

PREPARATION OF ORGANOSILICONE MODIFIED PALM OIL FATLIQUOR

by

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ABSTRACT

Fatliquoring is an important process in leather manufacture and these fatliquors are mainly chemical modification products of animal and vegetable oils. Palm oil, owing to its main characteristics and fatty acid composition is suitable as a raw material for fatliquor preparation. And organosilicone is increasingly used for leather production due to its excellent properties. In this paper, the organosilicone modified palm oil fatliquor was synthesized by amidation with diethanolamine, grafting with hydroxyl-terminated organosilicone, esterification with maleic anhydride and sulfiting with sodium bisulfite, in turn. The influence of the mass percentage of diethanolamine, hydroxyl silicone, maleic anhydride and sodium bisulfite on the emulsion stability and fatliquoring properties were explored; the reaction temperature and time were also studied. The FT-IR spectra analyses showed that the organosilicone chain segment was incorporated into the fatliquor molecule. The route of synthesis and the best conditions of preparing organosilicone modified palm oil fatliquor were determined. The result of applied experiments showed that this new type of fatliquor had excellent emulsion and dispersion characteristics, and the resultant leather was flexible and full.

RESUMEN

El engrase es un importante proceso en la fabricación del cuero y tales engrases son productos obtenidos principalmente por modificaciones químicas de aceites de origen animal o vegetal. Aceite de Palma [africana] debido a sus características primarias y composición de ácidos grasos es muy apropiado como materia prima para la preparación de engrases. Organosiliconas se utilizan cada vez más en la producción del cuero por sus excelentes propiedades. En este trabajo [se reportó] que el engrase resultante de la modificación del aceite de palma por síntesis por medio de amidación con dietanolamina, luego injertando una órgano-silicona terminando en un grupo hidroxílico, y esterificando con anhidromaleico y eventualmente sulfitando con bisulfito sódico. La influencia del porcentaje por masa de dietanolamina, hidroxisilicona, anhídrido-maleico y bisulfito de sodio sobre la estabilidad resultante de la emulsión y sus propiedades engrasantes fueron investigadas; el tiempo y temperatura de reacción también fueron estudiadas. Los análisis espectroscópicos por FT-IR demostraron que el segmento de la cadena conteniendo el silicio orgánico fue incorporado a la molécula del engrasante. La ruta de la síntesis y las condiciones óptimas en la preparación de engrases basados en aceite de palma modificado para contener silicona orgánica se determinaron. El resultado experimental de aplicación demostró que este nuevo tipo de engrasante tuvo excelentes características de emulsionabilidad y dispersión y que el cuero resultante es flexible y redondo.

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INTRODUCTION

Fatliquoring is one of the critical steps for garment and upholstery leather manufacturing, which makes the leather soft and imparts a pleasant feel. The physical characteristics of the leather such as break, extensibility and tensile strength, as well as comfort properties of the leather, depend on fatliquoring. The term fatliquors are used for the incorporation of oils and fats into the leather matrix in finely dispersed form of an emulsion. This is usually achieved by emulsification processes through the introduction of phosphate, sulfonate, and sulfite groups into the structure of oils and fats or by addition of surfactants to the composition of fatliquors.

A lot of research on fatliquors has been reported.¹⁻⁵ Oils and fats commonly used for fatliquoring operation in the leather production are neatsfoot oil, cod oil, sperm oil, castor oil, coconut oil, rapeseed oil, palm oil and wool grease. 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, and as well as the price advantage of palm oil.⁶ Palm oil has become a more and more important raw material for chemical industry. Now, China is the largest importer of palm oil, and the palm oil consumption would continue to increase along with economic development of China.^{7,8} Study on the main characteristics and the fatty acid composition of palm oil indicates that palm oil is suitable for preparing fatliquor.⁹⁻¹³

Organosilicone products, due to the obvious advantages of special flexibility, low surface energy, weather resistance, chemical inertness, and low glass transition temperature have a diversity of applications in leather chemical material preparations of fatliquor, finishing agent and functional auxiliaries.¹⁴⁻¹⁶ At present, organosilicone modified fatliquor is usually used as fatliquoring material for greatly improving the performance of leather.^{17,18} All of these silicon-modified fatliquors showed excellent properties such as the lower surface tension, special flexibility and chemical inertness. Meanwhile, the structure of palm oil contains 48%-52% unsaturated fat of total fat acids. Therefore, palm oil is better suitable as a raw material for preparing modified fatliquor. So, the objective of this study was to prepare modified fatliquor based on hydroxyl-terminated organosilicone and palm oil, which has been rarely reported on.

