at concentration 1, 3, 4, and 5 wt% was shown in Figure 5.23. The clay suspension at 1wt% showed significant precipitation of pigments at the bottom of the container while the suspension at the concentration of 3, and 4wt% presented negligible pigment settling. The good prevention of pigment sedimentation could be developed by applying bentone38 of 5wt%. The results show that the high population of organoclay attending in nail enamel gain more strong network to support the suspended pigment owing to at the each platelet edge of clay layer has hydrogen bond which can react to others layer building up the network structure. However, too high clay concentration might give high viscosity which is difficult brushing.

### 5.9.2 Bentone 27

Figure 5.24 indicated that the suspension at the concentration of 1, 3, and 4 wt% of bentone27 underwent precipitation of pigment at the bottom while concentration of above 5wt% can suspend its luster pigment even after 10 days. On account of clay concentration, there is soft gel at low clay content which can not carry the pigment in solution. In contrast to soft gel, strong gel is required to overcome the gravity force which pigment settling is corresponding.

### 5.9.3 Bentone 34

In Figure 5.25 reveals the same phenomenon as 5.9.2 and 5.9.3 that the suspension of 1, 3, and 4 wt% of bentone34 showed some sedimentation at the bottom of the container while at the suspension concentration of 5wt% can maintain its pigment suspension even after 10 days. On account of clay concentration, there is soft

gel at low clay content which can not carry the pigment in solution. In contrast to soft gel, strong gel is required to overcome the gravity force which pigment settling is corresponding.

**5.10 Evaluation of the formulated nail enamels on human**

The formulated nail enamels in Table 5.8 were blind tested on human as shown in Figure 5.26-5.28. From the test, films of the resulted nail enamels as well as commercial grade nail enamel appeared on human nail even after 10 days but about 20% of the total area of films had peeled off from the nail because of everyday life working. All of formulated and commercial films were durable for 10 days after brushing on human nail as shown in Figure 5.26. The results revealed that the our nail enamels showed durability on human nail comparable to the good commercial product i.e. Red Earth$^{TM}$. The data in questionnaire, we found that women of over 50% satisfied the pick up characteristics of nail enamel, which can be settled during transport to nail without enamel dripping which stain women's clothes. As nail enamel was applied on nail, more than 50% of women felt easily brush provided smooth and leveling film on nail. The solvents in nail enamel evaporated offering dried enamel film within 1 minute where is the satisfied drying time value to women of over than 70%. The women satisfied percentage on gloss characteristic is about 90% on the bentone34 formulated nail enamel while others two formulated nail enamel need to improve the gloss characteristics. Those women gave us a comment that they unsatisfied the gloss appearance which might be reduced gloss value by clay surfactant. We can develop this property by employing more glitter pigment to gain high light scattering. After 10 days, those women of 70% reported that on the enamel surface appeared obvious mark because of abrasion while some of them expressed no any mark on the film because their work occasionally damage the film.

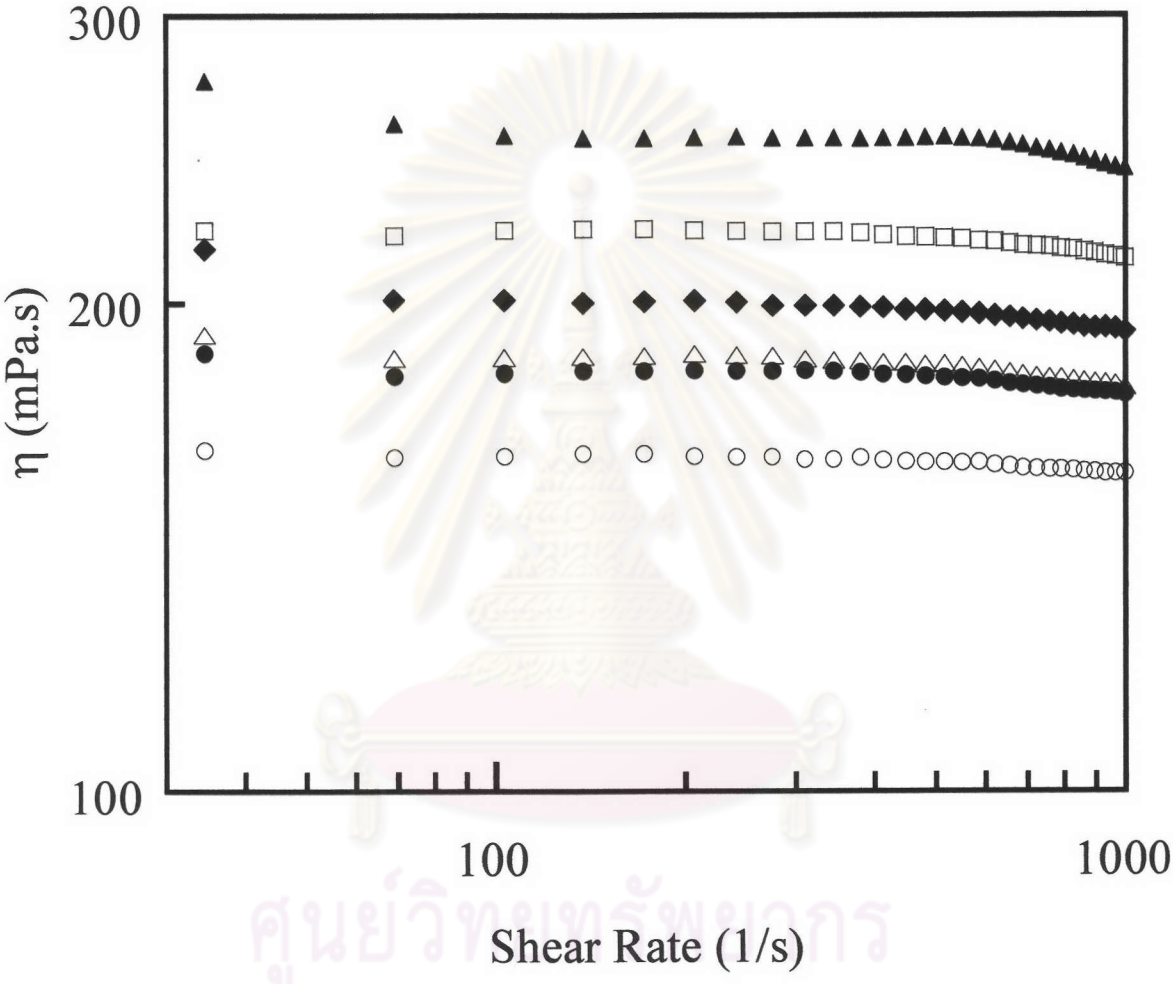



**Figure 5.1** Viscosity curves of CN solution at various contents of water:
(▲) 1 wt%, (□) 2 wt%, (◆) 3 wt%, (△) 4 wt%, (●) 6 wt%, (○) 10 wt%

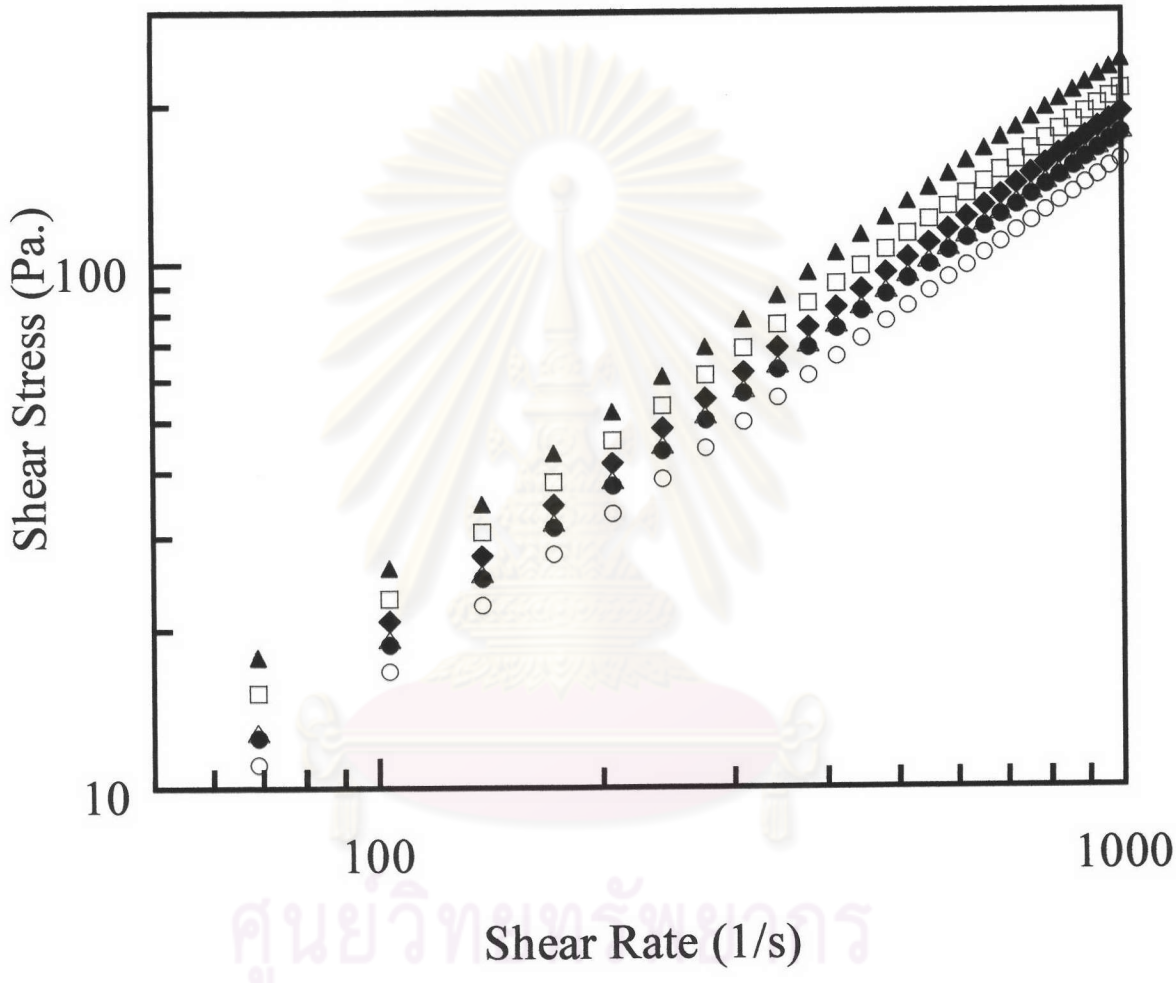



**Figure 5.2** Shear stress versus shear rate of CN solution at various contents of water: (▲) 1wt%, (□) 2 wt%, (◆) 3 wt%, (△) 4 wt%, (●) 6 wt%, (○) 10 wt%

