CHAPTER III

EXPERIMENTAL

Materials

1. Soybean oil fatty acids waste
2. Glacial acetic acid
   analytical grade; Riedel-de Haen
3. Hydrogen peroxide
   30 % volume for synthesis; Merck
4. Methyl alcohol
   analytical grade; J.T.Baker Inc.
5. Sulfuric acid (98 % w/w)
   analytical grade; BDH Chemicals Ltd.
6. Carbon tetrachloride
   analytical grade, Merck
7. Iodine trichloride (ICl_3)
   analytical grade; Fluka
8. Iodine (I_2)
   chemical grade; Fluka
9. Potassium Iodide (KI)
   analytical grade; BDH Chemicals Ltd.
10. Sodium thiosulfate ($Na_2S_2O_3$)
    analytical grade; Merck

11. Starch granule
    reagent grade; Sigma Chemicals company
12. Benzene
    analytical grade, J.T.Baker
13. Potassium hydrogen phthalate (KHP)
    analytical grade; Sigma Chemicals company
14. Hydrogen bromide in acetic acid (4.1 M)
    analytical grade; Fluka
15. Hexamethylpararosaniline hydrochloride (crystal violet)
    for indicator; Merck
16. Sodium bisulfite ($NaHSO_3$)
    analytical grade; Merck
17. Sodium metabisulfite ($Na_2S_2O_5$)
    analytical grade; Merck
18. Sodium sulfate (anhydrous)
    reagent grade; BDH chemicals company
19. Sodium hydrogen carbonate ($NaHCO_3$)
    reagent grade; Fluka
20. Diethyl ether
    reagent grade; J.T. Baker Inc.
21. Tergitol NP-9
    Union Carbide Thailand limited

Apparatus and Instrument

1. Apparatus for determining the Iodine Value (I.V.) of the oil,
    - 2-4 ml glass weighing scoops
    - 250 ml wide-necked glass bottles, which ground-glass stoppers
    - 50 ml burette, graduated in 0.1 ml

- stand and clamp for supporting burette.

2. Apparatus for determining the epoxy-group content of the epoxidized soybean oil methyl ester

    - 250 ml conical flask
    - 25 ml burette,graduated in 0.05 ml
    - stand and clamp for supporting burette.

3. Fourier-Transform NMR Spectrometer
   Bruker, model AC-F 200
4. Gas Chromatography-Mass Spectrometer (GC-MS)
   Fison Instruments, model Trio 2000 Equipped with a 8000 series GC
5. Fourier Transform Infrared Spectrometer (FTIR)
   Perkin-Elmer, model 1760 X
6. Universal testing machine
   model Instron 4302
7. Viscosity apparatus
   Hochler Instrument Co.,Inc., model K-234 A
8. Pour Point Apparatus
   HAAKE, model A82
9. Colorimeter
   Fisher, ASTM D1500
10. Flash point tester
    Herzog, ASTM D92
11. Scanning Electron Microscopy (SEM)
    model JSM 35CF

Procedure

1. Esterification of the Soybean oil fatty acids (SOFA)

Soybean oil fatty acids (278 g) was placed into a 2 litre round bottom flask. Methanol (320 g) and concentrated sulfuric acid (16 g, 5 % by weight of alcohol) were added. Then, the reaction flask was fitted with a condenser, stirred by a magnetic bar. The mixture was heated to 50° C for 2 hours. Then, it was poured into the separatory funnel to separate oil from methanol. The excess acid was washed out from the oil by 5 % sodium hydrogen carbonate solution. The product was called soybean oil methyl ester (SOME).

2. Preparation of peracetic acid solution and epoxidation of SOME [23-24]

A well stirred mixture of 46.7 ml of glacial acetic acid and 53.3 ml of 30 % hydrogen peroxide (mole ratio = 1:1) was heated at 60°C, for 4 hours and left overnight at room temperature. This solution is quite stable and may be stored for several week at 5°C without appreciable reduction in the peracetic acid content. SOME (20 g) was mixed with peracetic acid solution and maintained at 20°C or lower for about 4 hours with stirring. The solution was poured into cold water. The oil was separated and dissolved in ether. The ether solution was washed with water (3 x 100 ml), dried over anhydrous sodium sulfate, and filtered. Ether was evaporated and yielded red oil. In order to approach the appreciate epoxide yield content, the synthesized condition were varied as follow ;

- The mole ratio of the glacial acetic acid and hydrogen peroxide
- The temparature for generating peracetic acid
- The amount of peracetic acid solution per 20 g of SOME

The effect of $AcOH:H_2O_2$ mole ratio, peracetic acid generating temperature and the amount of peracetic acid solution per SOME were studied under condition which were shown in Table 3.1. The product was called epoxidized soybean oil methyl ester (ESME).