EXPERIMENTAL

Methods and Procedures

Materials

All reagents were commercially available and were used without further purification. Palm oil, food grade, average molecular weight was $840 \text{ g}\cdot\text{mol}^{-1}$, was purchased from Yantai Tianmao Edible Oil Co., Ltd.(China). Hydroxyl-terminated

silicone oil, industrial grade, average molecular weight was $388 \text{ g}\cdot\text{mol}^{-1}$, was obtained from Bluestar New Chemical Materials Co., Ltd.(China). Isopropyl alcohol, diethanolamine, sodium methoxide, maleic anhydride, and sodium bisulfite were analytical reagent grade, purchased from Nanjing Chemical Reagent Co., Ltd. (China).

Preparation of Silicone Modified Fatliquor

The preparation reaction was carried out in 250-mL flasks with mechanical stirrer, reflux condenser, dropping funnel and thermometer. The procedure for the preparation of organosilicone modified palm oil fatliquor was as follows: 100g palm oil was mixed with the desired amount of diethanolamine in the presence of sodium methoxide as the catalyst, the system was refluxed with stirring at the reaction temperature for a certain time. After amidation reaction, the suspension resulting was cooled to 85°C , different amounts of hydroxy-terminated silicone oil was added dropwise via a dropping funnel over a period of 30 minutes and continued to stir for a certain time. Then the above reaction mixture was cooled to 50°C , an appropriate amount of maleic anhydride was dissolved while stirring, and heated gradually to the reaction temperature when maleic anhydride dissolved, the solution was stirred for 210 minutes to finish the reaction. The resultant of esterification was cooled to 85°C , sodium bisulfite solution was sluggishly added drop by drop for approximately 60 minutes, then continued to react for 180 minutes at the same temperature with stirring. Finally, appropriate solids-content of obtained fatliquor was adjusted by adding water. The resulting mixture was the desired organosilicone modified palm oil fatliquor.

Fourier Transform Infrared Spectra

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.

Fatliquoring Processes

The crust leather used for fatliquoring processes were wet chrome tanned pigskins and goatskins, and the chemicals used for the processing were commercial grade except the fatliquor. The wet blue skins were washed in a drum with running water at 35°C for 10 minutes. Then the skins were retanned with 3% chrome retanning agent with 100% float at 35°C for 120 minutes. After the retanning was finished the skins were washed with running water at 35°C for 10 minutes. Next the retanned skins were neutralized completely to pH 6.0-6.5 by addition of sodium bicarbonate to a 150% float at 35°C . The neutralized skins were washed with 300% float at 40°C for 20 minutes and then drained. The neutralized skins were dyed and fatliquored with organosilicone modified palm oil fatliquor simultaneously. The fatliquor used was 12% of the

pickled weight. During dyeing and fatliquoring, the temperature was maintained at 40°C, and the float was 100%. After 60 minutes of dyeing and fatliquoring, the bath was fixed to pH 3.0-3.5 by addition of formic acid. The fatliquored skins were washed with running water at room temperature, and then dried.

RESULTS AND DISCUSSION

Amidation Reaction of Palm Oil with Diethanolamine

The free diethanolamine present in the reaction mixture was determined by volumetric titration. The sample was quenched to stop the reaction and dissolved in isopropanol in a 100-mL Erlenmeyer flask, then, bromophenol blue as indicator was added to the flask. The sample was titrated with a 0.1 mol·L⁻¹ HCl in isopropanol to a yellow end point. The percentage of conversion of diethanolamine was calculated from the following formula:

$$\%conversion_t = (1 - V_t/V_0) \times 100\%$$

where, V_t was the volume (mL) of HCl used in the titration of the sample at reaction time t , V_0 was the volume (mL) of HCl used in the titration of the original unreacted sample. Throughout this particular investigation, the molar ratio of palm oil to diethanolamine was fixed at 1.0:1.0 and 1.0:1.2, respectively. Concurrently, reaction temperature was 110°C and 120°C, respectively. The effect of molar ratio and reaction temperature on conversion rate of diethanolamine is shown in Figure 1.

