



## Synthesis of Fatliquor from Palm Oil and Hydroxyl-Terminated Organosilicon

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Leather making processes usually require the addition of fatliquoring agents to separate the leather fibers from each other for promoting leather hand feeling and softness. The fatliquoring agents are mainly chemically modified products of animal and vegetable oils. In terms of the fatty acid components, palm oil is suitable as a raw material for fatliquoring agent preparation. Organosilicon has been increasingly used in leather making process due to its excellent properties. In this paper, an organosilicon modified palm oil fatliquoring agent was synthesized by 4 step processes *i.e.*, amidation with diethanolamine, grafting with low molecular weight hydroxy-terminated silicone oil, esterification with maleic anhydride and sulfonation with sodium bisulfite. The molar ratio of reactants, reaction temperature and time on conversion rate of diethanolamine in amidation were explored. In grafting action, esterification and sulfonation, the influence of the mass percentage of reactants on the emulsion stability and fatliquoring properties of the final product was explored. Simultaneously, the reaction temperature and time on conversion rate of hydroxy-terminated silicone oil in grafting action and maleic anhydride in esterification were investigated. The FT-IR spectra analyses showed that under optimal conditions the goal resultants were obtained. The route of synthesis and the best conditions of preparing organosilicon modified palm oil fatliquor were determined.

**Key Words:** Palm oil, Organic silicon, Fatliquor, Leather.

### INTRODUCTION

In leather making processes transformation of hide and skin into leather requires several chemical and mechanical steps to remove noncollagenous matter in pretanning operation. In the tanning operation, the purified matrix is tanned by chrome tanning agents, vegetable tannins, or syntans. In order to produce soft leather, after tanning the leather is processed through a fatliquoring step, which is designed to introduce oils and fats into the leather matrix preventing the adhesion of fibers. Fatliquoring is one of the critical step for garment and upholstery leather manufacturing, which makes the leather soft and has a pleasant feel. The physical characteristics of the leather, as well as comfort properties of the leather, depend on fatliquoring<sup>1</sup>. The term fatliquoring agents, which are used for bringing oils and fats into the leather-fiber network, are emulsifying mixtures<sup>2,3</sup>. Emulsification of fatliquoring agent is usually achieved by introduction of phosphate, sulfonate and sulfite groups, *etc.*, into the structure of oils and fats or by addition of surfactants to the composition of fatliquoring agent.

Although any oil or fat can be used as raw material for producing fatliquoring agent, the most commonly used oils and fats are those of neatsfoot oil, cod oil, sperm oil, castor oil, coconut oil, rapeseed oil and palm oil, *etc.*<sup>4-6</sup>. These have a

similar basic chemical structure consisting of triglycerides. Palm oil is the most economical vegetable oil in the world oils market, for yield of the oil palm fruit and oil are the highest as compared to other oil plants<sup>7</sup>. Palm oil has become an important raw material for cosmetics, personal care products, pharmaceutical and industrial areas<sup>8,9</sup>. Palm oil contains a high proportion of palmitic acid as well as considerable quantities of oleic acid and linoleic acid which give it a higher unsaturated fatty acid content<sup>10-13</sup>. The fatty acid component of palm oil proves it suitable for use as raw material for synthetic fatliquoring agent<sup>14</sup>.

Organosilicon is the compound containing the silicon-oxygen bond (-Si-O-Si-), the intermolecular forces of organosilicon are much weaker than that of hydrocarbons. Due to the characteristics of relatively nontoxic, special flexibility, weather resistance and chemical inertness, *etc.* organosilicon is widely used in manufacturing of leather chemicals.

This paper described preparation of organosilicon modified fatliquoring agent based on hydroxyl-terminated organosilicon and palm oil, which has been seldom reported. First the palm oil was amidated with diethanolamine and the amidated compound was then grafted with hydroxyl-terminated organosilicon and then maleic anhydride and sodium bisulfite as hydrophilic segments were added in turn to improve

the hydrophilicity of the fatliquoring agent. The influence factors of input ratio, reaction temperature and temperature, *etc.*, on conversion rate of reactants and the properties of the obtained fatliquoring agent were investigated in detail. The structure of the resultant was characterized by FT-IR and the properties the obtained fatliquoring agent were studied by application tests.