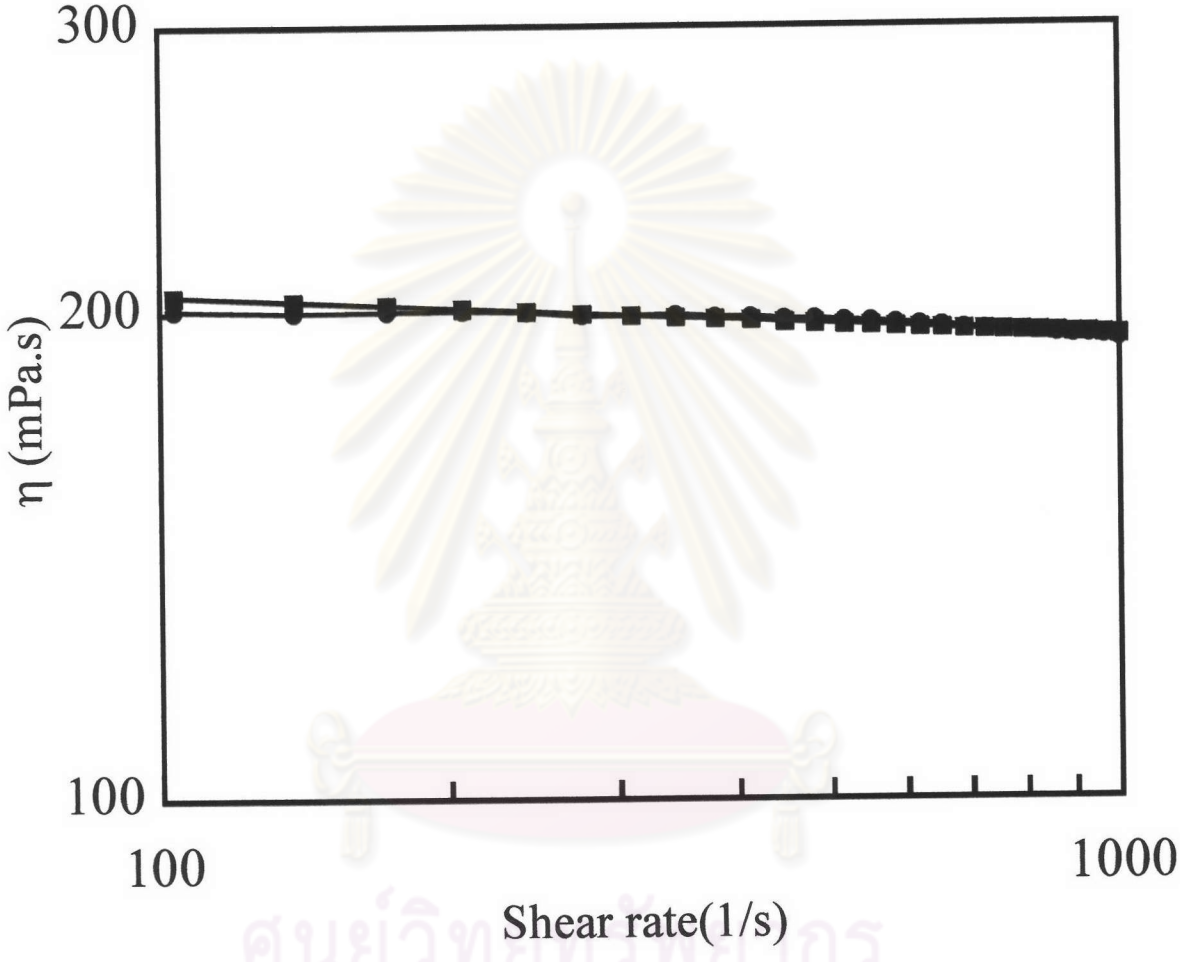



**Figure 5.3** Viscosity versus shear rate of CN solution at water content of 3wt%: (●) 3wt%, (■) Carreau model

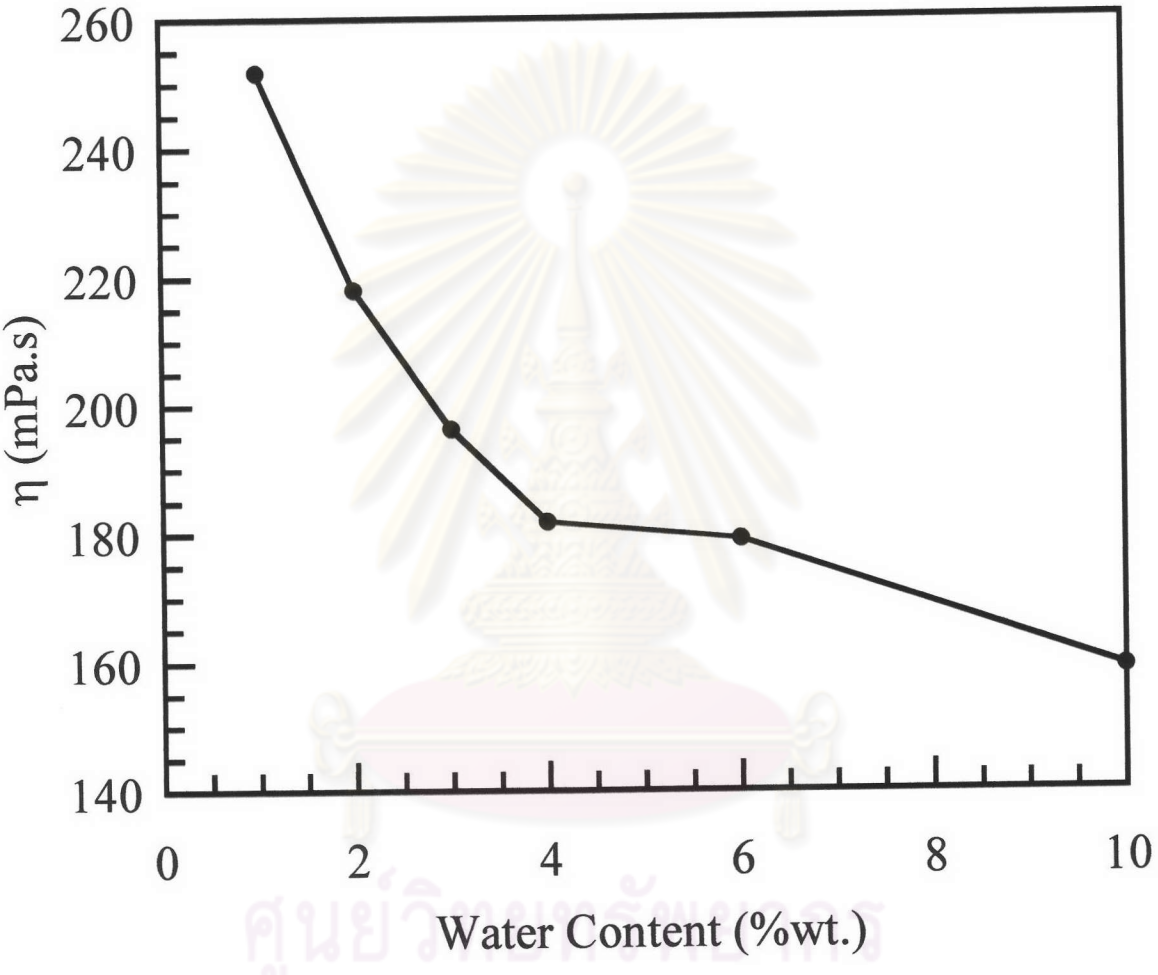



**Figure 5.4** Viscosity of CN solution at various water contents at shear rate 620 (1/s).

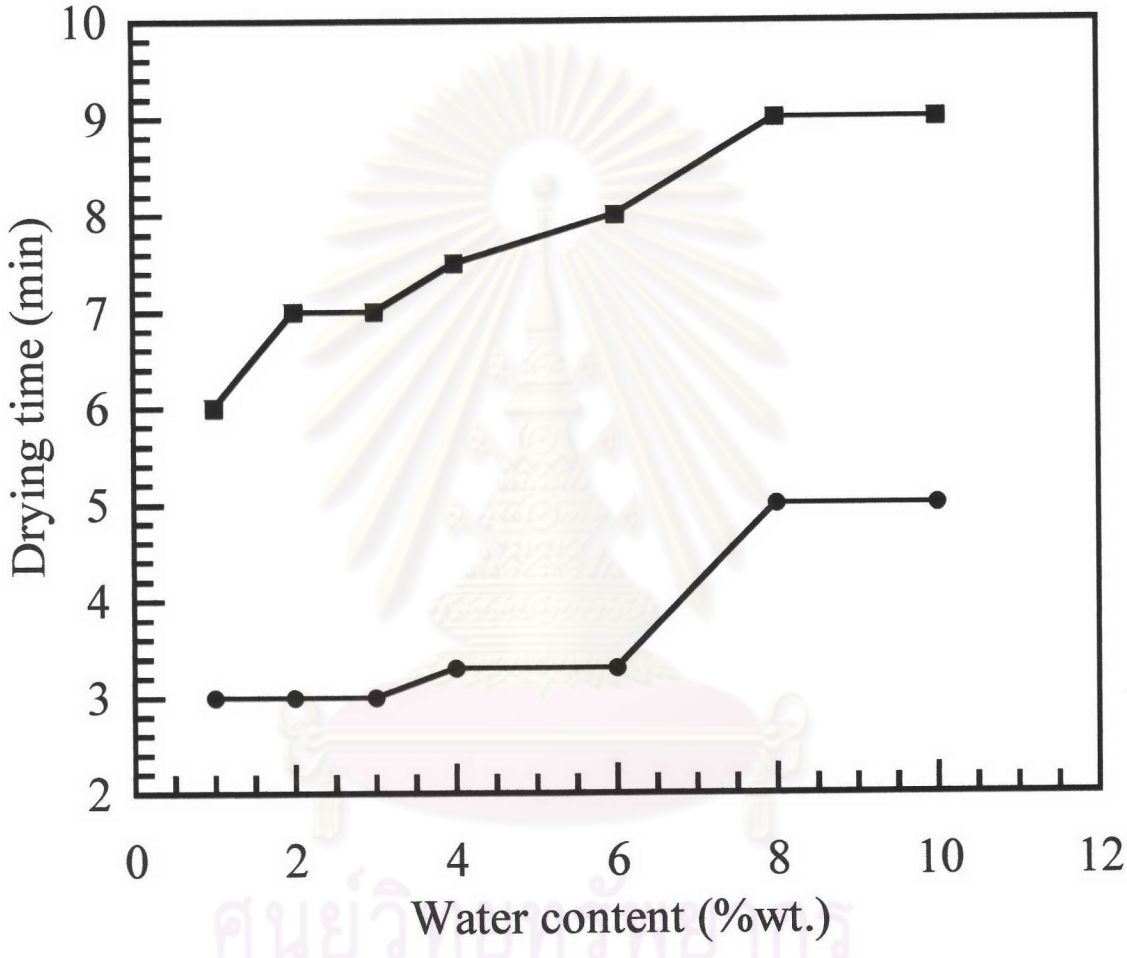



**Figure 5.5** Drying time of CN solution at two different relative humidity: (■) 90%RH, ( ●) 50%RH

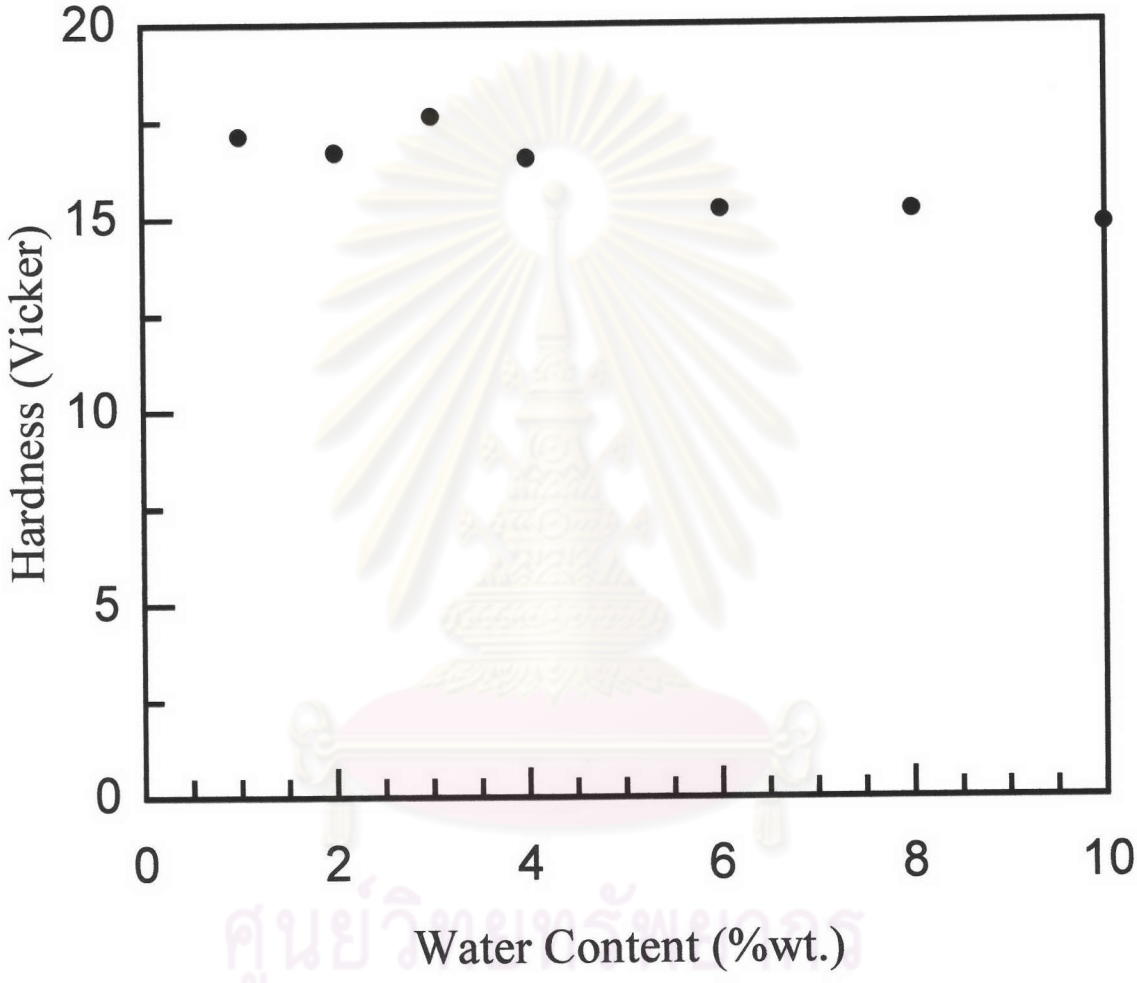



**Figure 5.6** Hardness of CN film at various water contents.

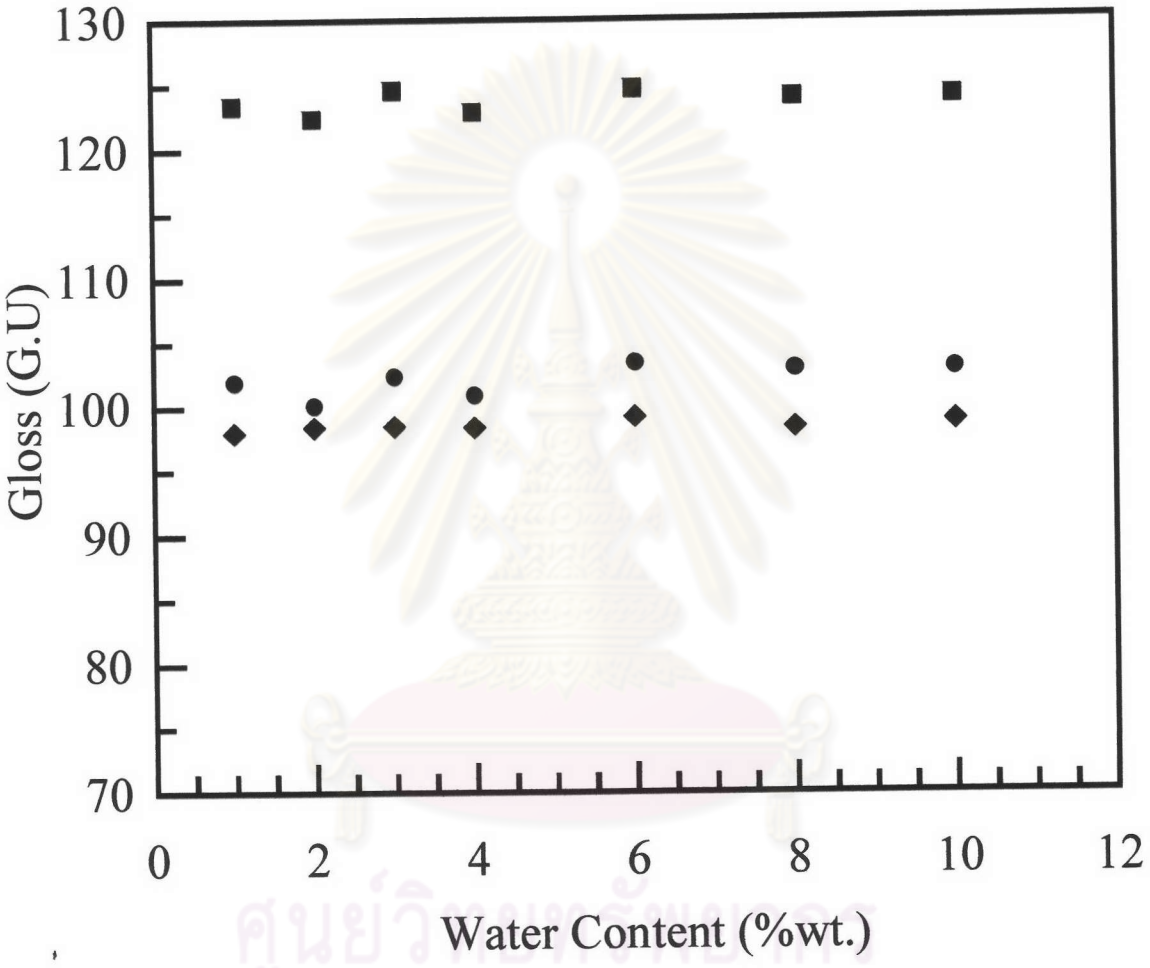
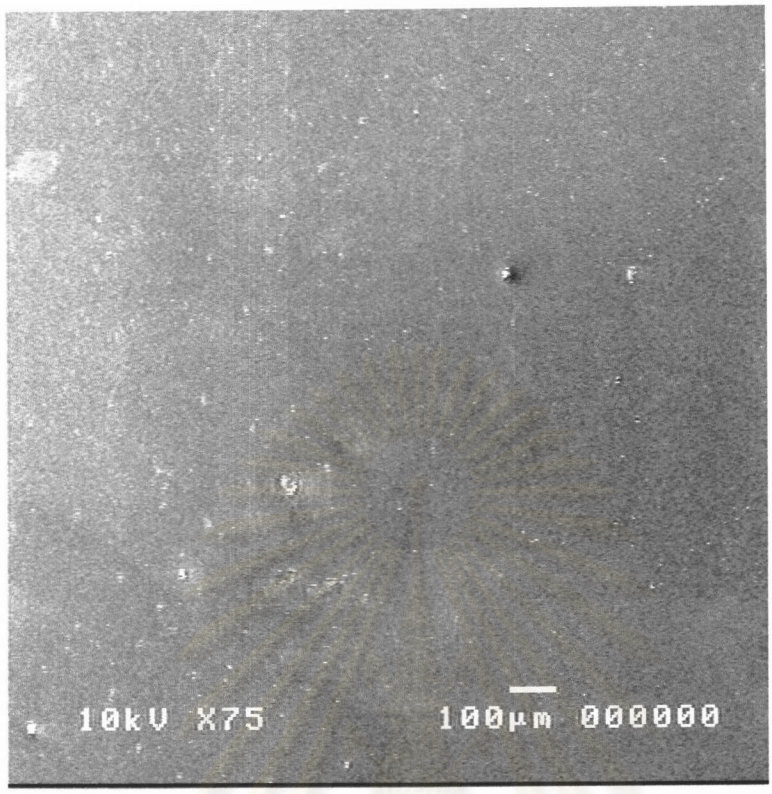
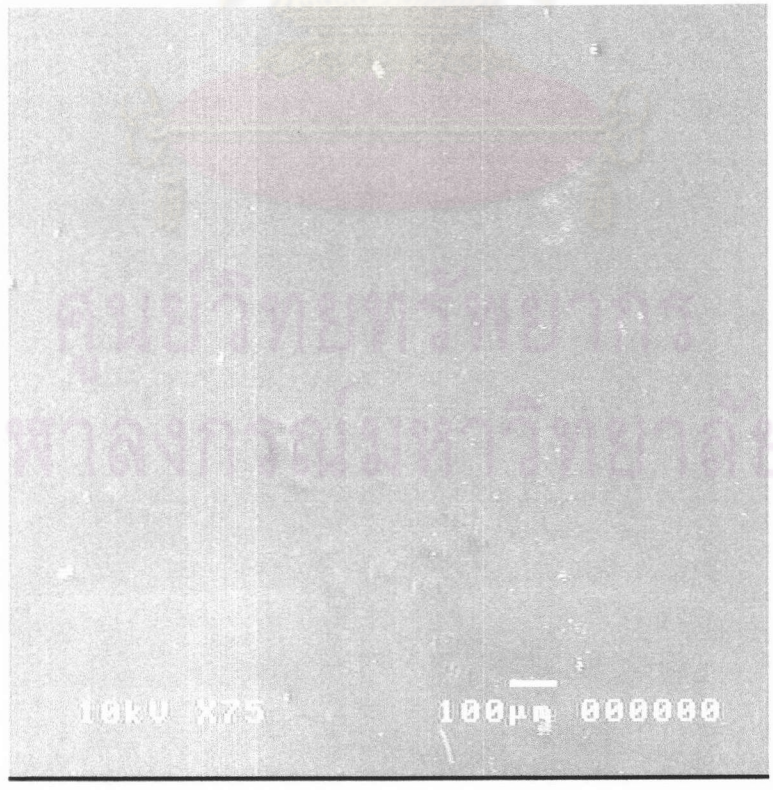



**Figure 5.7** Gloss of CN films at different reflection angles:
(■) 60 Geometry, (●) 20 Geometry, (◆) 85 Geometry




(a)