Figure 1 graphically illustrated the relationship between conversion rate of diethanolamine and input ratio during reaction time at varying temperature with fixed catalyzer concentration. The curves were very similar to each other in behavior, except the conversions of different reaction conditions. When reaction time was prolonged, the conversion

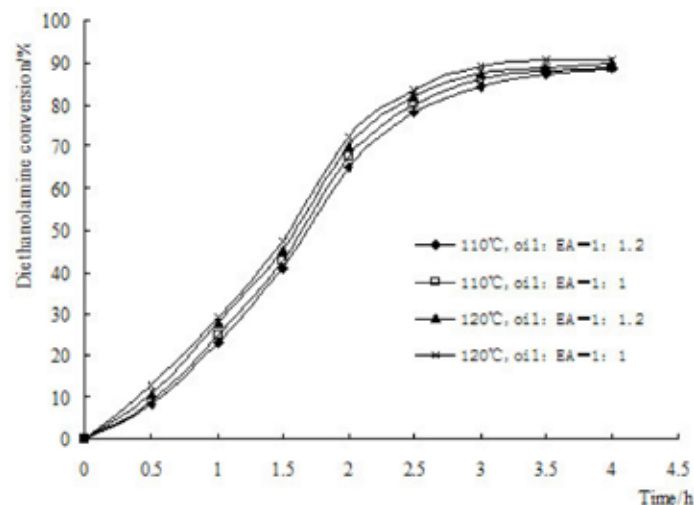


Figure 1. Time-conversion curves of diethanolamine.

rate of diethanolamine increased markedly; amidation reaction approached equilibrium at 180 minutes. An increase in temperature results in an increased conversion rate of diethanolamine; conversion rate enhancement was detected when the reaction temperature was increased from 110°C to 120°C with fixed input ratio after 180 minutes of reaction. However, increasing the input ratio of diethanolamine tended to diminish the conversion at the same reaction temperature and time.

The amido group of fatty alkanolamide which was the resultant of amidation reaction was capable of cross-linking with collagen through the formation of hydrogen bonds, and able to complex with trivalent chromium ions, which enhance the combination of the obtained fatliquor. More importantly, the hydroxyl of the fatty alkanolamide introduced by diethanolamine was reactive group grafting with hydroxyl-terminated silicone oil. In order to obtain satisfactory conversion rate of diethanolamine and hydroxyl content of amidation resultant, the synthesis process parameters can be optimized as a molar ratio between palm oil and diethanolamine of 1.0:1.2, a reaction temperature of 120°C, and a reaction time of 180 minutes.

In order to verify the structure of the optimization resultant of amidation, the FT-IR spectra of palm oil and amidation resultant have been compared. The FT-IR spectrum of the palm oil was shown in Figure 2. The bands located at about 3008cm⁻¹, 2929cm⁻¹ and 2854cm⁻¹ were attributed to the C-H stretching vibration. Following these signals, there was a strong band at about 1747cm⁻¹ corresponding to the C=O stretching vibration of the carboxylic group; the band located at about 1463cm⁻¹ was due to the C-H bending vibration, the band located at about 1172cm⁻¹ represented the C-O stretching vibration; and the shoulder signal at 725cm⁻¹ was attributed to the (CH₂)_n skeleton vibration. The FT-IR spectrum of the optimization resultant of amidation was shown in Figure 3, which provided a different picture. The Figure 3 displayed characteristic absorption at about 3300cm⁻¹ corresponding to the hydroxyl group stretching vibration; absorption at about 1643cm⁻¹ corresponding to the C=O stretching vibration of the amido group; and absorption at 1126cm⁻¹ corresponding to the C-N stretching band. Compared to Figure 2, the C=O absorption band at about 1741cm⁻¹ became smaller in Figure 3. These indicated that the alkanolamide was synthesised by the progress of the amidation reaction between palm oil and diethanolamine at the optimum reaction conditions.

Graft Organosilicone onto Amidation Resultant

Since Si-O bond was partially ionic, chemical reactivity of the silanol group (Si-OH) is stronger than the alcoholic hydroxyl(C-OH). The Si-O bonds can be easily cleaved by strong acids or with strong bases, so hydroxy-terminated silicone oil was reactive to the intermolecular condensation between hydroxyl groups with amidation resultant containing