## EXPERIMENTAL

All reagents used in preparation of organosilicon modified fatliquor were commercially available and were used without further purification. Palm oil (average molecular weight was 840 g mol<sup>-1</sup>), food grade, was purchased from Yantai Tianmao Edible Oil Co., Ltd. (China). Hydroxy-terminated silicone oil (average molecular weight was 388 g mol<sup>-1</sup>), industrial grade, was obtained from Bluestar New Chemical Materials Co., Ltd. (China). Isopropyl alcohol, diethanolamine (EA), sodium methoxide, benzene, maleic anhydride and sodium bisulfite were analytical reagent grade, purchased from Nanjing Chemical Reagent Co., Ltd. (China). The chemicals used in fatliquoring application tests except the fatliquor were commercial products.

Fourier transform infrared (FT-IR) spectra of the resultants were recorded to determine the structure of the resultants by a Tensor 27 spectrophotometer (BRUKER OPTICS, Switzerland) using potassium bromide (KBr) discs prepared from powdered samples mixed with dry KBr at room temperature.

The Muffle furnace (SX-10-12, Shanghai Hongji Instrument LD., Ltd., China), vacuum drying oven (PH-240A, Cany precision instruments Co., Ltd., China) and the high speed centrifuge (GT10-2, Beijing Medical Centrifuge Factory, China) were used to measure the content of SiO<sub>2</sub> in the resultant of hydroxyl-terminated silicone oil grafting reaction.

**Preparation of hydroxyl-terminated organosilicon modified palm oil fatliquoring agent:** 100g palm oil, desired amount of diethanolamine with 0.3 wt % sodium methoxide based on mass of palm oil as catalyst were charged into a 250 mL four-necked flask, equipped with a mechanical stirrer, a dropping funnel, a reflux condenser and a thermometer. The materials were refluxed with stirring at the reaction temperature for a certain time. After amidation, the suspension resulting was cooled to reaction temperature, then hydroxy-terminated silicone oil was added dropwise over 0.5 h and continued to react for various times. The grafting organosilicon reaction resultant was cooled to 50 °C, an appropriate amount of maleic anhydride was dissolved and the solution was stirred at 95 °C for 3.5 h. The resulting ester was cooled to 85 °C, sodium bisulfite solution was slowly added drop wise over *ca.* 1 h, then remained for 3 h.

The performance of the prepared fatliquoring agents under difference reaction conditions were studied through fatliquoring application tests on chrome tanned pig skins and goat skins according to the general processes of garment leather.

## RESULTS AND DISCUSSION

**Amidation of palm oil:** The course of the synthesis of alkanolamide by palm oil react with diethanolamine (EA) was followed by volumetric titration of the free diethanolamine

present in the reaction mixture. The changes of the conversion rate of diethanolamine was determined in a isopropanol medium using 0.1 mol L<sup>-1</sup> HCl solution as titrating agent and bromophenol blue as indicator. The percentage of conversion of diethanolamine was calculated from the following formula:

$$\% \text{ conversion}_t = (1 - V_t/V_0) \times 100 \%$$

where, V<sub>t</sub> was the volume (mL) of HCl of the sample at reaction time t, V<sub>0</sub> was the volume (mL) of HCl of the original unreacted sample. The effect of molar ratio and reaction temperature on conversion rate of diethanolamine was shown in Fig. 1.

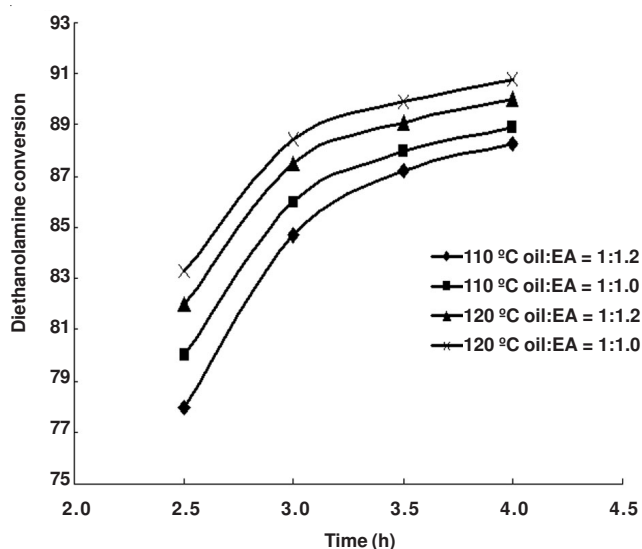


Fig. 1. Time-conversion curves of diethanolamine

As shown in Fig. 1, molar ratio and reaction temperature greatly affected the conversion rate of diethanolamine. When the molar ratio of palm oil to diethanolamine remained on 1.0:1.0 and 1.0:1.2, respectively, the conversion rate of diethanolamine increased with the reaction temperature was increased from 110 to 120 °C. Besides, the conversion of diethanolamine has been found to be affected by the input amount of diethanolamine. At the same reaction temperature and time, the transferring percentage of diethanolamine diminished as increasing the input amount of diethanolamine.