Table 3.1 The various operating conditions for the ESMEs preparing.

Parameters studied	$AcOH:H_2O_2$ mole ratio	Temperature (°C)	Amount of peracetic acid solution per 20 g of SOME (ml)
$AcOH:H_2O_2$ mole ratio	1:1	60	100
	2:1	60	100
	4:1	60	100
	5:1	60	100
	6:1	60	100
	8:1	60	100
	10:1	60	100
Temperature (°C)	5:1	30	100
	5:1	40	100
	5:1	50	100
	5:1	60	100
	5:1	80	100
	5:1	100	100
Amount of peracetic acid solution per 20 g of SOME (ml)	5:1	60	50
	5:1	60	75
	5:1	60	100
	5:1	60	125
	5:1	60	150

To find the optimum condition, the following parameters were determined : conversion, iodine value, and epoxy content.

2.1 Conversions

The conversions were determined by C^{13}-NMR method. From the C^{13}-NMR spectrum of SOME and synthesized ESMEs which were shown in Figures A3 and A10-A25, it could be seen the signals of methyl ester ($O\text{-}CH_3$) at 51.2 ppm and olefinic carbons ($C{=}C$) at the interval 123.8-132.3 ppm. Owing to olefinic carbons are the reactive site for the epoxidation reaction, therefore the peak area ratio of olefinic carbons and methyl ester signals should indicate the % conversion of the reaction as the following equation.

$$\chi = \left(1 - \frac{A_p}{A_s} \right) \times 100$$

where χ is the conversion of the reaction
A_p is the peak area ratio of the product (ESME)
A_s is the peak area ratio of the starting material (SOME)

2.2 Iodine Value (I.V.) [24]

Iodine Value (I.V.) of the SOFA and ESMEs were determined by IUPAC (Method II.D.7) procedure. The weight of fat to be taken varies according to its expected iodine value in the following way :

Iodine Value expected	Weight to be taken for test (g)
<5	3.00
5-20	1.00
21-50	0.40

continued

51-100	0.20
101-150	0.13
151-200	0.10

The appropriate quantity of fat was weighed to about 0.1 mg in the glass weighing scoop. The fat was dissolved by adding 15 ml of carbon tetrachloride into the bottle. Then the bottle was added exactly 25 ml of the Wijs reagent, inserted the stopper,shaked gently and leaved in the dark place for 1 hour.

At the end of this time, 20 ml of 100 g/l potassium iodide solution and 150 ml of water were added. The mixture was then titrated with 0.1 N sodium thiosulfate solution using 10 g/l of starch solution as indicator.

The iodine value (I.V.) is given by the formula.

$$\text{I.V.} = \frac{12.69 \times T \times (V_1 - V_2)}{m}$$

where V_1 is the number of ml of the standardized sodium thiosulfate solution for blank

V_2 is the number of ml of the standardized sodium thiosulfate solution for test portion

T is the exact normality of the sodium thiosulfate solution used

m is the mass, in g, of the test portion

2.3 Epoxy-Group Content [24]

The epoxy-group content of the ESMEs was determine by IUPAC (Method II.D.20) procedure. The fat (0.3-0.5 g) was into a 250 ml conical flask , and then 10 ml of benzene was added with stirring by magnetic bar.

Consequently, not more than 0.1 ml of the indicator solution (crystal violet 1 g/l in acetic acid) was added. The reaction flask was equipped with a stopper and a burette in such a manner that the tip of the burette was just touched the surface of the solution (in order to avoid loss of hydrogen bromide). The reaction mixture was stirred and titrated with the hydrogen bromide acetic solution until a bluish-green colour persists for 30 seconds (control the speed of the stirrer so as to avoid splashing.

The percentage (t) of epoxy-group oxygen in the fat is given by the formula :

$$t = \frac{1.60 \times V \times T}{m}$$

Where V is the number of millitre of the standardized hydrogen bromide acetic acid solution used for titration,

T is the the exact normality of the hydrogen bromide acetic acid solution used,

m is the mass in gram of the test portion.