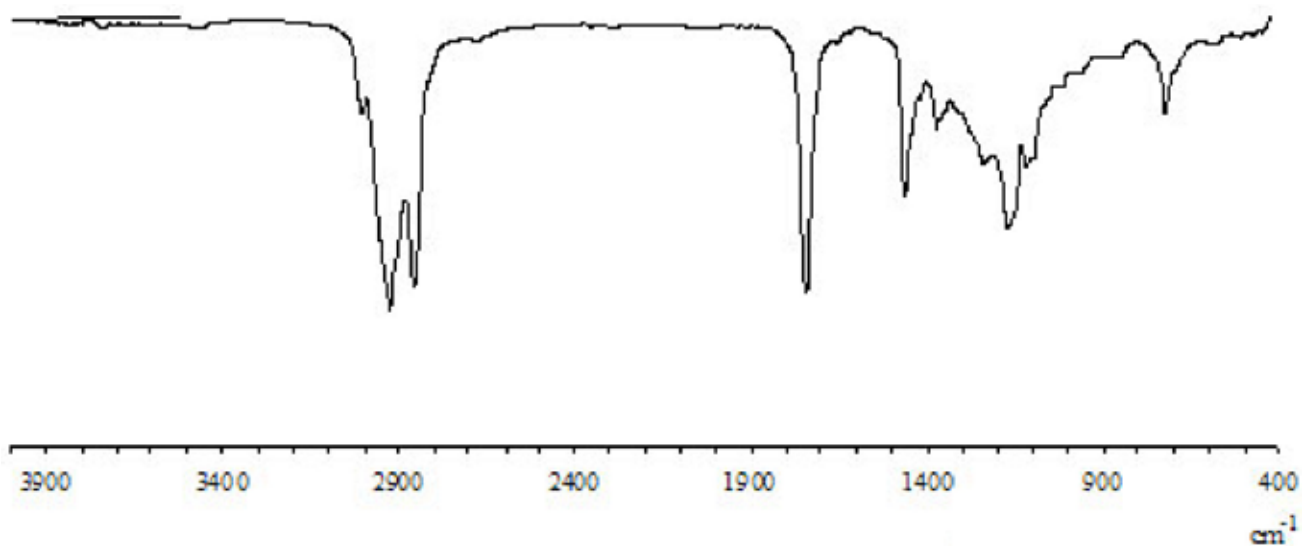


Figure 2. FT-IR spectrum of palm oil.

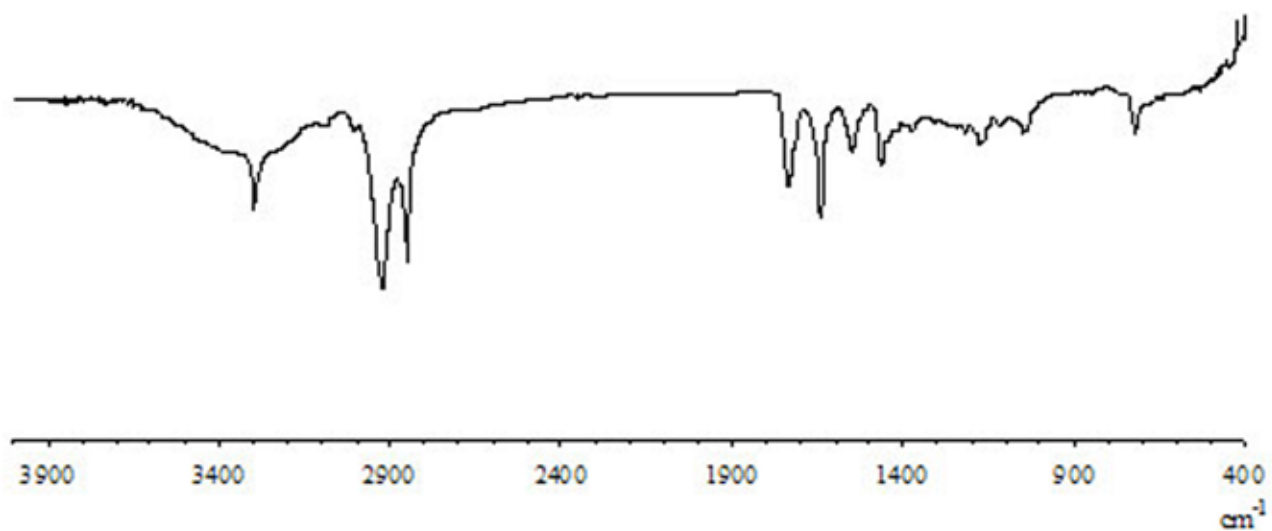


Figure 3. FT-IR spectrum of amidation product.