The results of laboratory experiments showed that the molar ratio of palm oil and diethanolamine was 1.0:1.2, the reaction temperature was 120 °C and the reaction time was 3.5 h, the conversion rate of diethanolamine was 89 %. The infrared spectrum analysis proved the alkanolamide was synthesized under the optimization reaction conditions. The sample of amidation resultant was washed with saturation salt aqueous solution and dried for the infrared spectrum analysis. The FT-IR spectra of palm oil and amidation resultant have been compared in Fig. 2.

The spectral line 1 was the palm oil and the spectral line 2 was amidation resultant in the Fig. 2. The FT-IR spectrum of the optimization amidation resultant displayed characteristic absorption of the hydroxyl group at about 3300 cm<sup>-1</sup> and absorption of the C-N band at 1126 cm<sup>-1</sup>. By condensation reaction with the hydroxyl which was introduced by amidation the hydroxyl-terminated silicone oil could be grafted onto the molecular of fatty alkanolamide.

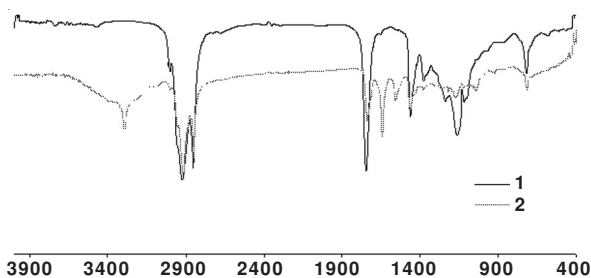


Fig. 2. FT-IR spectrum of palm oil and amidation product; 1 FT-IR spectrum of palm oil, 2 FT-IR spectrum of amidation product

### Grafting reaction of hydroxyl-terminated silicone oil:

The effects of reaction temperature and time were studied by measuring silicon content of the resultant. The sample was washed carefully with deionized water and then desiccated with vacuum drying oven. The dried sample was dissolved in benzene, the unreacted hydroxyl-terminated silicone oil was separated by centrifugal separation (45 min with 4000 revolutions per min). The silicon content of the resultant sample was analyzed by oxidizing roasting method. The percentage of conversion of hydroxyl-terminated silicone oil was calculated from the following formula:

$$\% \text{ Conversion} = (\text{g/G}) \times 100$$

where, g was SiO<sub>2</sub> weight of the sample, G was SiO<sub>2</sub> theoretical weight of the sample.

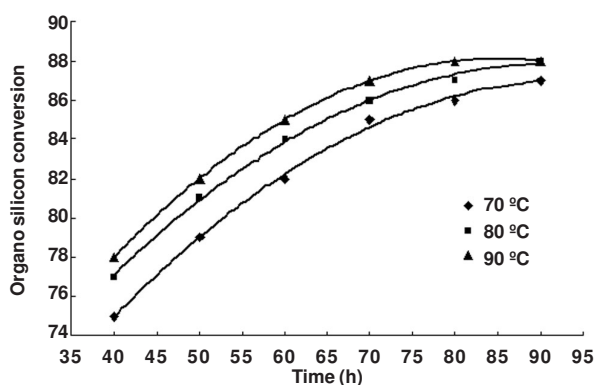


Fig. 3. Time-conversion curves of organosilicon.

The effect of reaction temperature and time on conversion rate of hydroxyl-terminated silicone oil was shown in Fig. 3. The conversion of hydroxyl-terminated silicone oil was increase with the increase of reaction temperature and holding time and increase more quickly with the reaction temperature. When reaction temperature was 70 °C, the conversion reached 87 % after reacting 1.5 h. When reaction temperature was 80 °C, the conversion reached 88 % after reacting 1.5 h. When reaction temperature was 90 °C, the conversion reached 88 % after reacting 80 min. The best reaction temperature was 80-90 °C and time was 1.5 h.