(b)

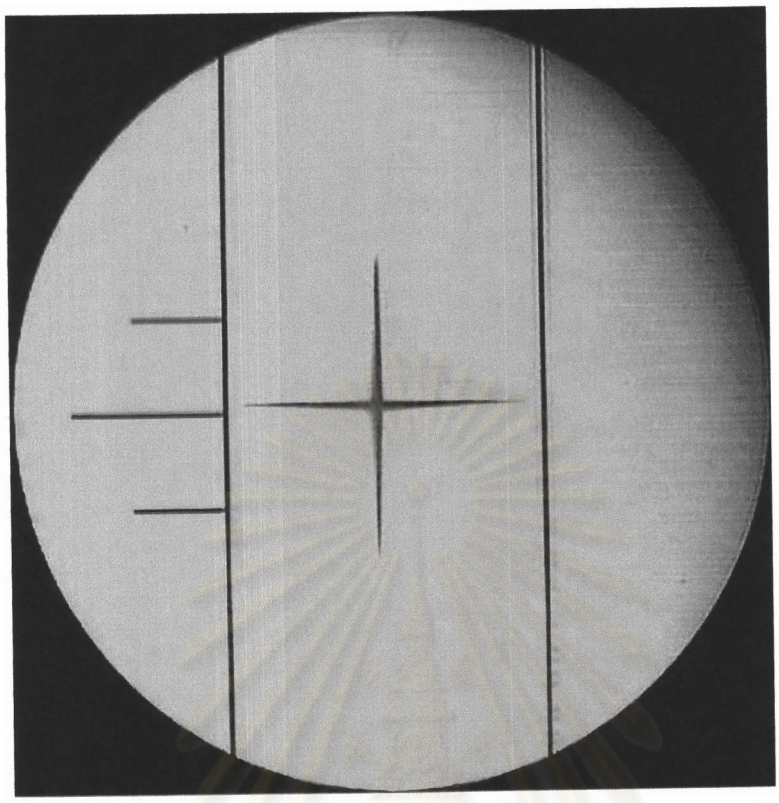
**Figure 5.8** SEM micrographs of two different water contents on CN films:
(a) 1wt%, and (b) 10wt%

**Table 5.1** Effect of various adhesion promoters on CN films.

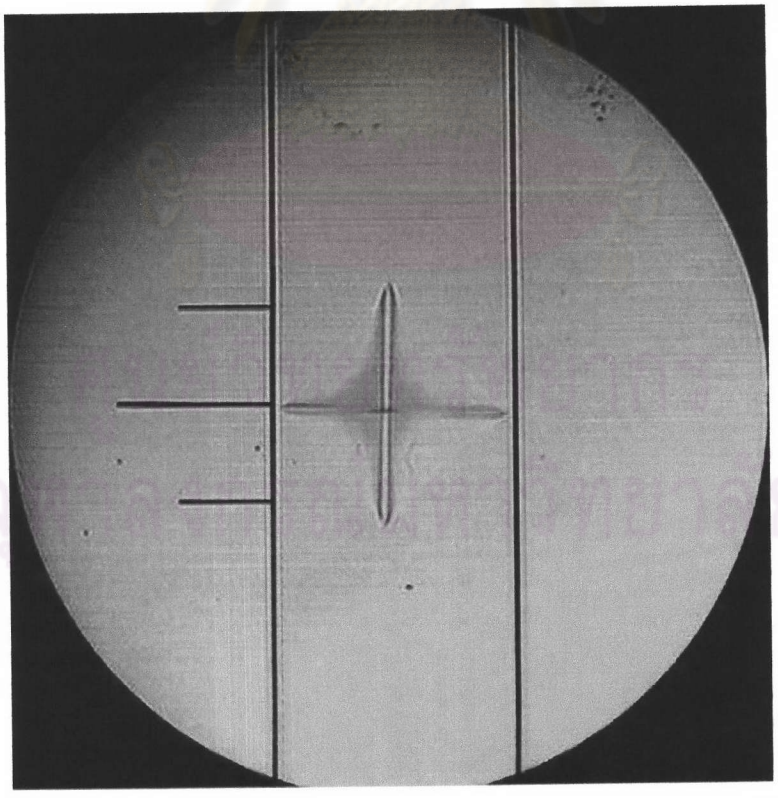
| Resin Type | Area of adhesion (%) | | | |
|---|---|---|---|---|
| | % adhered area I | % adhered area II | % adhered area III | Average |
| SD 603 | 7 | 2 | 6 | 5 |
| Silicone | 100 | 100 | 100 | 100 |
| ER-912 | 73 | 83 | 95 | 84 |
| EPO 828 | 85 | 100 | 80 | 88 |
| Benzoxazine | 100 | 95 | 100 | 98 |
| Red Earth™ | 100 | 100 | 100 | 100 |

**Table 5.2** Effect of maleic resin on adhesion properties of CN films.

| Maleic content (wt%.) | Area of adhesion (%) | | | |
|---|---|---|---|---|
| | % adhered area I | % adhered area II | % adhered area III | Average |
| 10 | 73 | 83 | 95 | 84 |
| 8 | 86 | 93 | 83 | 87 |
| 5 | 91 | 100 | 100 | 97 |
| 2 | 90 | 85 | 100 | 92 |
| 0 | 85 | 100 | 80 | 88 |



(a)



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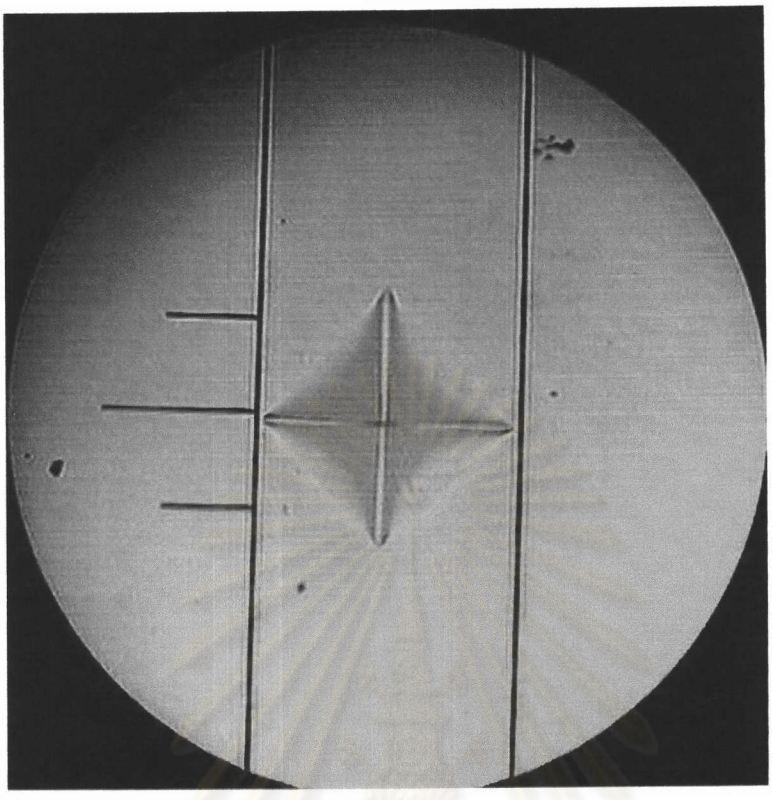

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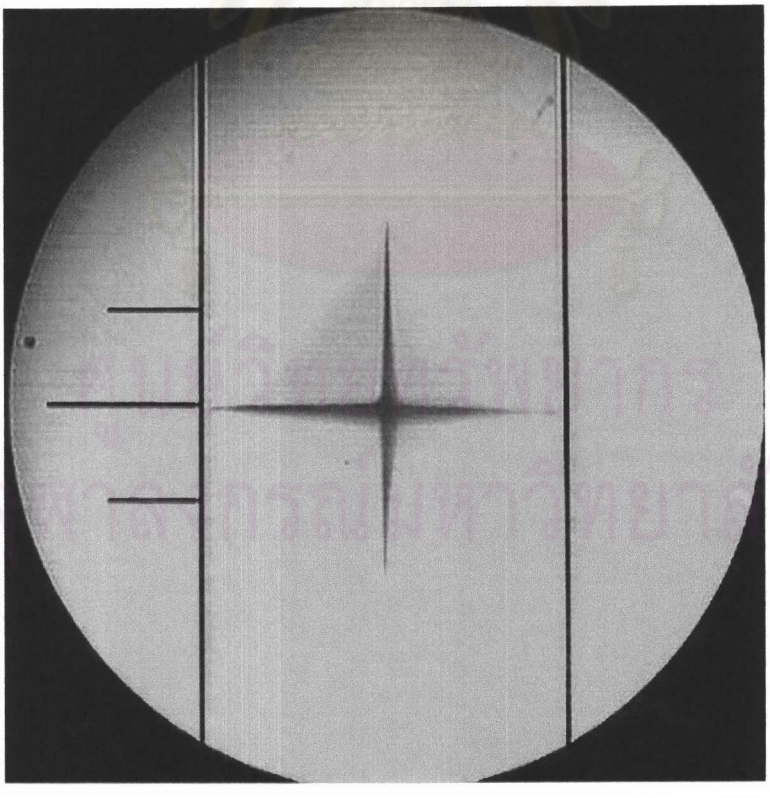
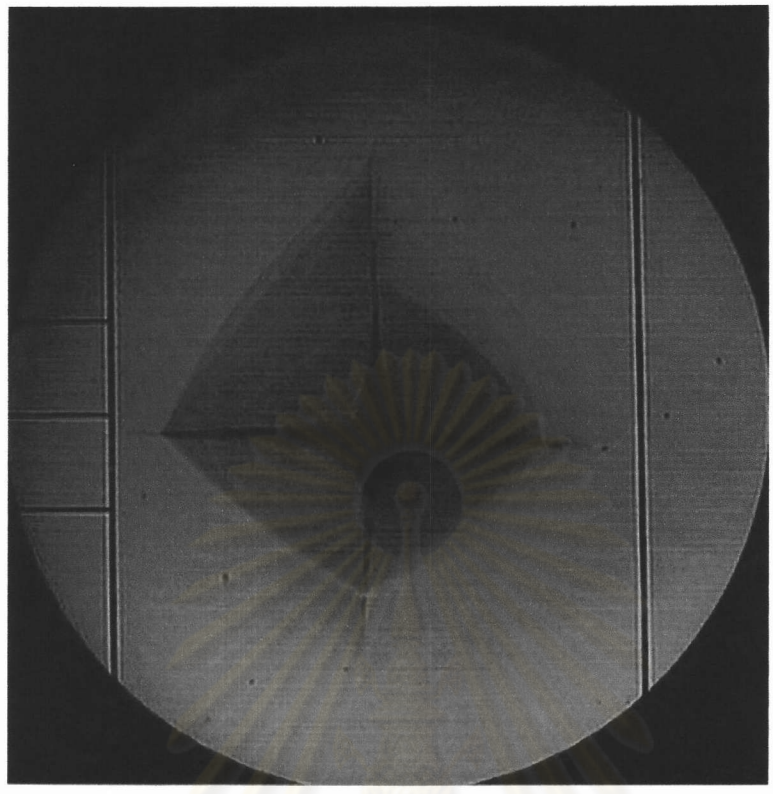
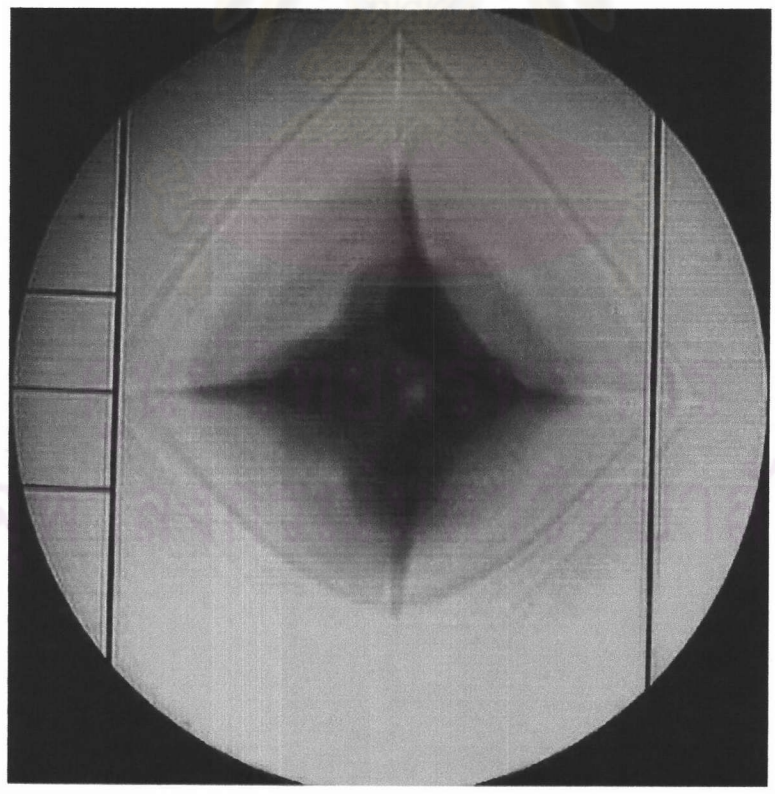


(d)



(e)



(f)

**Figure 5.9** Effect of maleic resin content on hardness of CN films:
(a) no adhesion promoter, (b) 10wt%, (c) 8wt%, (d) 5wt%, (e) 2wt%, and (f) epoxy 10wt%