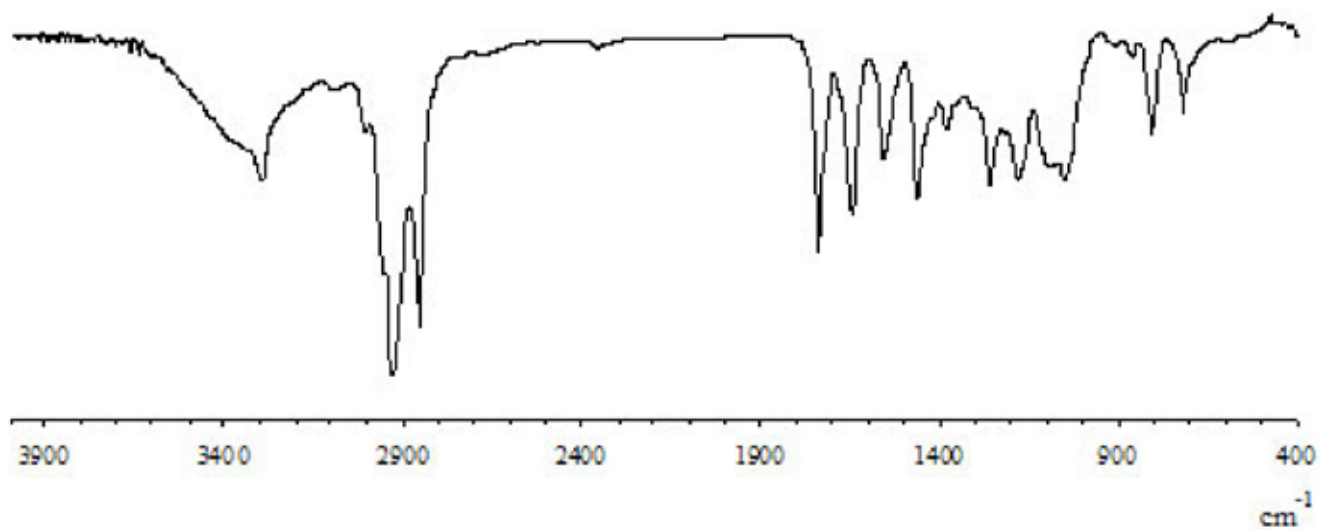


Figure 4. FT-IR spectrum of hydroxyl silicone modified product.

free hydroxyl. Terminal hydroxyl groups provide reactive sites that allow the organosilicone segment to attach to the modification resultant of palm oil via Si-O-C band. In order to prevent self-condensation, hydroxy-terminated silicone oil was added drop by drop over time.

The silicone content in the fatliquor had obvious effects on both properties of the fatliquor and the cost of production. It can be seen that the flexibility of the fatliquor increased with the amount of silicone in fatliquor, but self-emulsifying capacity of the fatliquor got worse and the cost of production increased with an increasing in the content of the silicon. The influence of the dosage of hydroxy-terminated silicone oil on the emulsion stability of the fatliquor and the hand feelings of the fatliquored leather were investigated. The results were shown in Table 1.

Emulsion stability and fatliquoring application on pigskins and goatskins garment leather of the final products of different dosage of hydroxy-terminated silicone oil, 10%, 15% and 20%(mass ratio of hydroxy-terminated silicone oil to palm oil) were tested.

In Table 1, it was found that the fatliquor emulsion was stable, and with good acid and alkali resistance, when the mass ratio of hydroxy-terminated silicone oil was lower than 15%. The stability of fatliquor emulsion decreased when the mass ratio of hydroxy-terminated silicone oil was 20%. The results of fatliquoring application experiments showed that the fatliquored leather possessed a slippery feel and excellent softness when the mass ratio of hydroxy-terminated silicone oil was 15%, and performance of the fatliquored leather was poor when the mass ratio of hydroxy-terminated silicone oil was 10%. According to the results of emulsion stability and fatliquoring application experiments, the mass ratio of hydroxy-terminated silicone oil to palm oil to was determined between 10-15%.

The FT-IR spectrum of the optimization resultant of graft organosilicone was shown in Figure 4. The FT-IR spectra showed characteristic absorption at 1261cm^{-1} corresponding to Si-O-Si group(Si-O bending vibration); following this signal, there was a shoulder signal at 1100cm^{-1} corresponding to Si-O-C group(Si-O stretching band), and the band located at about 808cm^{-1} corresponding to the Si-C stretching vibration. It can be observed from the FT-IR spectrum that the hydroxy-terminated silicone oil has been successfully grafted with the amidation resultant of the palm oil (due to the reaction between -OH groups of the reactants) under the optimized reactions conditions.