The emulsion stability of the final product and the hand feelings of the fatliquored leather were main parameters for investigated the amount of hydroxyl-terminated silicone oil in grafting organosilicon reaction. The effect on the amount of hydroxyl-terminated silicone oil was qualitatively tested by emulsion stability and hand feeling experiments. The results were shown in Table-1. The fatliquor emulsion was stable when the mass ratio of hydroxyl-terminated silicone oil was lower

than 15 % and with good acid and alkali resistant. But the stability of fatliquor emulsion became deteriorative when the mass ratio of hydroxy-terminated silicone oil was 20 %. The performances of final products were tested by fatliquoring application experiments. Hand feeling and softness of the fatliquored leather were contrasted. The performances were better when the mass ratio of hydroxy-terminated silicone oil was 15 % than it was 10 %. According to the results of qualitative experiments, the mass ratio of hydroxy-terminated silicone oil to palm oil was determined between 10-15 %.

TABLE-1  
EFFECTS OF THE MOUNT OF HYDROXYL SILICONE

Test parameter	Hydroxyl silicone dosage (g per 100 g palm oil)			
	10	15	20	
Emulsion stability (after 24 h)	1:9 dilution	Stable	Stable	Floating oil
	1:4 dilution	Stable	Stable	Floating oil
	1:2 dilution	Stable	Stable	Stratified
	Acid resistant (1 mol L <sup>-1</sup> hydrochloric acid aqueous)	Stable	Stable	Stratified
	Alkali resistant (1 mol L <sup>-1</sup> ammonia water)	Stable	Stable	Stratified
Fatliquoring performance	Hand feeling of leather	Moderate	Good	-
	Softness of leather	Moderate	Good	-

**Esterification of maleic anhydride:** In esterification reaction the esterification rate of maleic anhydride was used as major factor for determining reaction time. The esterification rate of maleic anhydride was analyzed by measuring the acid value and saponification value of the reaction mixture. The esterification rate of maleic anhydride at 85 and 100 °C was shown in Fig. 4. In this study the esterification did not use catalyst, the main resultant of esterification was maleic monoester. When reaction temperature was 85 °C the esterification rate of maleic anhydride was 44 % after reacting 4 h. When reaction temperature was 100 °C the esterification reaction reached equilibrium after reacting 3.5 h. Therefore, reaction temperature and reaction time can be determined at 100 °C and for 3.5 h, respectively.

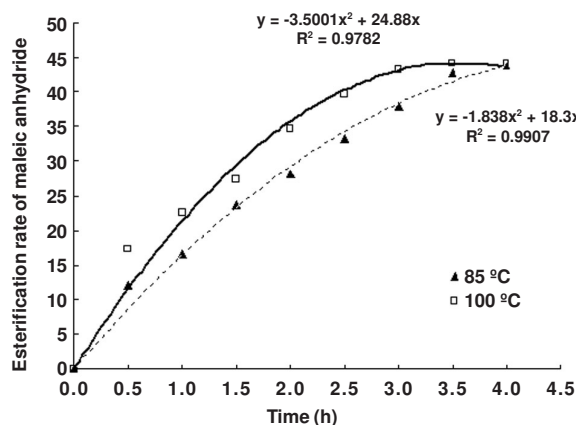


Fig. 4. Times-esterification rate of maleic anhydride

TABLE-2  
EFFECTS OF AMOUNT OF MALEIC ANHYDRIDE

Test parameter	Maleic anhydride dosage (g/100 g palm oil)			
	15	20	25	30
Esterification rate of maleic anhydride (%)	45.3	43.6	42.1	40.3
Emulsifying performance of final product	Emulsifiable	Emulsified lightly	Emulsified lightly	Emulsified lightly
Emulsion stability (1:9 dilution, after 24 h)	Floating oil	Stable	Stable	Stable

TABLE-3  
EFFECTS OF SODIUM BISULFITE DOSAGE ON PERFORMANCE OF FINAL PRODUCTS

Test parameter	Sodium bisulfite dosage (g/100 g palm oil)				
	15	20	25	30	35
Emulsifying performance of final product	Emulsified difficulty	Emulsifiable	Emulsified lightly	Emulsified lightly	Emulsified lightly
Emulsion stability (1:9 dilution, after 24 h)	Stratified	Stable	Stable	Stable	Stable
The absorption (exhaustion) of fatliquoring	-	Very goods	Good	Medium	Moderate

Table-2 showed the results on maleic anhydride amount affecting the final product emulsion stability under the optimum reaction temperature and time. With maleic anhydride mass rate increasing, the esterification ratio of maleic anhydride decreased gradually, but the emulsion stability of the fatliqor was improved. When the maleic anhydride mass ratio was 20 %, the emulsion stability of the fatliqor met the requirement of fatliqor emulsified.