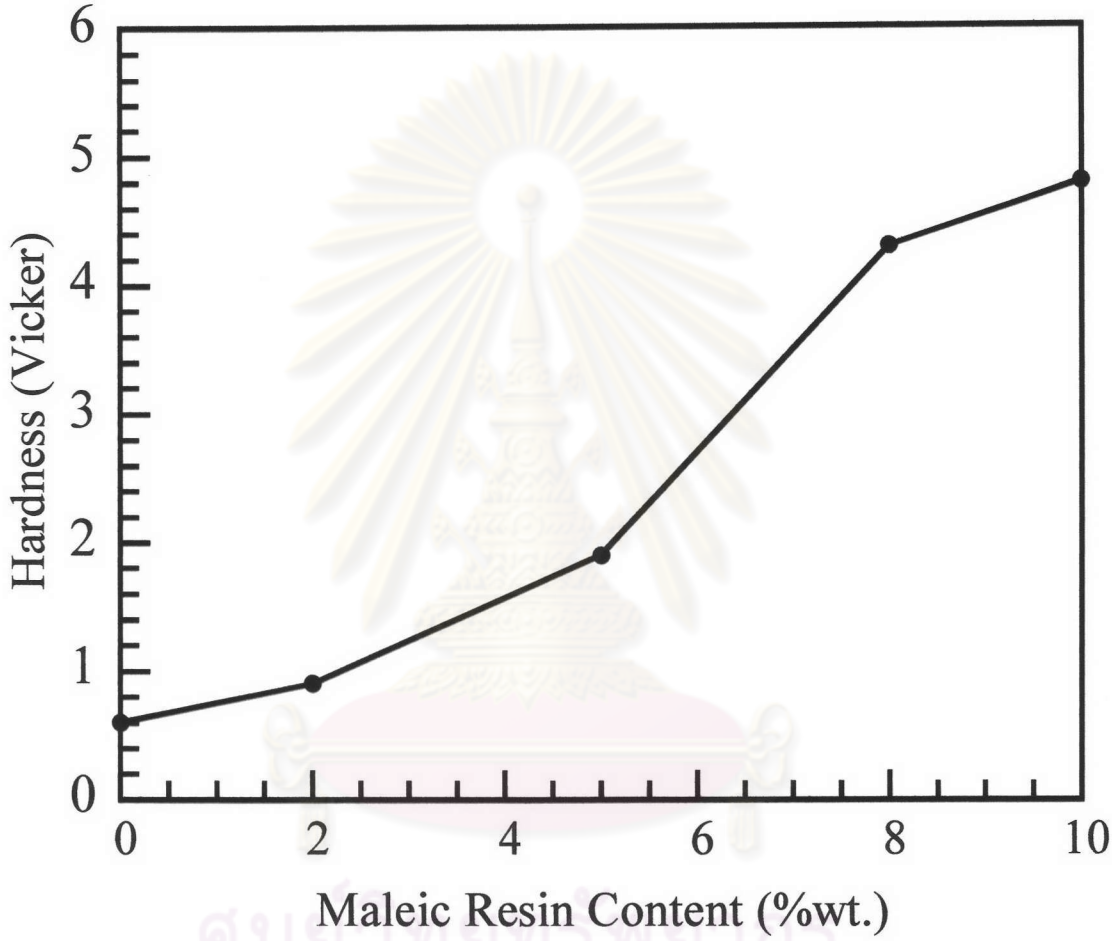



**Figure 5.10** Effect of maleic-epoxy resin mixtures on hardness in CN films.

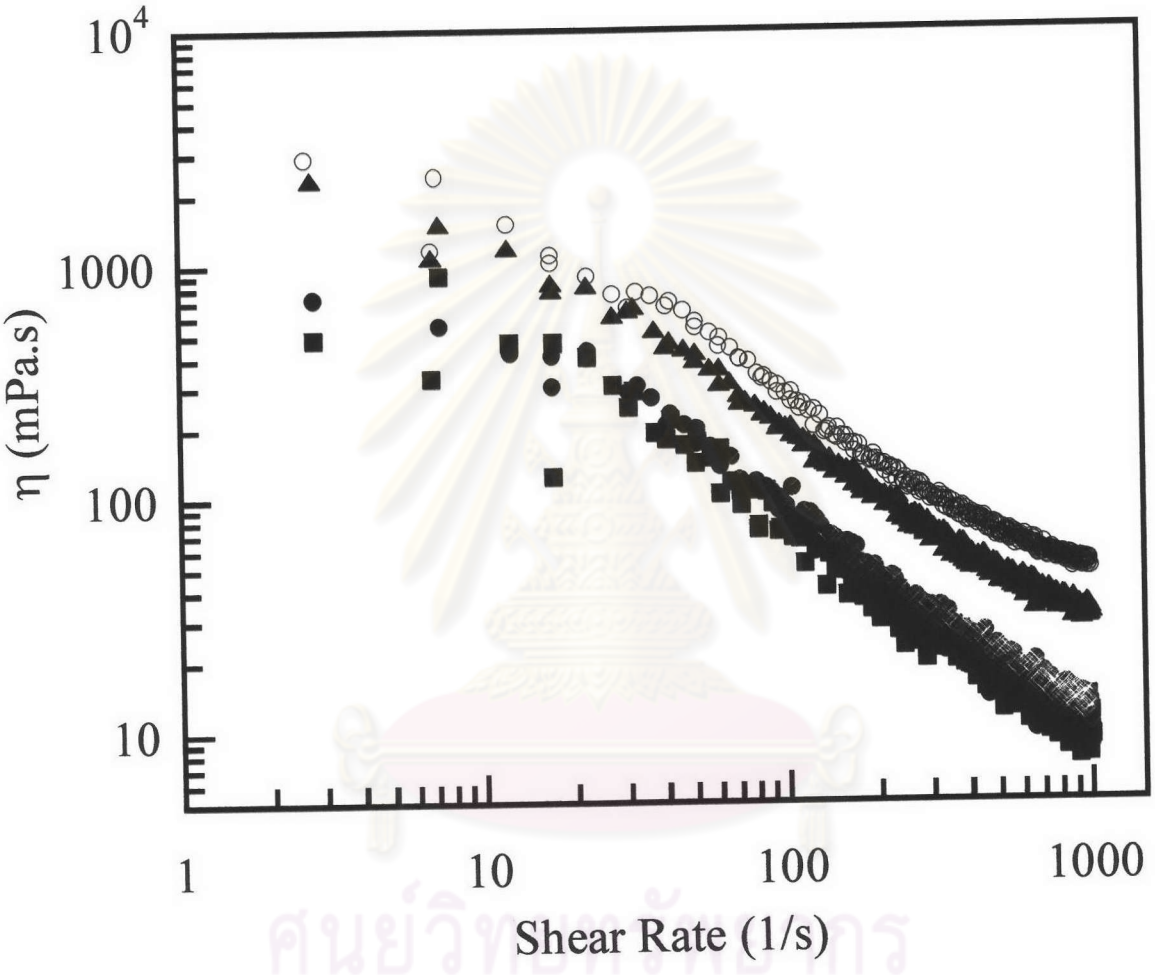



**Figure 5.11** Viscosity of 8wt% bentone38 in toluene at various mixing times using a mechanical stirrer at a speed of 650 rpm:
(○) 48hr, (▲) 24hr, (◇) 14hr, (■) 8hr, and (●) 4hr

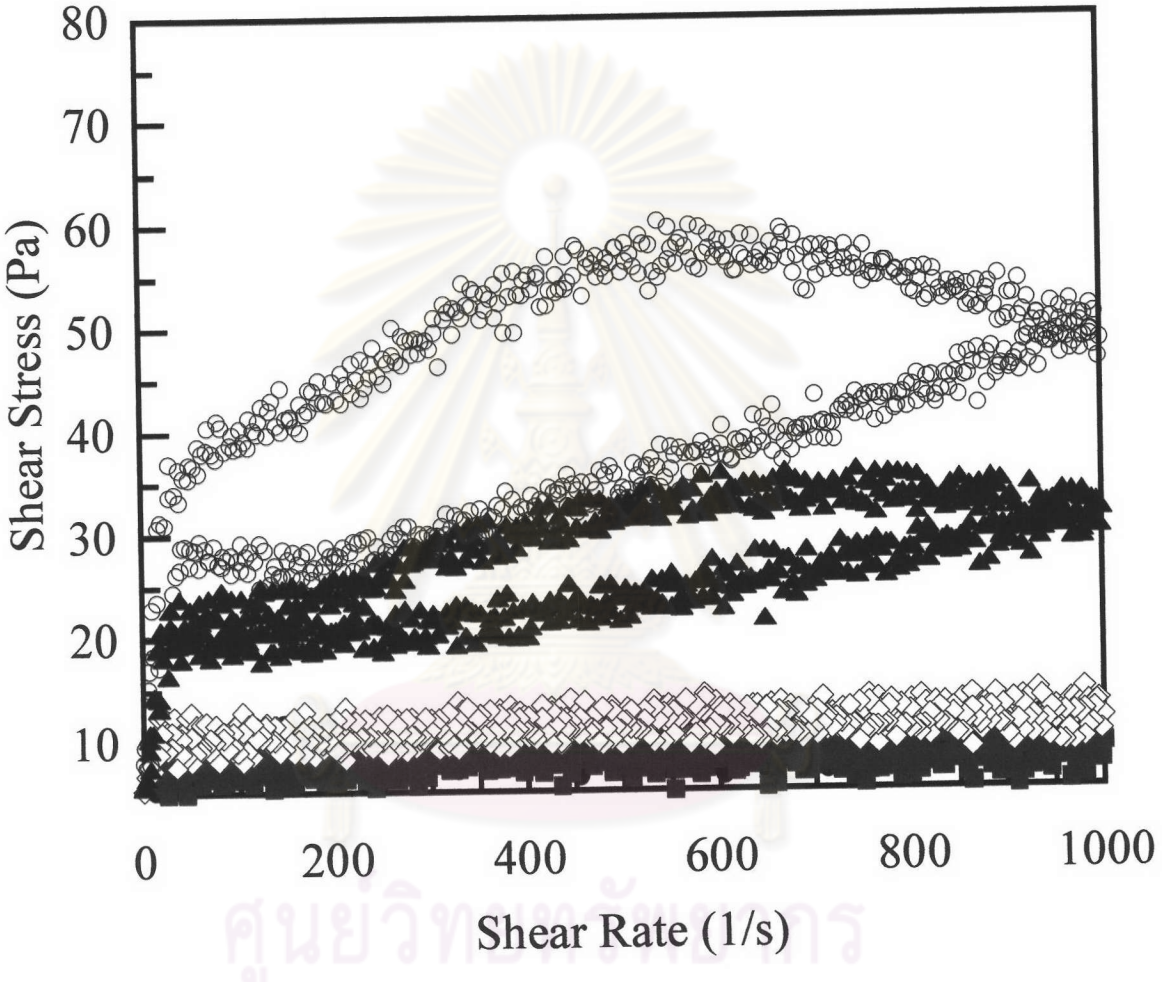



**Figure 5.12** Hysteresis of 8wt% bentone38 in toluene at various mixing times using a mechanical stirrer at a speed of 650 rpm:
(○) 48hr, (▲) 24hr, (◇) 14hr, (■) 8hr, and (●) 4hr

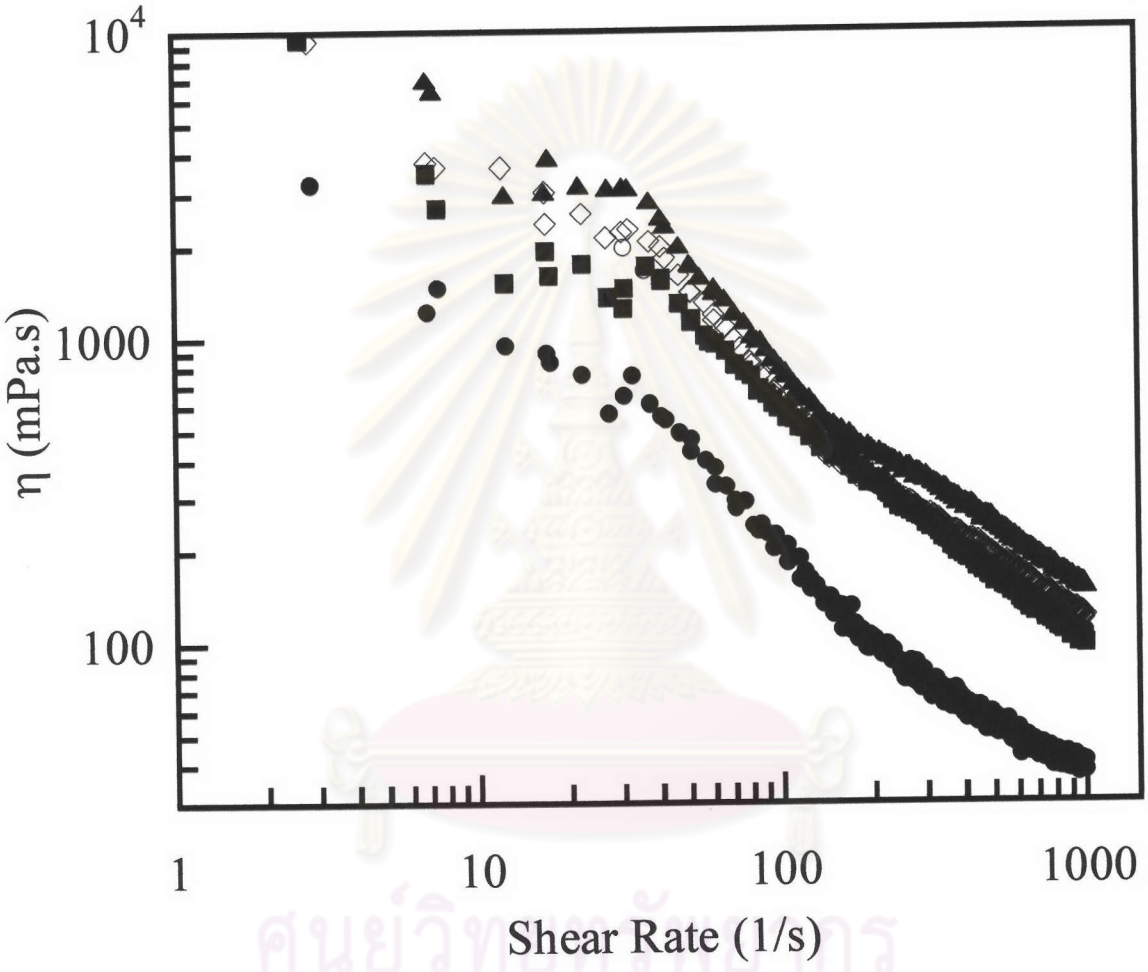



**Figure 5.13** Viscosity of 8wt% bentone38 in toluene at various high speed shear rates using a homogenizer for 5 minutes:
(▲) 24000 rpm, (◇) 21500 rpm, (■) 13500 rpm, (○) 9500 rpm, and (●) 6500 rpm

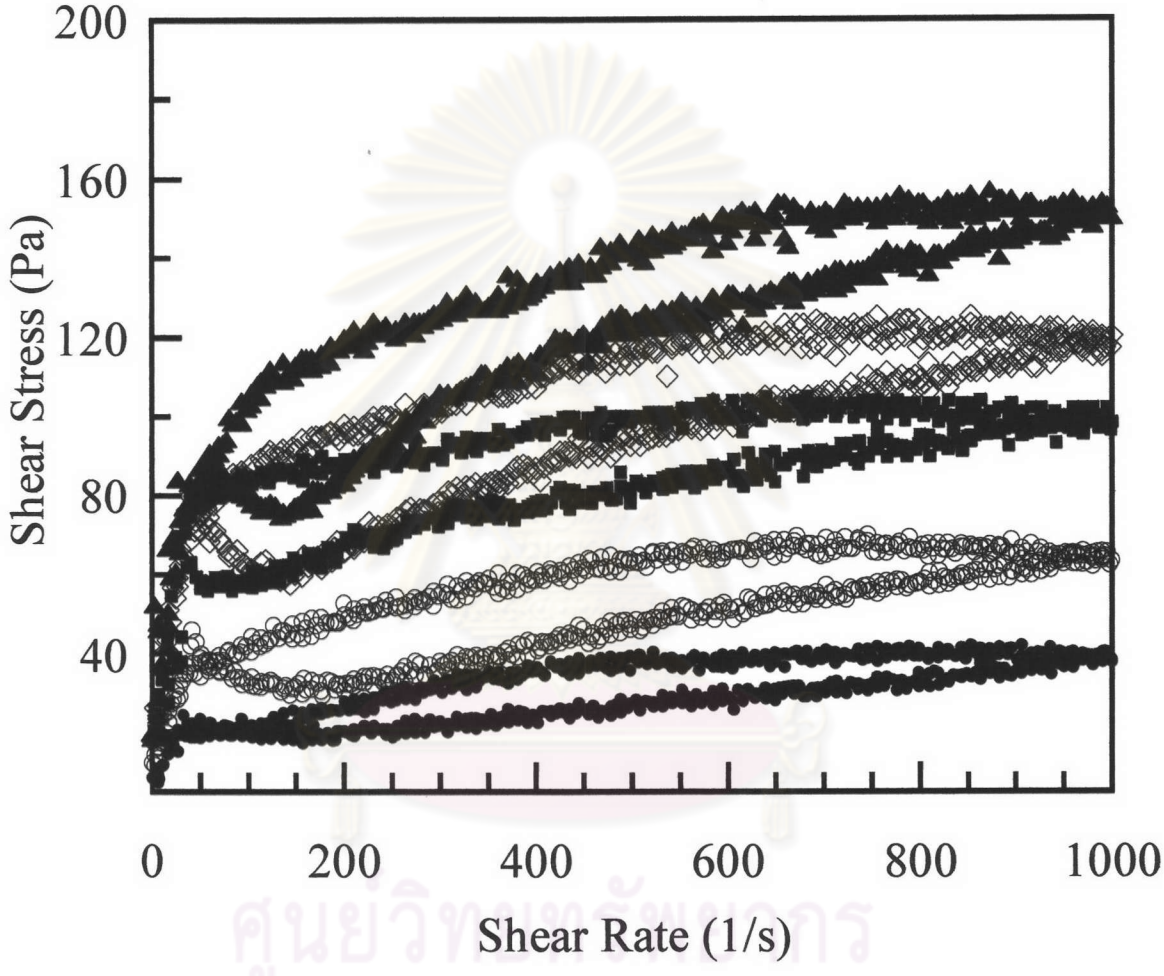



**Figure 5.14** Hysteresis of 8wt% bentone38 in toluene at various high speed shear rates using a homogenizer 5 minutes:
(▲) 24000 rpm, (◇) 21500 rpm, (■) 13500 rpm, (○) 9500 rpm, and (●) 6500 rpm