Esterification with Maleic Anhydride

The esterification of the grafting organosilicone resultant with maleic anhydride was performed for increasing the fatliquor emulsion capability. The esterification rate of maleic

TABLE 1

Effects of Hydroxyl Silicone Dosage on Emulsion Stability and Fatliquoring Performance of Final Products

Emulsion stability (after 24 hours) and fatliquoring performance	Hydroxyl silicone dosage (g/100g palm oil)		
	10	15	20
1: 9 dilution	Stable	Stable	Floating oil
1: 4 dilution	Stable	Stable	Floating oil
1: 2 dilution	Stable	Stable	Stratified
Acid resistant			
($1\text{mol}\cdot\text{L}^{-1}$ hydrochloric acid aqueous)	Stable	Stable	Stratified
Alkali resistant			
($1\text{mol}\cdot\text{L}^{-1}$ ammonia water)	Stable	Stable	Stratified
Oil feeling (hands) of leather	Moderate	Good	—
Softness of leather	Moderate	Good	—

anhydride was determined by measuring the acid value and saponification value of the reaction mixture. Sample (0.5-1.0g) was taken from the reaction mixture of esterification reaction and dissolved in 50mL 95% alcohol in a 250-mL Erlenmeyer flask. Titration was carried out using 0.1M NaOH standard solution as titrant, and phenolphthalein alcohol solution (1% wt) as indicator. First, the sample was titrated to red, while red can keep 30 seconds, the consumption volume of NaOH solution was recorded as $V_1\text{mL}$. Second, added $V_1\text{mL}$ of NaOH solution into the sample and reflux condensed for 2 hours at 80°C . Then the hot sample was titrated until red just disappeared by 0.1M HCl standard solution; the consumption volume of HCl solution was recorded as $V_2\text{mL}$. The esterification rate of maleic anhydride was calculated from the following formula:

$$R\% = \frac{V_1 - V_2 \times \frac{C_2}{C_1}}{V_1 + \left(V_1 - V_2 \times \frac{C_2}{C_1} \right)} \times 100\%$$

where, R was esterification rate of maleic anhydride, V_1 was the volume (mL) of NaOH standard solution, V_2 was the volume (mL) of standard HCl solution, C_1 was the molar concentration of standard NaOH solution, C_2 was the molar concentration of HCl standard solution, $V_1 - V_2 \times \frac{C_2}{C_1}$ was ester content of the sample.

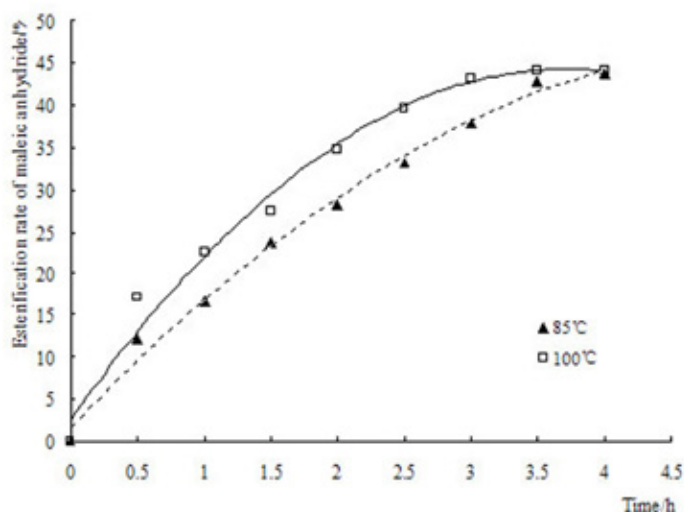


Figure 5. Time-esterification rate of maleic anhydride

Without catalyst, the main esterification resultant of maleic anhydride was monoester, so the highest esterification rate of maleic anhydride was 50%. The calculation of esterification rate of maleic anhydride at different temperatures was shown in Figure 5. It can be seen from the experimental data that the esterification reaction between maleic anhydride and grafting organosilicone resultant occurred. When reaction temperature was 85°C, the esterification was slow and the esterification rate of maleic anhydride was 44% after 240 minutes. When reaction temperature was 100°C, the esterification was accelerated, and the esterification reaction reached equilibrium basically after 210 minutes. Therefore, reaction temperature can be determined at 100°C, and reaction time for 210 minutes. The emulsion stability of the final product with different maleic anhydride dose under the optimum reaction temperature and time was studied, with the results shown in Table 2. The emulsion aspect was classified according to Table 2; with the increase of maleic anhydride dose, the esterification rate of maleic anhydride decreased gradually, but the emulsion stability of the final product was improved. When the maleic anhydride dose was 20%, the emulsion stability of the final product can meet the requirement of emulsified fatliquor.