**Sulfonation of sodium bisulfite:** Sulfonation is a common approach for improving the emulsifying property and uptake amount of fatliqor. The investigation of sodium bisulfite amount was shown in Table-3. It proved that the amount of sodium bisulfite could significantly change emulsifying property and uptake amount of fatliqor. With the amount of sodium bisulfite increasing the fatliqor emulsion became stable but uptake amount was decrease. The emulsion stability and uptake amount of fatliqor should be considered synthetically while the sodium bisulfite amount was determined. Among the experimental parameters in the Table-3, it could be known that the emulsion stability and uptake amount of the fatliqor could be meet operation requirement when the sodium bisulfite amount was 20-25 g/100 g palm oil.

silicone oil was grafted onto the molecular of amidation resultant. The spectral line 2 was the optimization resultant of esterification. Contrasted with line 1, the absorption peak of -OH at  $3309\text{ cm}^{-1}$  decreased obviously. The strong absorption at  $1741\text{ cm}^{-1}$  and  $1645\text{ cm}^{-1}$  belonged to C=O group of ester and C=C group of maleate, respectively. The FT-IR spectrum implied the maleic anhydride reacted with the grafting organosilicon resultant. The spectral line 3 was the optimization resultant of sulfonate. The absorption bands at  $1188\text{ cm}^{-1}$  and  $1051\text{ cm}^{-1}$  belonged to  $\nu_{\text{as}}\text{SO}_3$  and  $\nu_{\text{s}}\text{SO}_3$  of  $-\text{SO}_3^-$  group, respectively. And the absorption peak of C=C group of maleate at  $1645\text{ cm}^{-1}$  decreased obviously. These implied that  $-\text{SO}_3^-$  was grafted onto the molecular of the final product.

## Conclusion

The novel method of synthesis hydroxy-terminated silicone oil modified palm oil fatliqor was investigated. The effects of molar ratio of palm oil and diethanolmine, reaction temperature and reaction time on diethanolmine conversion rate were studied. Under the optimum reaction conditions, the conversion rate of diethanolmine was 89 %. The effects of reaction temperature and time on hydroxyl-terminated silicone oil conversion rate were studied. Under the optimum reaction conditions, the conversion rate of hydroxyl-terminated silicone oil could reach 88 %. The amount of hydroxy-terminated silicone oil was determined by emulsion stability and hand feeling experiments. The mass ratio of hydroxy-terminated silicone oil to palm oil was 10-15 %, the emulsion of final product was stable, the fatliqored leather had excellent hand feeling and softness. The esterification rate and amount of maleic anhydride were studied. Under the optimum reaction temperature and time, when the mass rate was 20 %, the esterification rate of maleic anhydride was more than 43 %. The amount of sodium bisulfite on emulsifying property and uptake amount of the final product was investigated. The sodium bisulfite amount was determined 20-25 g/100 g palm oil according to the test results.

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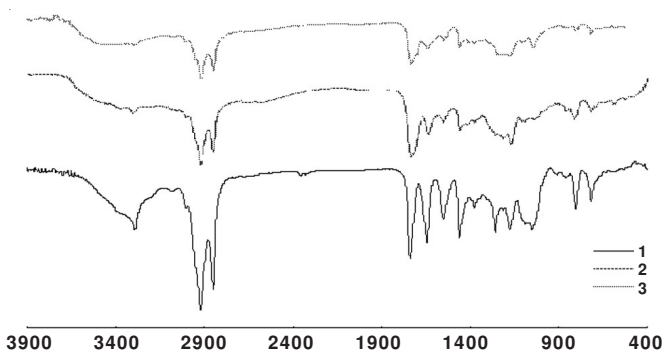


Fig. 5. FT-IR spectrum of reaction resultants, 1 Grafting organosilicon on resultant, 2 Esterification resultant, 3 Sulfonation resultant

The FT-IR spectrum of the optimization resultants of graft organosilicon, esterification and sulfonation reaction were shown in Fig. 5. The spectral line 1 was the optimization resultant of graft organosilicon, showed characteristic absorption at  $1261\text{ cm}^{-1}$  corresponding to Si-O-Si group,  $1100\text{ cm}^{-1}$  corresponding to Si-O-C group and  $808\text{ cm}^{-1}$  corresponding to the Si-C band<sup>15</sup>. The FT-IR spectrum showed the hydroxy-terminated

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