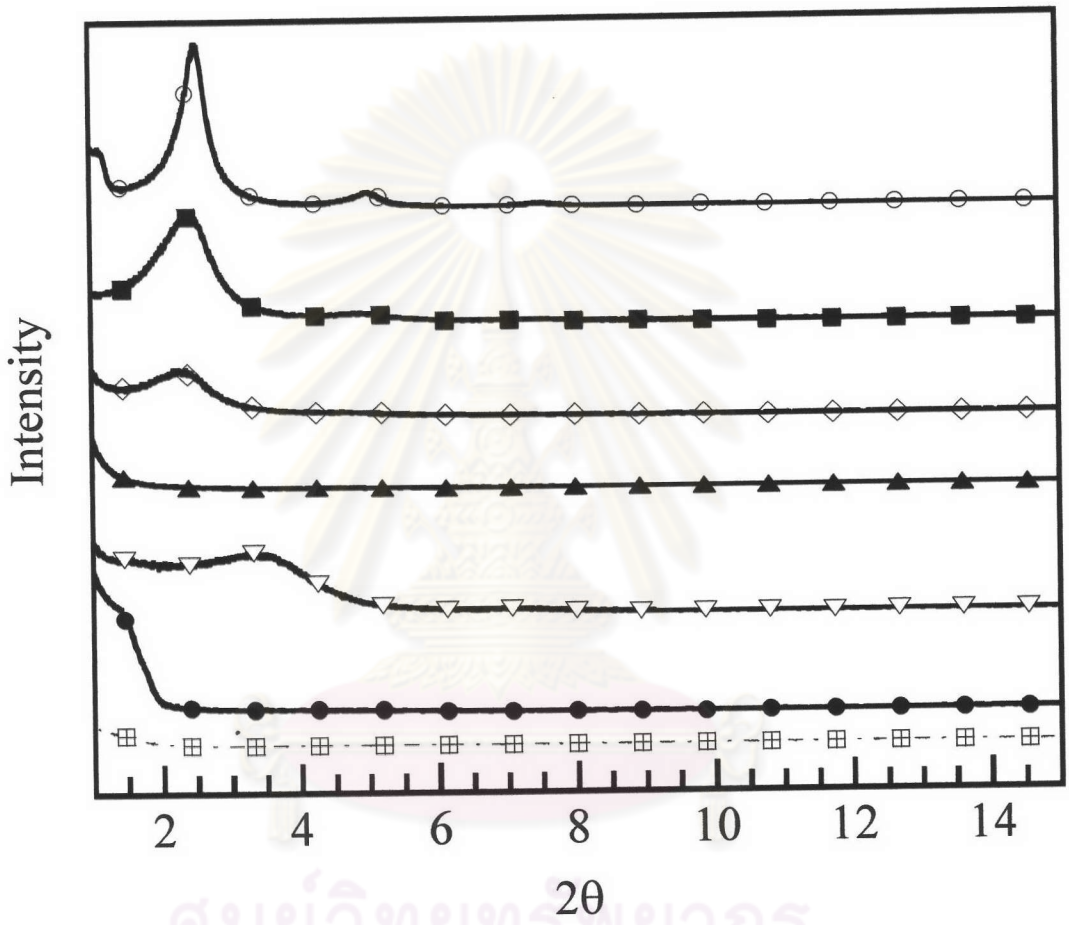



**Figure 5.15** XRD patterns of bentone38 in CN nail enamel films:
(○) 5wt%, (■) 3wt%, (◇) 1wt%, (▲) 0.35wt%, (▽) powder,
(●) unfilled film, and (⊞) slide glass

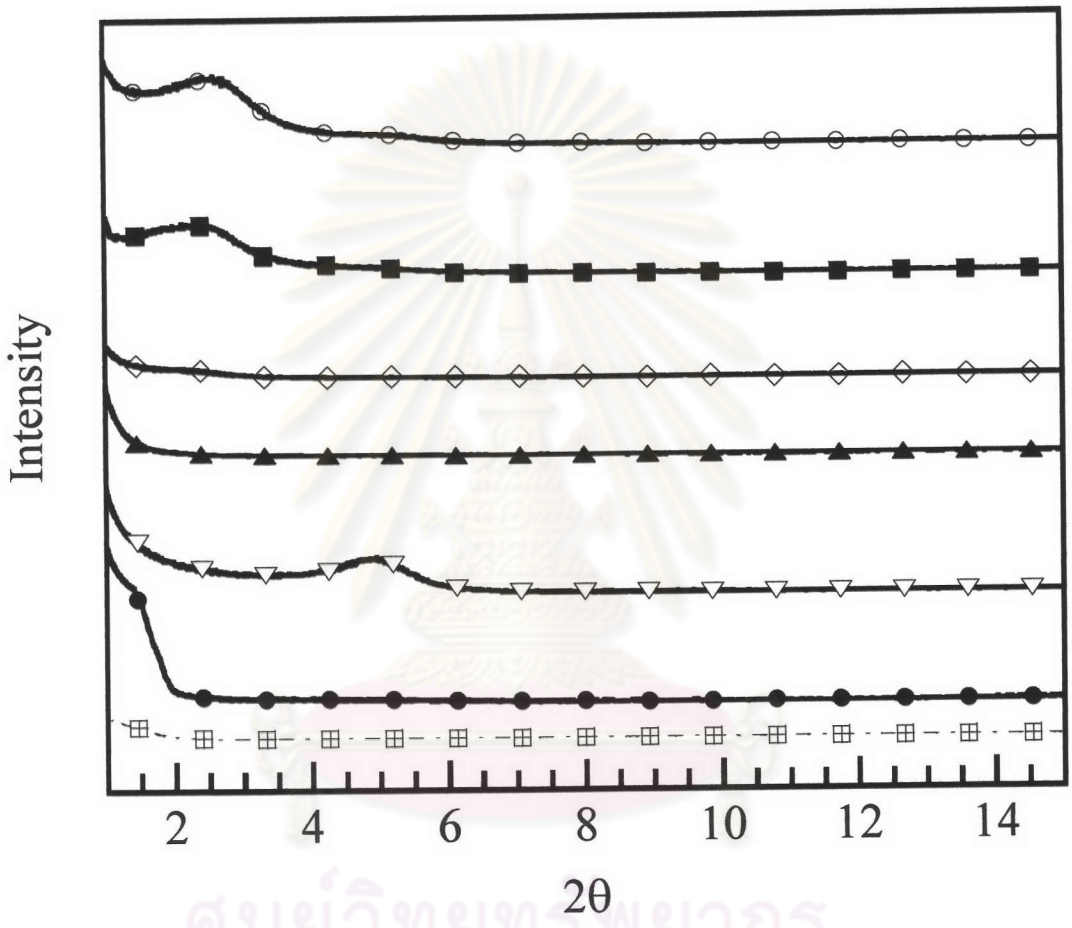



**Figure 5.16** XRD patterns of bentone27 in CN nail enamel films:
(○) 5wt%, (■) 3wt%, (◇) 1wt%, (▲) 0.35wt%, (▽) powder,
(●) unfilled film, and (⊞) slide glass

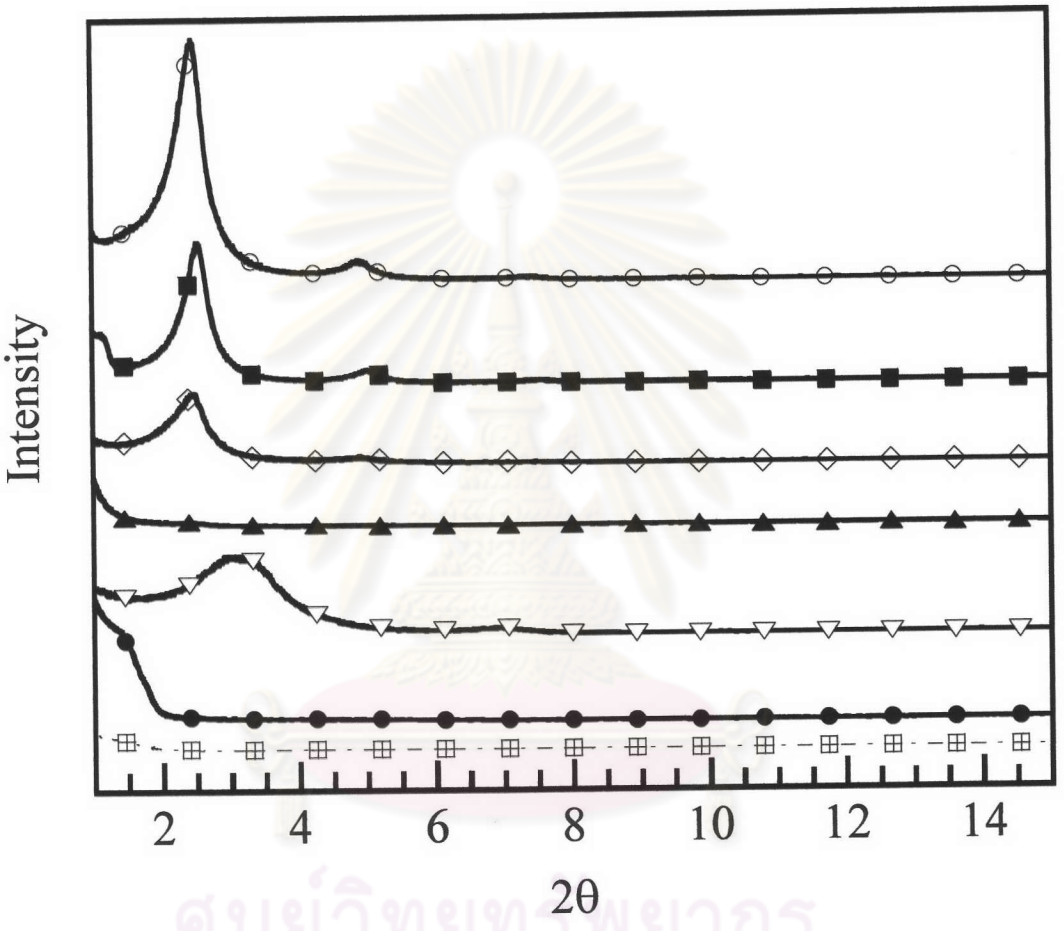
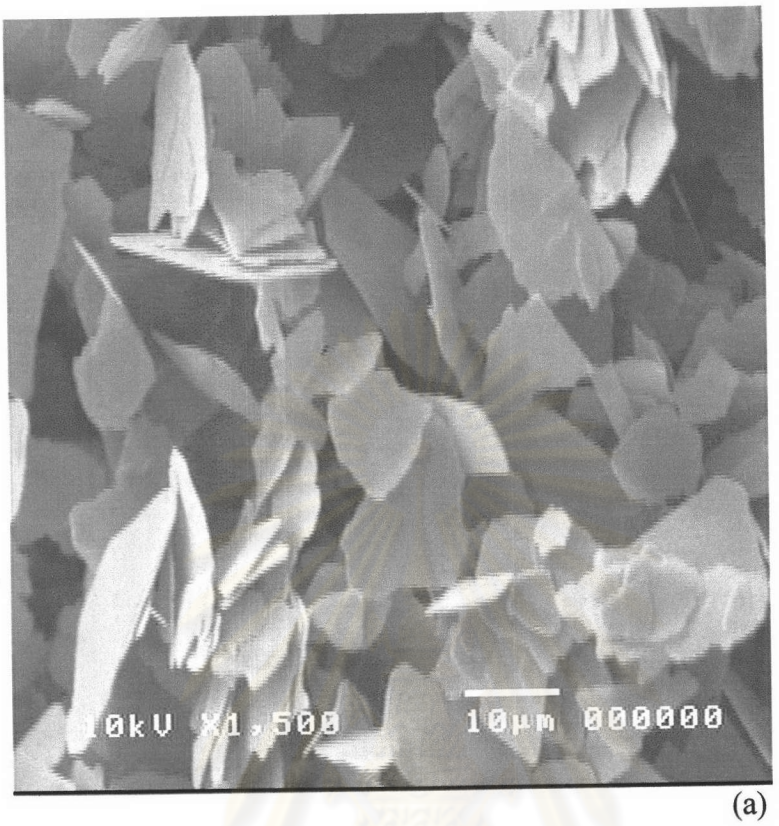


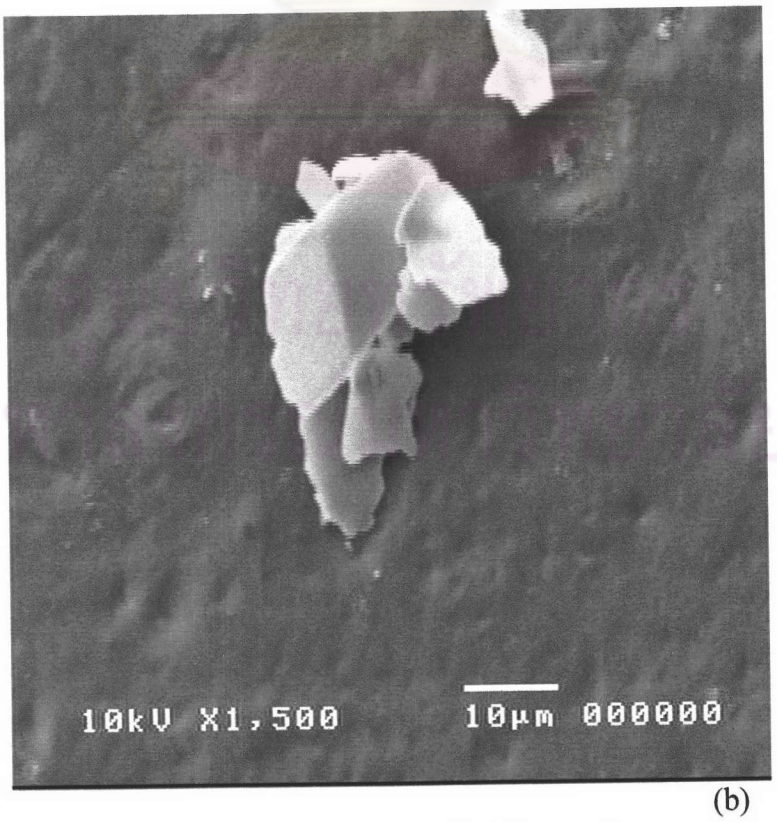

**Figure 5.17** XRD patterns of bentone34 in CN nail enamel films:
(○) 5wt%, (■) 3wt%, (◇) 1wt%, (▲) 0.35wt%, (▽) powder,
(●) unfilled film, and (⊞) slide glass

**Table 5.3** d-Spacing of clay interlayer in CN nail enamel films prepared by homogenizing at high shear rate of 9500 rpm for 5 minutes.

| Sample | 2θ | θ | sin (θ) | d-Spacing (Å) | Δ d(Å) |
|---|---|---|---|---|---|
| Ben38 powder | 3.39 | 1.70 | 0.030 | 26 | - |
| Ben38 5wt% | 2.55 | 1.28 | 0.022 | 35 | 9 |
| Ben38 3wt% | 2.39 | 1.20 | 0.020 | 37 | 11 |
| Ben38 1wt% | 2.26 | 1.13 | 0.019 | 39 | 13 |
| Ben38 0.35wt% | - | - | - | - | Exfoliated |
| Ben27 powder | 4.96 | 2.48 | 0.040 | 18 | - |
| Ben27 5wt% | 2.45 | 1.23 | 0.020 | 36 | 18 |
| Ben27 3wt% | 2.35 | 1.18 | 0.019 | 38 | 20 |
| Ben27 1wt% | - | - | - | - | Exfoliated |
| Ben27 0.35wt% | - | - | - | - | Exfoliated |
| Ben34 powder | 3.06 | 1.53 | 0.030 | 29 | - |
| Ben34 5wt% | 2.55 | 1.28 | 0.022 | 35 | 6 |
| Ben34 3wt% | 2.48 | 1.24 | 0.022 | 36 | 7 |
| Ben34 1wt% | 2.45 | 1.23 | 0.020 | 36 | 7 |
| Ben34 0.35wt% | - | - | - | - | Exfoliated |



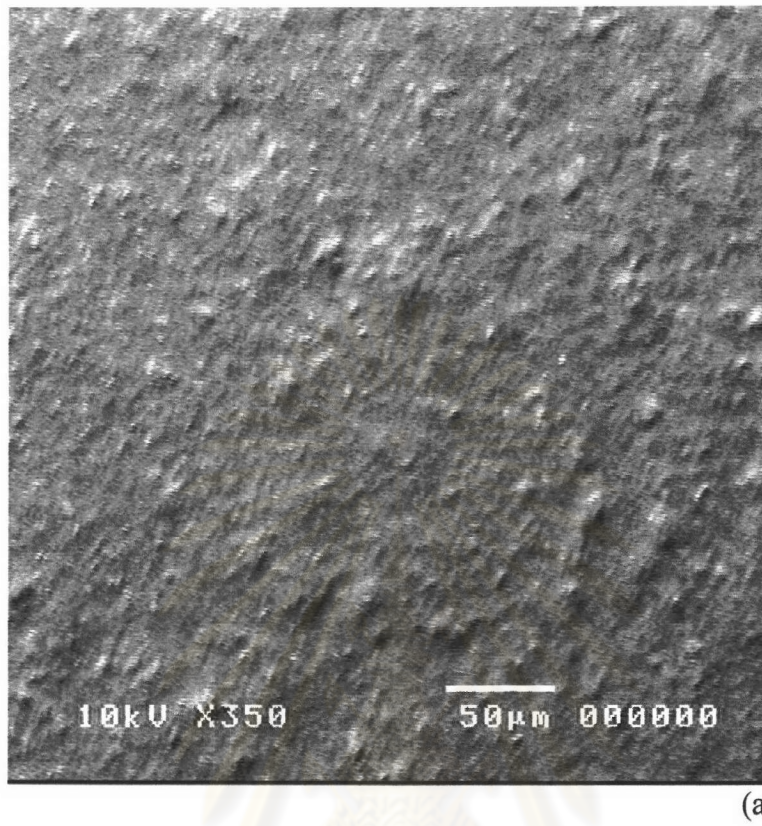

(a)