The FT-IR absorption spectrum of the optimization resultant of esterification was shown in Figure 6. After esterification reaction, the absorption peak of stretching vibration of $-OH(3309\text{cm}^{-1})$ decreased obviously, and the absorption peak of maleic anhydride at 1850cm^{-1} and 1781cm^{-1} disappeared. Additionally, strong absorption bands appearing at 1741cm^{-1} and 1645cm^{-1} belonged to $C=O$ group of ester and $C=C$ group of maleate, respectively. These implied that an esterification happened between maleic anhydride and the grafting organosilicone resultant, while carboxylic acid group and active carbon-carbon double bond were introduced into esterification resultant.

Preparation of Sodium Sulphonated Ester

To meet the emulsification requirement of fatliquoring operation on fatliquor, the resultant of esterification with maleic anhydride should be sulfonated to improve the emulsifying properties of the final product. The reaction generally takes place between sodium bisulfite and carbon-carbon double bond, which conjugated with carbonyl in maleic acid monoester, is a nucleophilic addition reaction. With the formation of monoester, the uniform distribution of π electrons was destroyed, so the α -carbon connected with free carboxyl had more positive charge. While the sulfur atom of nucleophilic reagent NaHSO_3 had a lone electron pair, the nucleophilic addition reaction was prone to be taken between both reactants if the attack of the SO_3^{2-} anions at the α -C atom of the ethylene bond. As the result of electron attracting effect of $-\text{COOR}$ group, addition of sulfonic group mainly takes place on the more positively charged carbon atom; the reaction mechanism was similar to the Michael addition.

Sulfonation could improve the emulsifying properties of the final product and uptake of fatliquor; the emulsifying properties of final products and uptake of fatliquors of different sodium bisulfite content were shown in Table 3. As can be seen from Table 3, when the amount of sodium bisulfite was enough for all the maleic acid monoester to be sulfonated, the final product was easy to emulsify but there was less uptake of fatliquor in application test. If the amount of sodium bisulfite was 15g, the sulfonate rate of maleic acid monoester was less than 40%, the emulsion capability could not meet the

TABLE 2

Effects of Maleic Anhydride Dosage on Emulsion Stability of Final Products

Maleic anhydride dosage (g/100g 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 hours)	Floating oil	Stable	Stable	Stable