3. Preparation of Sulfonated soybean oil methyl esters (SSME)

The ESME (20 g) was placed in a 250 ml three-necked round bottom flask, which was fitted with a condenser, a dropping funnel and a thermometer. Subsequently, the saturated aqueous solution of sodium bisulfite (20 g) was added gradually and maintained at 90 ° C for 24 hours, with stirring. The reaction mixture was allowed to cool to room temperature, and then the oil layer (SSME) was separated and dried with andhydrous sodium sulfate. The characteristics of SSME was determined by ^{13}C-NMR and IR.

The same reaction was repeated with addition of nonionic surfactant (tergitol NP-9, 1 g). The abbreviation name of this product was SSME+5 % NP-9.

4. Hydrolysis of ESME

ESME (2 g) was hydrolyzed by sodium hydroxide solution (2 g in 50 ml water) in a 250 ml round bottom flask fitting with a condenser. The reaction mixture was heated at 90 °C for 6 hours, after which was cooled to ambient temperature, and poured into a separatory funnel. The excess base was neutralysed with the hydrochloric solution, and then extracted by diethyl ether (2 x 25 ml). The ether extract was washed with water, dried over anhydrous sodium sulfate, and filtered. The filtrate was evaporated. The characteristic of hydrolyzed ESME was determined by ^{13}C-NMR.

5. Commercial sulfonated oil (CSO)

Commercial sulfonated oil was made by oxidative sulfitation of the fish oil in the presence of cobalt naphthenate. The fish oil (800 g) and cobalt naphthenate (1 g) were placed in a 2 litre of flsk which was equipped with an inlet tube. The reaction mixture was stirred vigorously and heated to 60°C with bubbling air through therein. The reaction temperature was maintained at 60°C for 6 hours. Then 40 g of tergitol NP-9 was added and followed by adding the saturated aqueous solution of sodium metabisulfite (100 g) gradually to the reaction mixture at 90°C. The stirring was continued until the reaction mixture was clear. Finally, the pH of the product was adjusted to about 7.0 by 50% aqueous solution of sodium hydroxide.

In this study, the soybean oil methyl ester was also changed to sulfonated product by commercial procedure in order to compare the lubrication capability of the leather with the product which was synthesized by epoxide pathway. The abbreviation name of the sulfonated soybean oil methyl ester by this procedure was SSME*.

6. Fatliquoring process

Before the fatliquor was introduced into the fibers of leathers, the hides had been taken into several steps of the process for changing them to leathers as shown in Figure 3.1. In the step of fatliquoring process, the incorporation of fatliquor into the leather was done by putting the cow wet blue leather (100 g) in a rotating drum and performed the following steps :

Operation	%	Addition	Control
Wash	200	water at 35°C	
	0.5	ALCHEM CSA[a]	
	0.3	formic acid	30 min., pH 3.6
Drain & new float	200	water at 35°C	
	2.5	NA 113[a]	60 min., pH 7.0
Drain & wash	200	water	10 min.
Drain & new float	200	water at 35°C	
	12	faliquor[b]	60 min.
	1	formic acid	30 min., pH 3.6
Drain & wash	200	water	10 min.
Hang to dry			

[a] auxiliary agents (Trade name)