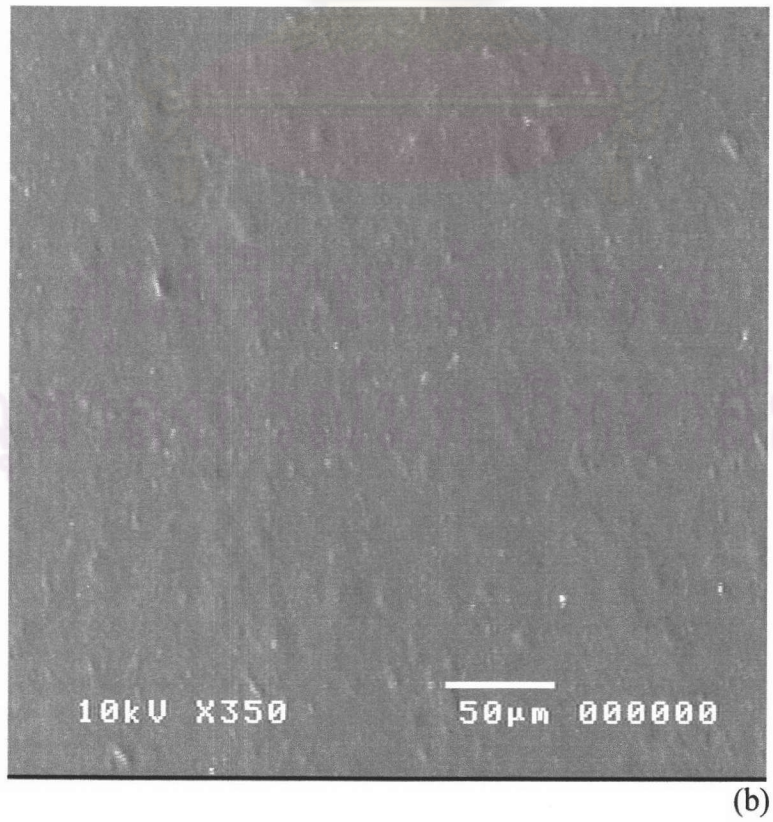

(b)

**Figure 5.18** SEM micrographs of pigmented nail enamel:

(a) titanium dioxide coated mica, and (b) commercial nail polish




(a)




(b)

**Figure 5.19** SEM micrographs of two different preparation methods for formulated nail enamel: (a) motor stirring, and (b) homogenizing

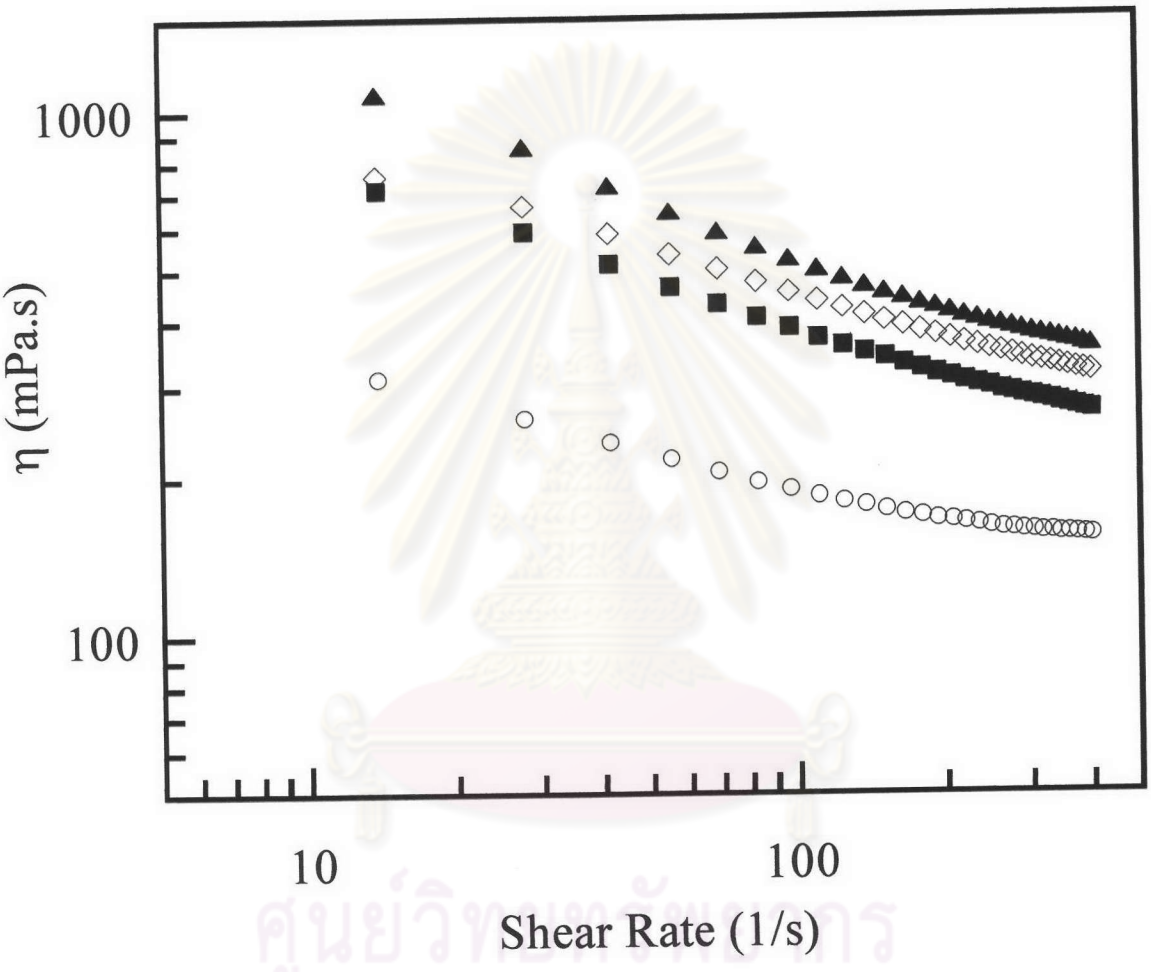



**Figure 5.20** Non-newtonian flows of nail enamel using various thixotropes at 5wt %: (▲) bentone27, (◇) bentone34, (■) bentone38, and (○) Red Earth™

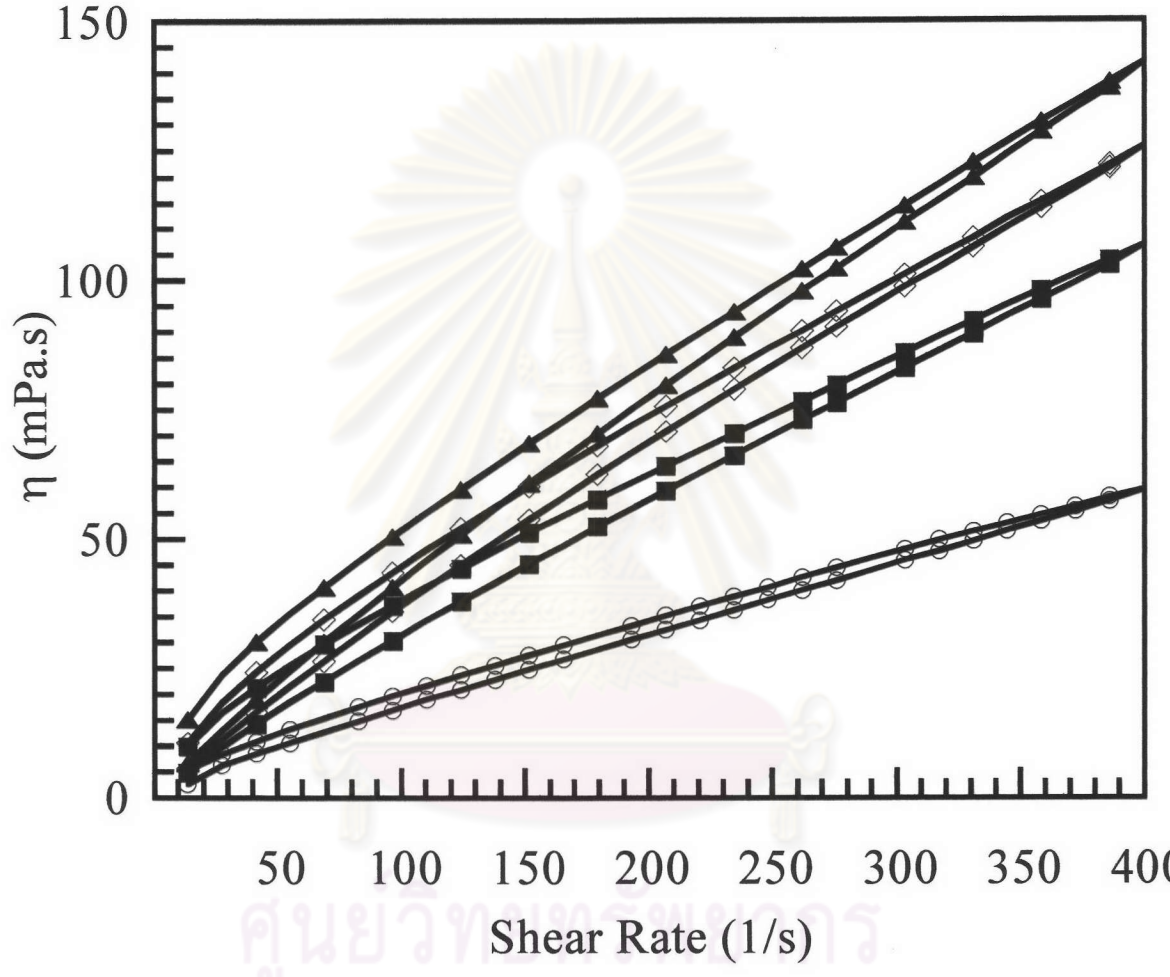



**Figure 5.21** Effect of types of clays on thixotropic behaviors of formulated nail enamel at 5wt %:
(▲) bentone27, (◇) bentone34, (■) bentone38, and (○) Red Earth™

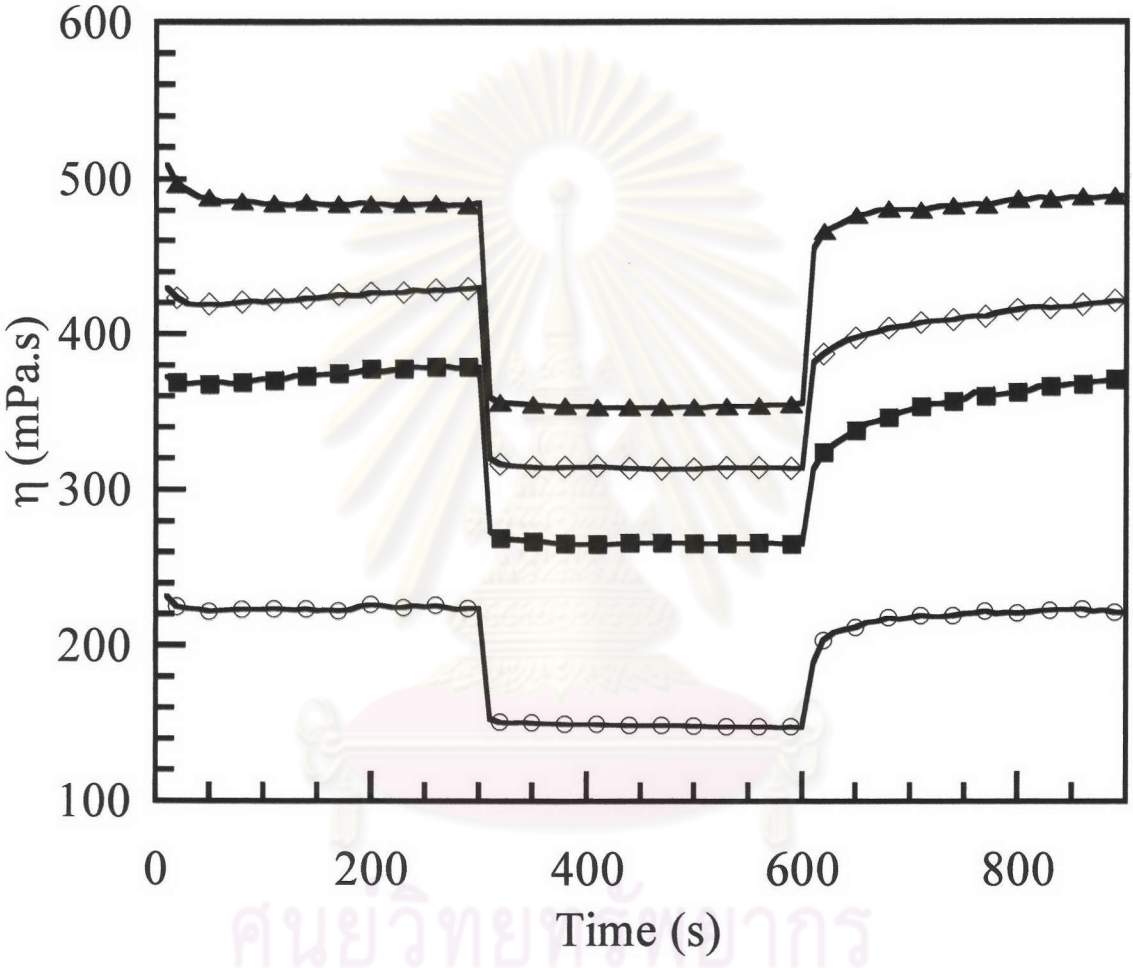



**Figure 5.22** Step shearing 4/400/4 (1/s) for thixotropic test of the result nail enamel at 5wt %: (▲) bentone27, (◇) bentone34, (■) bentone38, and (○) Red Earth™

**Table 5.4** Thixotropic index of various organoclay in nail enamel.

| Nail enamel Type | T.I. |
|---|---|
| Ben38 | 1.4 |
| Ben27 | 1.4 |
| Ben34 | 1.4 |
| RedEarth™ | 1.5 |

**Table 5.5** Recovery time at 90% viscosity of various organoclay in nail enamel.

| Nail enamel Type | $\eta_0$ (mPa.s) | 90% $\eta_0$ | Recovery time (sec) |
|---|---|---|---|
| Ben38 | 378.6 | 340.74 | 56.6 |
| Ben27 | 484.6 | 436.14 | 8.13 |
| Ben34 | 429.7 | 386.73 | 19.3 |
| RedEarth™ | 223.8 | 201.42 | 18.8 |

**Table 5.6** Drying time of various organoclay in nail enamel.

| Nail Enamel | Time of Drying (min.) | | | | | |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | Average |
| Clear nail enamel | 3.0 | 3.0 | 3.3 | 3.3 | 3.0 | 3.12 |
| Ben 38 | 4.0 | 4.0 | 4.0 | 3.5 | 3.5 | 3.80 |
| Ben 27 | 3.5 | 3.5 | 3.5 | 4.0 | 4.0 | 3.70 |
| Ben 34 | 4.0 | 4.0 | 4.0 | 3.5 | 3.5 | 3.80 |
| Red Earth™ | 3.5 | 3.5 | 4.0 | 4.0 | 4.0 | 3.80 |

**Table 5.7** Gloss of various organoclay in nail enamel at 60 °.

| Nail Enamel | Gloss (G.U) |
|---|---|
| Clear nail enamel | 122.5 |
| Ben 38 | 56.8 |
| Ben 27 | 29.8 |
| Ben 34 | 76.7 |
| Red Earth™ | 74.2 |

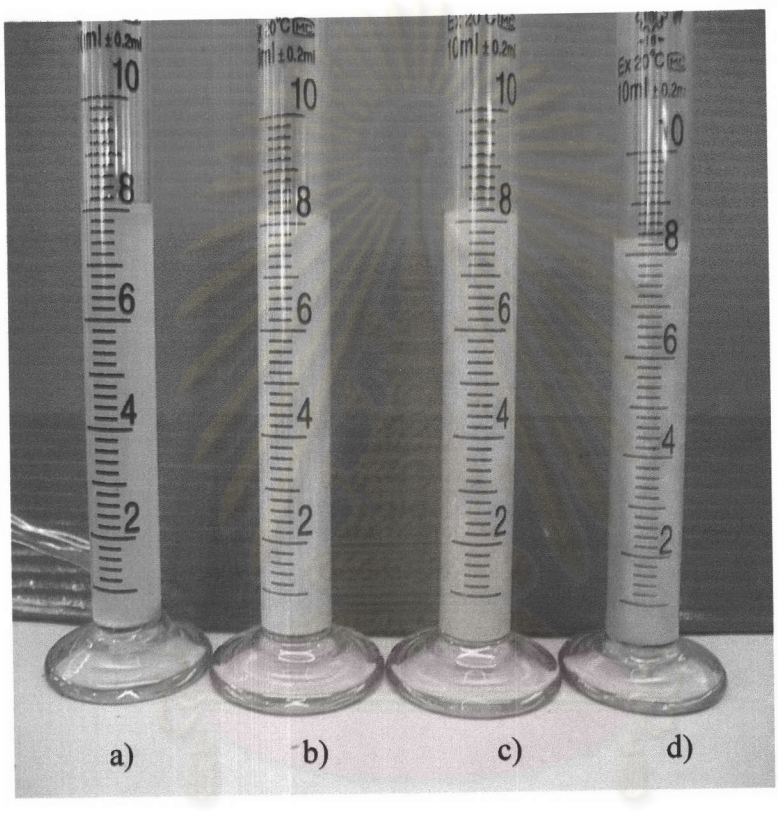



**Figure 5.23** Sedimentation of formulated nail enamel at various contents of bentone38 (at day $10^{th}$):
(a) 1wt%. (b) 3wt%. (c) 4wt%., and (d) 5wt%.

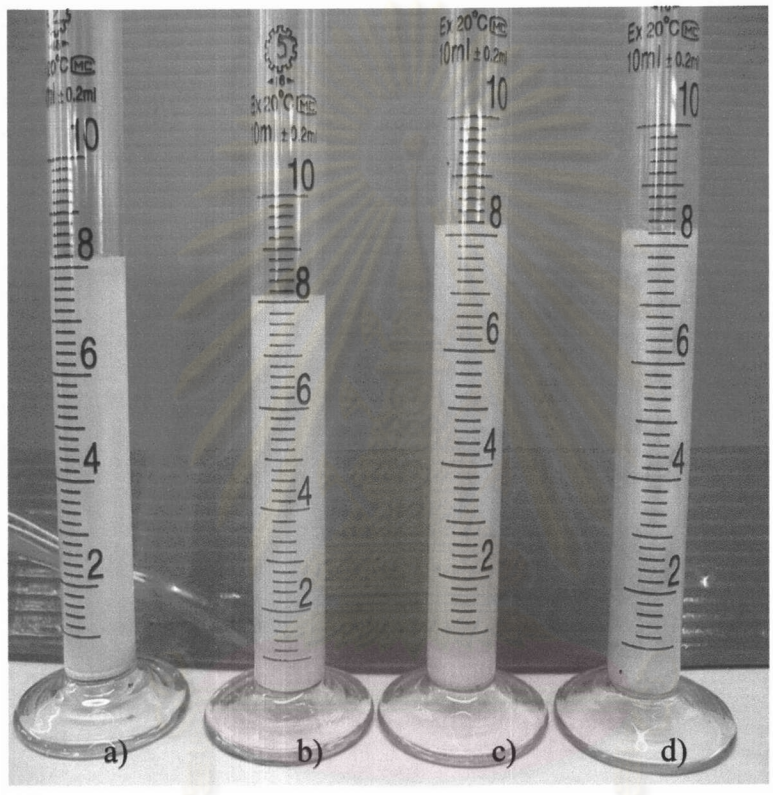



**Figure 5.24** Sedimentation of formulated nail enamel at various content of bentone27 (at day 10th):
(a) 1wt%. (b) 3wt%. (c) 4wt%., and (d) 5wt%.

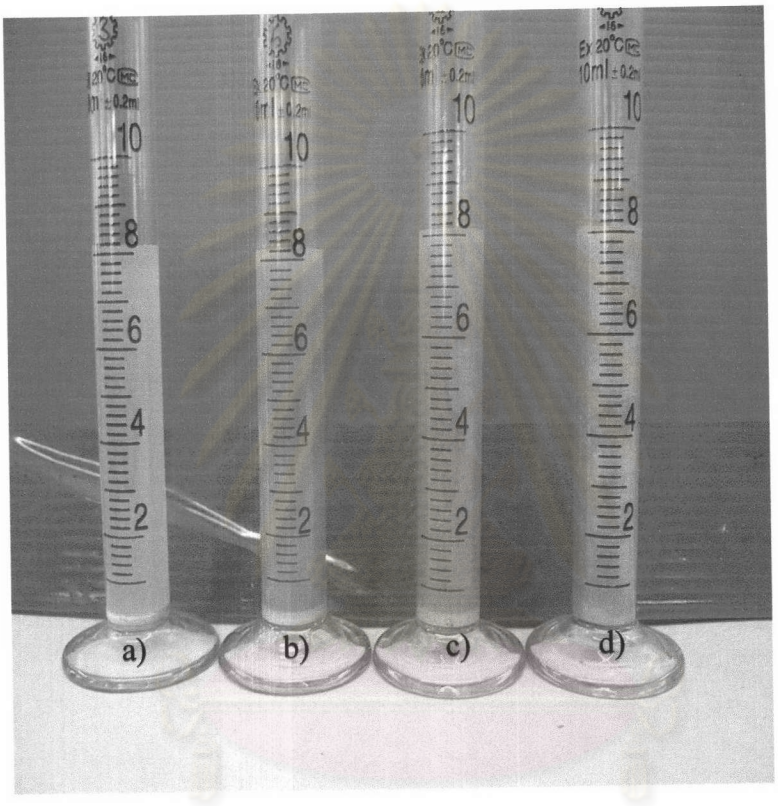
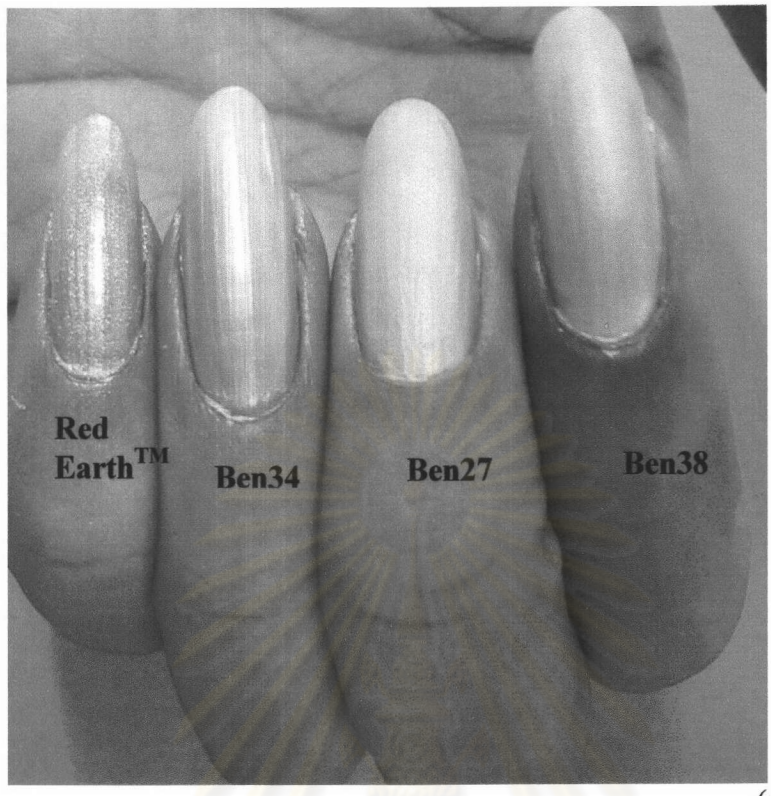



**Figure 5.25** Sedimentation of formulated nail enamel at various content of bentone34 (at day 10th):
(a) 1wt%. (b) 3wt%. (c) 4wt%., and (d) 5wt%.

**Table 5.8** Formulated of nail enamels.

| **Ingredients** | **wt %** | | |
|---|---|---|---|
| | **A** | **B** | **C** |
| Cellulose nitrate | 10 | 10 | 10 |
| Maleic resin | 5 | 5 | 5 |
| Epoxy resin | 5 | 5 | 5 |
| Dibutyl phthalate | 5 | 5 | 5 |
| Ethyl alcohol | 5 | 5 | 5 |
| Butyl acetate | 15 | 15 | 15 |
| Ethyl acetate | 20 | 20 | 20 |
| Toluene | 29 | 29 | 29 |
| Bentone 38 | 5 | - | - |
| Bentone 37 | - | 5 | - |
| Bentone 34 | - | - | 5 |
| Pigments | 1 | 1 | 1 |

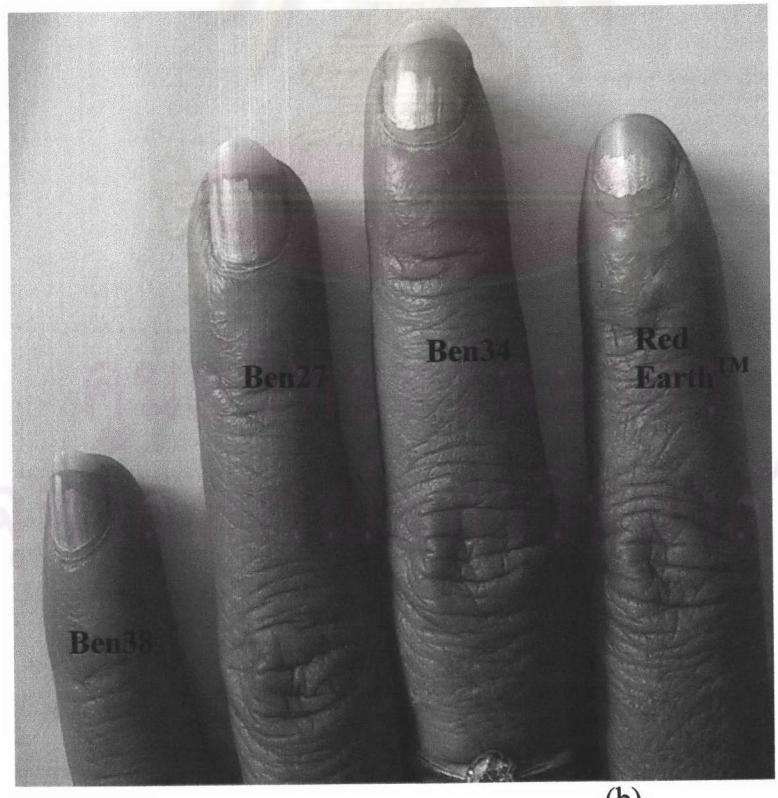



(a)


(b)

**Figure 5.26** Comparative test on human of formulated nail enamels of various suspending agents:
(a) 1 day (b) 10 days

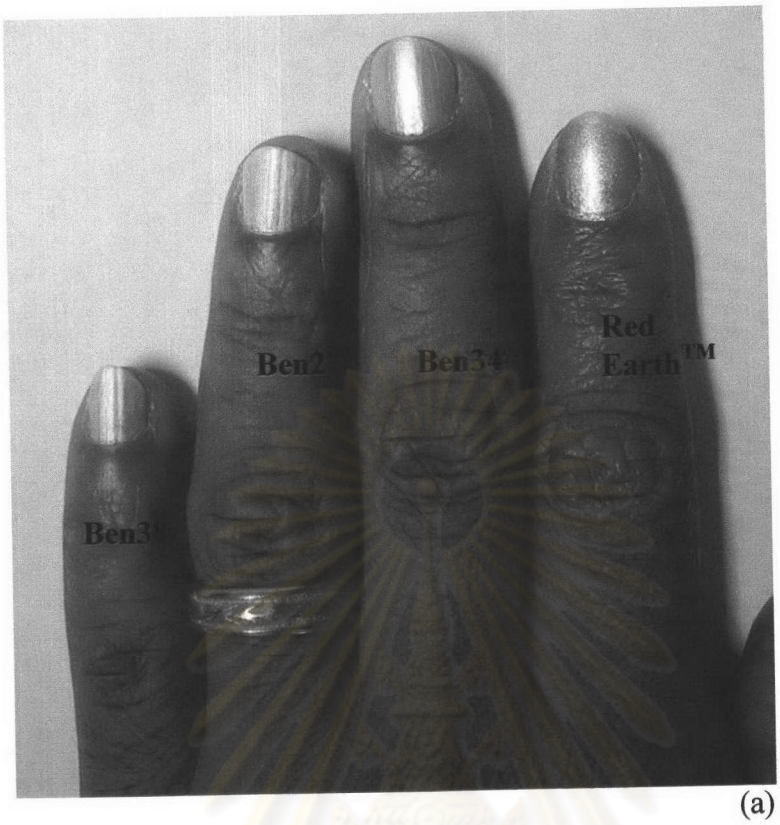

(a)




(b)

**Figure 5.27** Comparative test on human of formulated nail enamels of various suspending agents:

(a) 1 day (b) 10 days




(a)


(b)

**Figure 5.28** Comparative test on human of formulated nail enamels of various suspending suspending agents:

(a) 1 day (b) 10 days

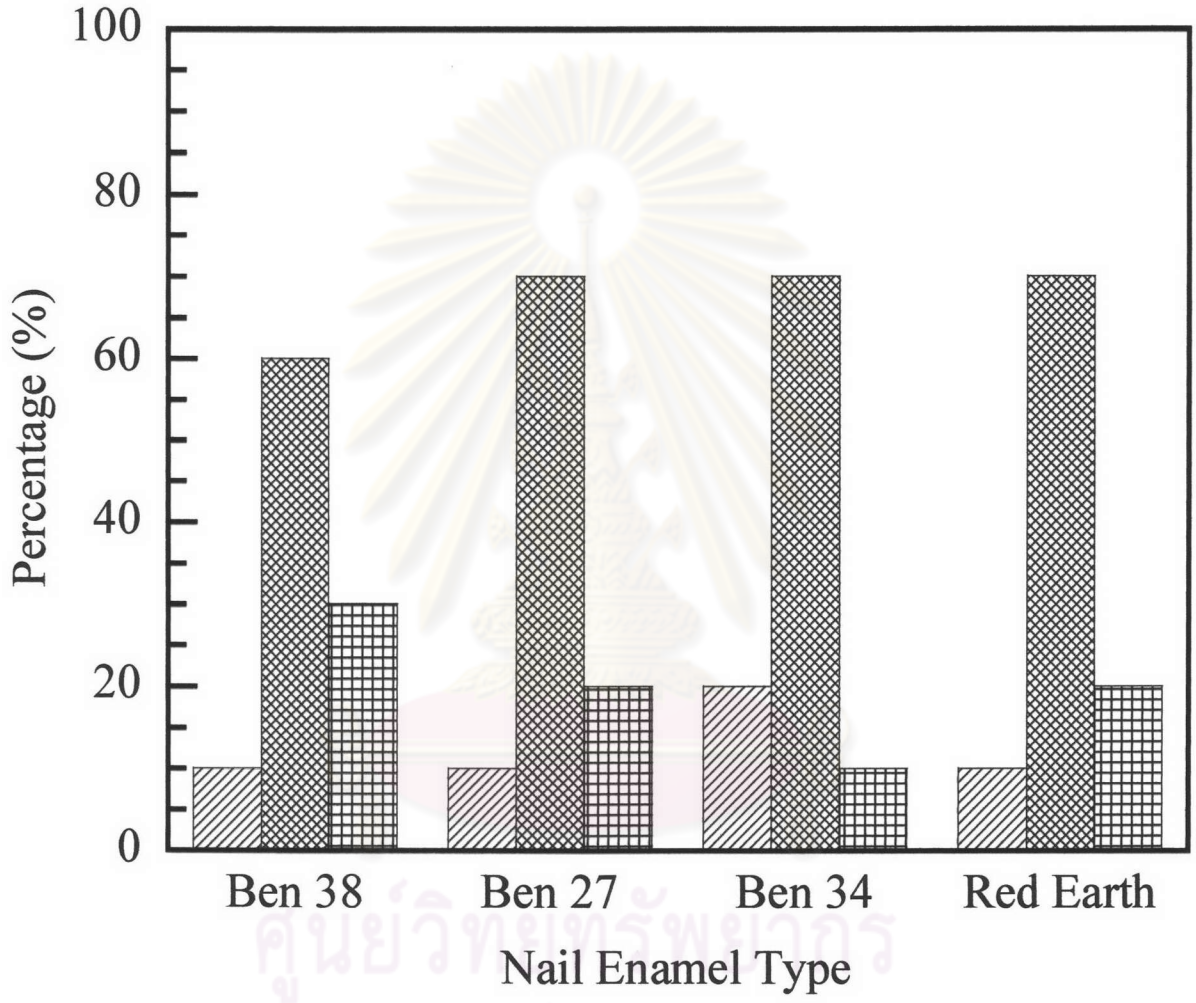



**Figure 5.29** Human satisfaction on pick up characteristic of formulated nail enamel: (▨) dripping, (▩) settle, and (▦) lump