[b] synthesize in the laboratory

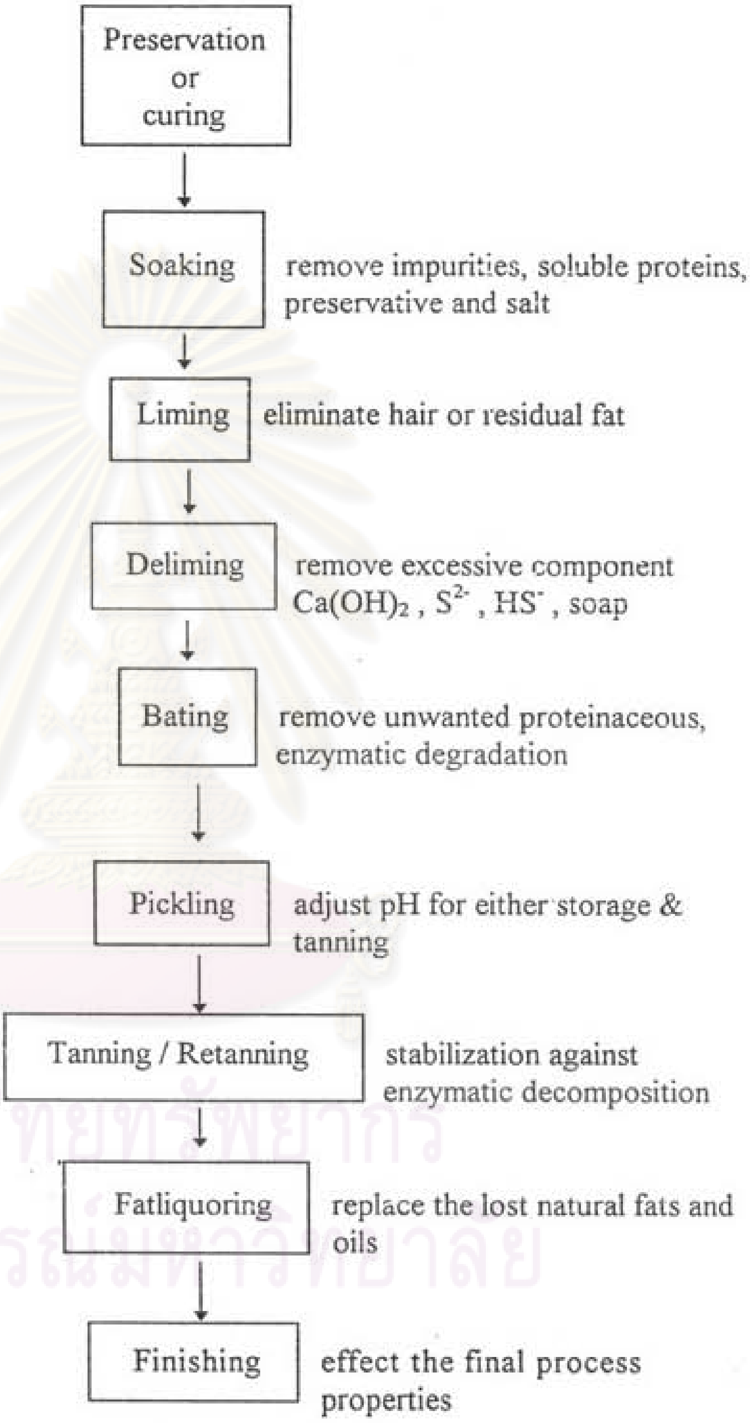


Figure 3.1 The overall process of leather production

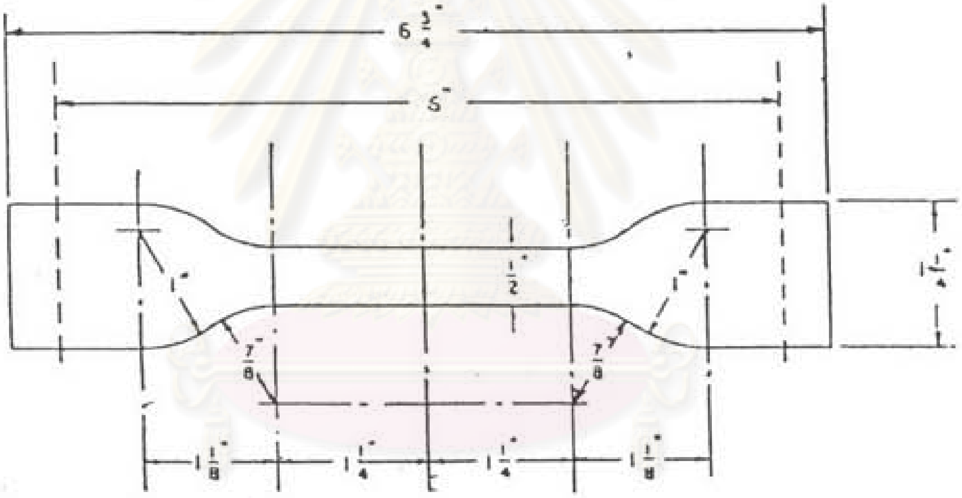
Faliquors used in this study were SSME, SSME+5 % NP-9, SSME* and CSO were used in the fatliquoring formulation. Therefore, each fatliquor was incorporated into the leather as described above.

7. Mechanical testing

Mechanical properties of unfatliquored and fatliquored cow leather were measured by the following ASTM test methods as follows :

ASTM D2209-90 Standard test method for tensile strength of leather

ASTM D2211-64 Standard test method for elongation of leather



in.	mm.	in.	mm.
1/2	12.7	1 1/4	31.8
7/8	22	6	152
1	25.4	6 3/4	171
1 1/8	28.6		

Figure 3.2 Schematic of tensile strength and elongation of test specimen

<u>Conditions</u>

Temperature : 23.0 °C

Relative humidity : 50.0 %

Speed of testing : 10.0 in/min.

Gage length : 63.6 mm

Distance between grips : 102±3.2 mm