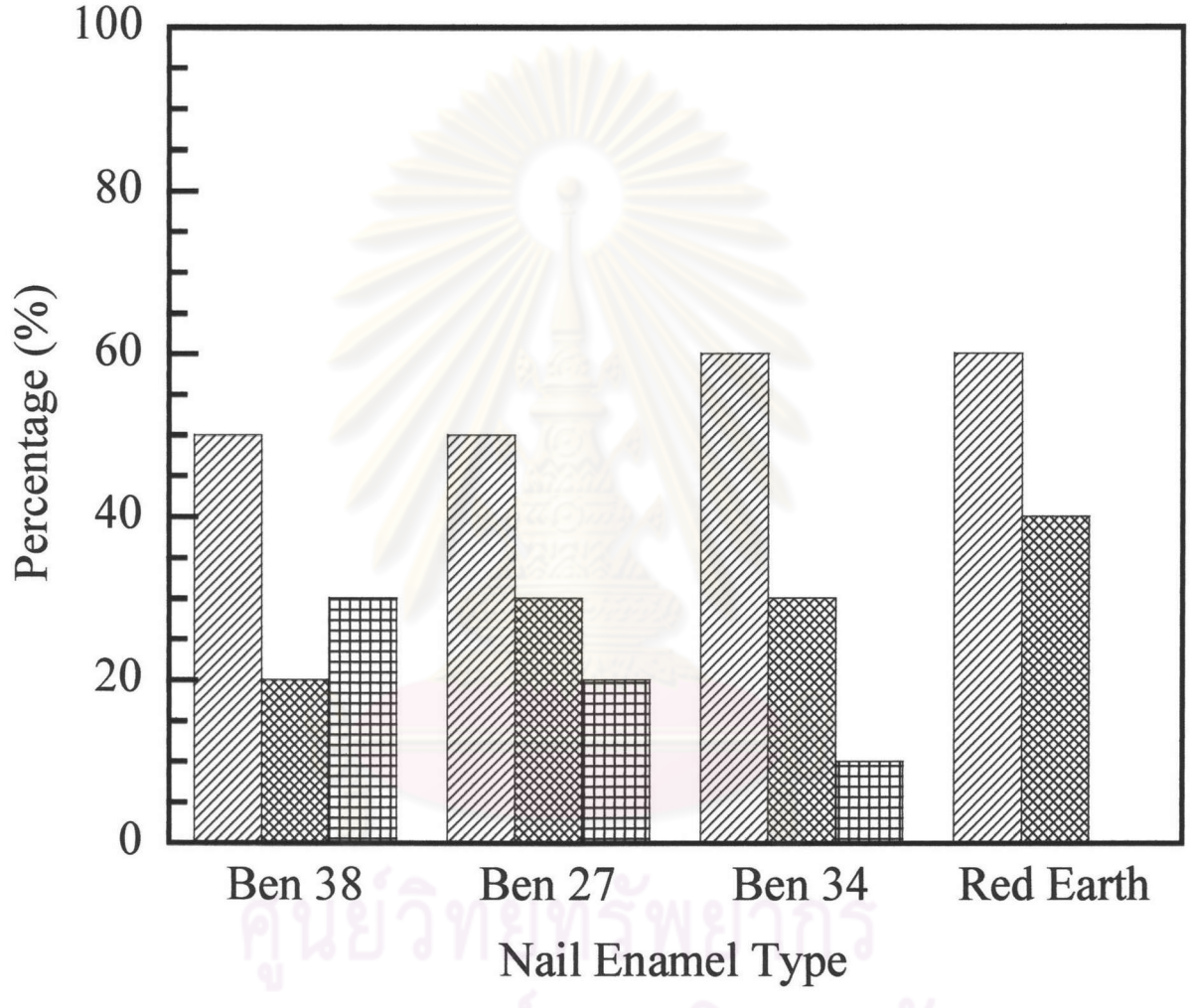





**Figure 5.30** Human satisfaction on ease of brushing characteristic of formulated nail enamel: (▨) easy, (▩) preferable, and (▦) difficult

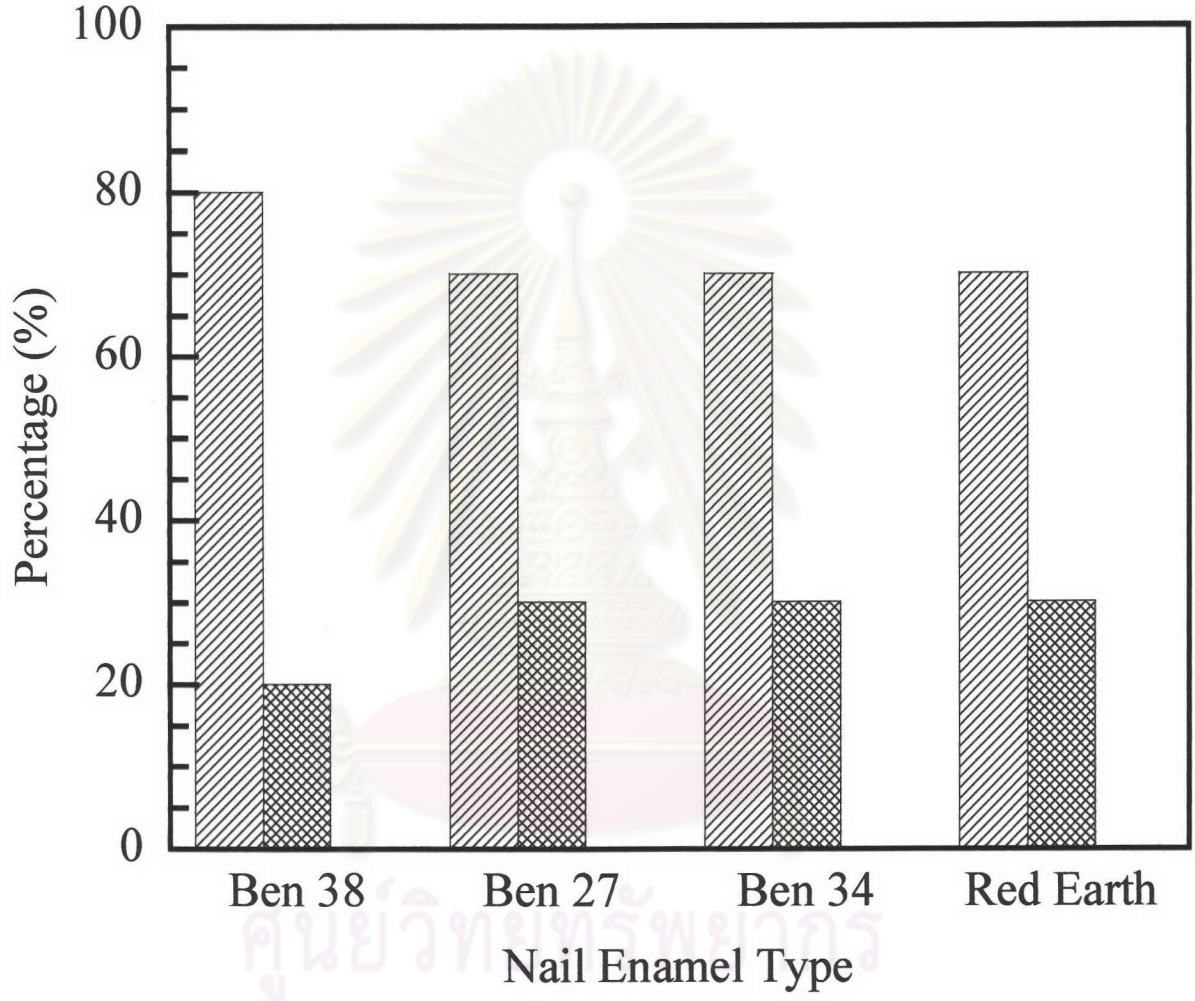





**Figure 5.31** Human satisfaction on drying time characteristic of formulated nail enamel: (▨) < 1 min., (▩) 1-4 min., and (▦) > 5 min.

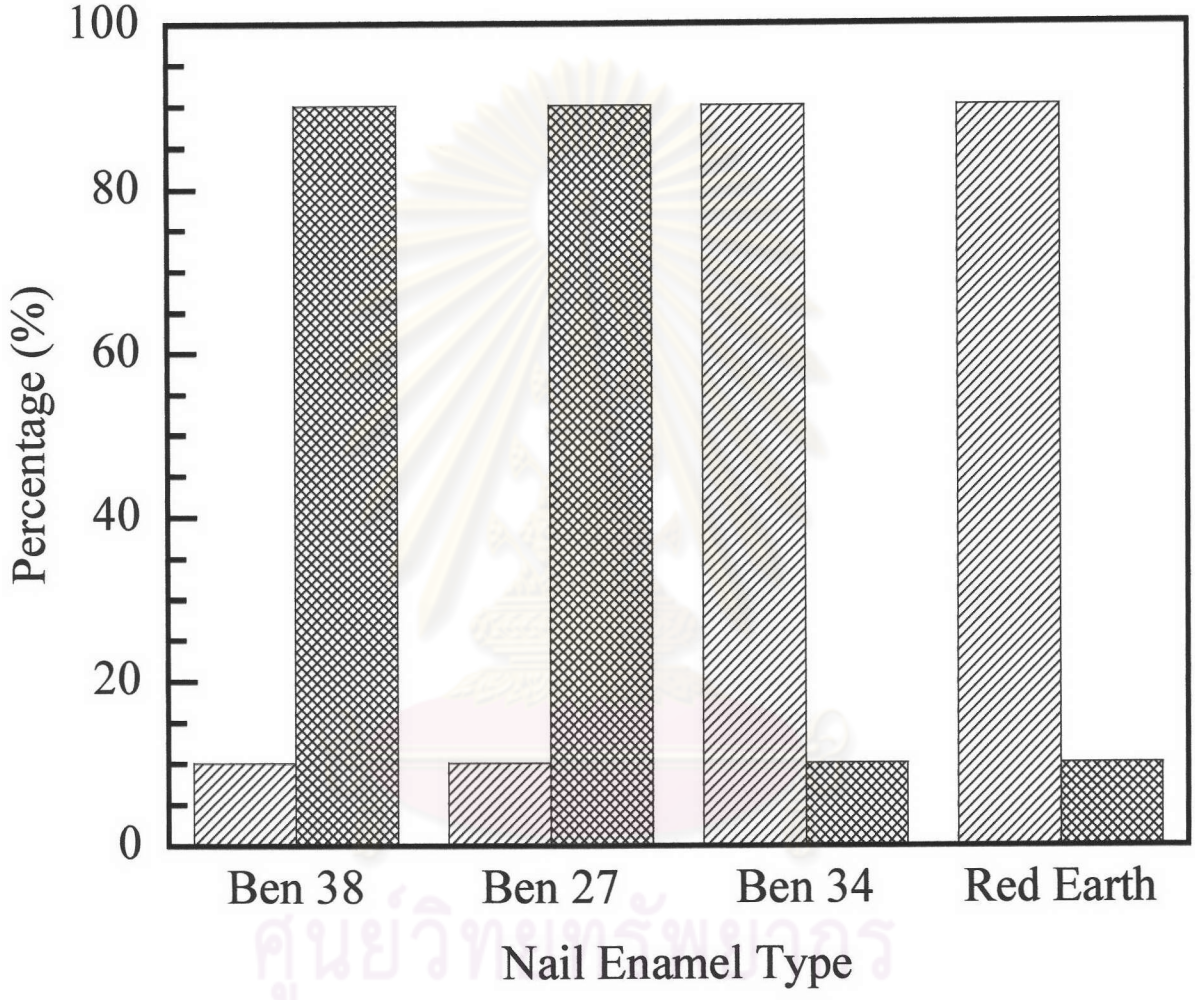



**Figure 5.32** Human satisfaction on gloss characteristic of formulated nail enamel: (▨) satisfied, and (▩) unsatisfied

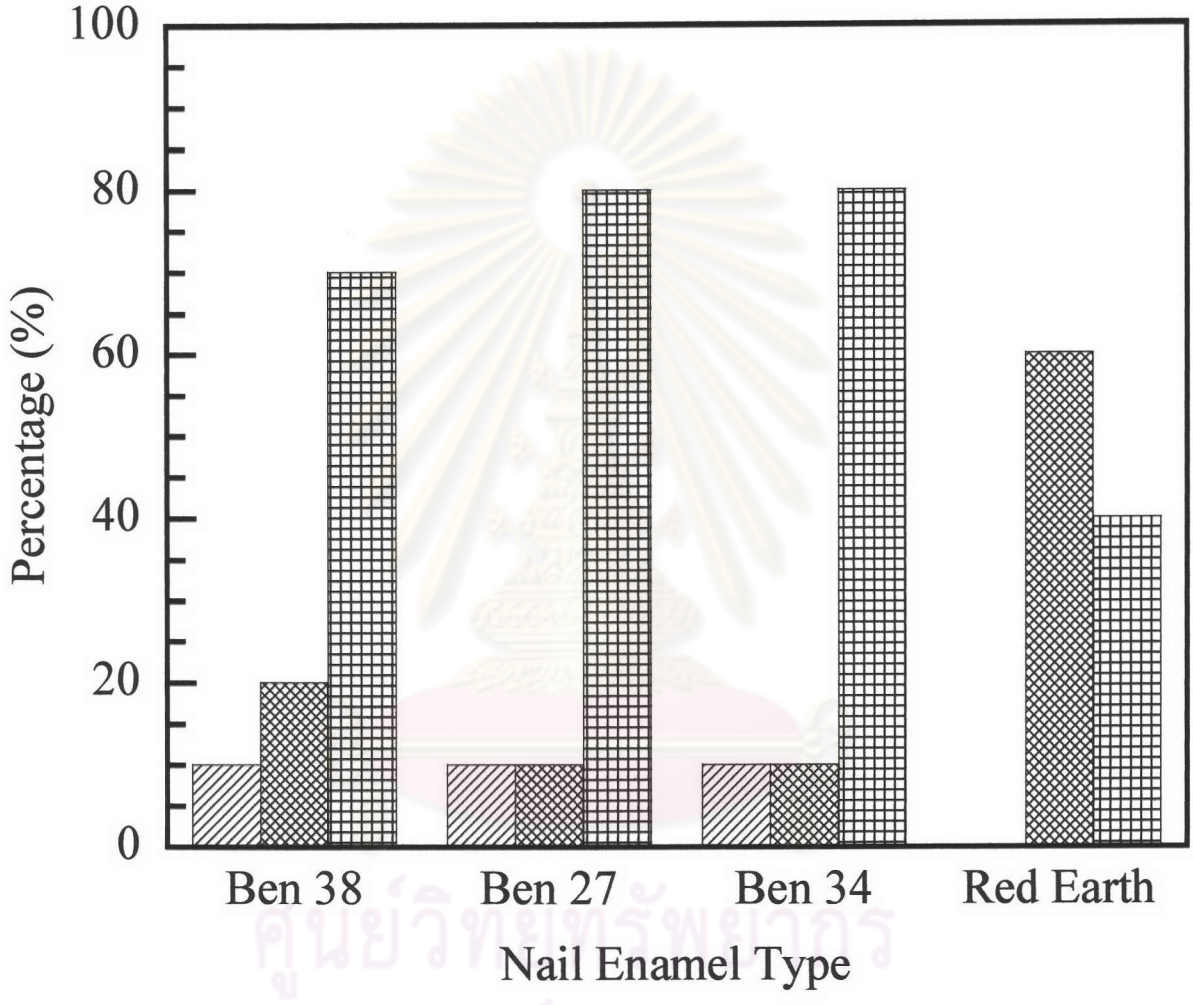





**Figure 5.33** Human satisfaction on abrasion characteristic of formulated nail enamel: (▨) no abrasion, (▩) a little bit of abrasion, and (▦) obviousness