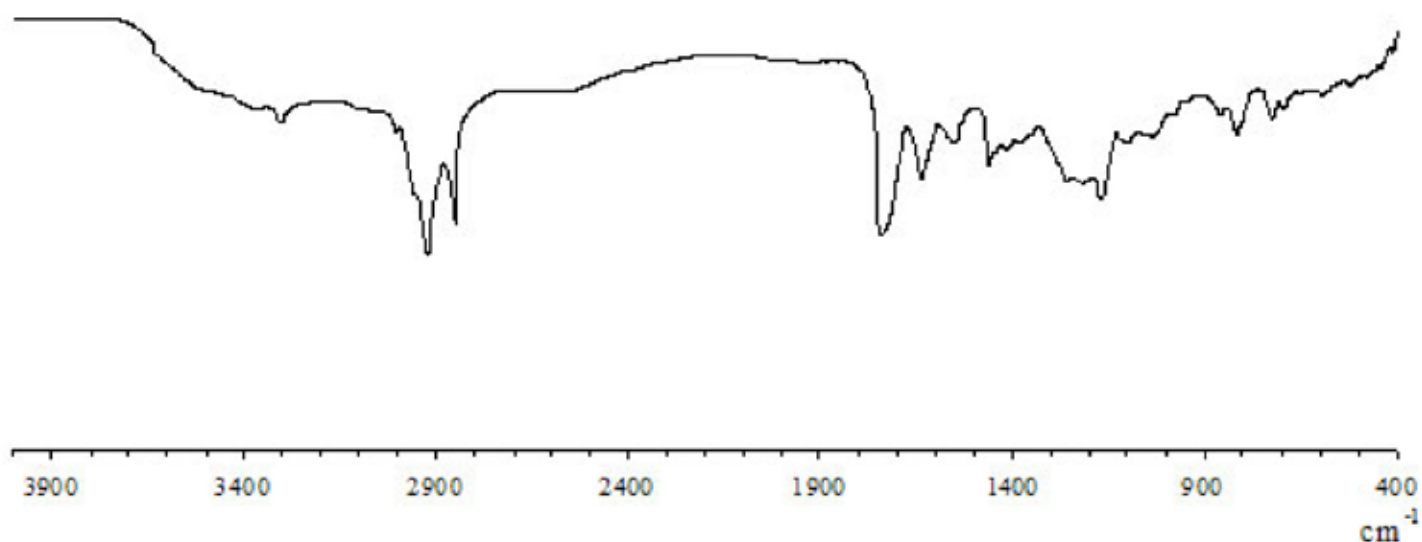


Figure 6. FT-IR spectrum of maleic anhydride esterification product.

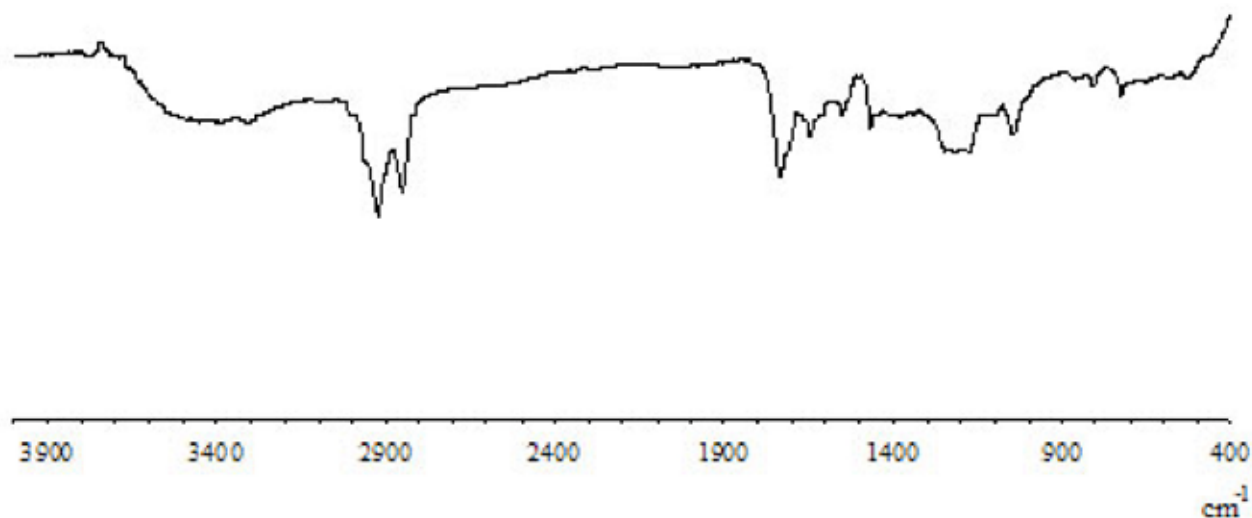


Figure 7. FT-IR spectrum of sulfited reaction product.

TABLE 3

Effects of Sodium Bisulfite Dosage on Performance of Final Products

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

TABLE 4

**Physical and Chemical Properties
of Organic Silicone Modified
Palm Oil Fatliquoring**

Properties	Performance
Appearance	Yellowish color paste
Solid-content(%)	≥60
Electrical of active ingredient	Anion
pH(1: 9 dilution)	6.5-7.5
Emulsion stability (1: 9 dilution)	>24 hours
Acid resistance	Good
Salt resistance	Good

requirement. By comprehensively surveying the emulsion stability of final product and uptake of fatliquor in fatliquoring operation, the sodium bisulfite amount was determined at 20-25g per 100g palm oil, so the sulfonate rate of maleic acid monoester was about 70%.

The FT-IR absorption spectra of the optimization resultant of sulfonate is shown in Figure 7. After sulfonation reaction, the absorption bands appeared at 1188cm^{-1} and 1051cm^{-1} belonged to $\nu_{\text{as}}\text{SO}_3$ and $\nu_{\text{s}}\text{SO}_3$ of $-\text{SO}_3^-$ group, respectively. Additionally, the absorption peak of C=C group of maleate (1645cm^{-1}) decreased obviously. These implied that $-\text{SO}_3^-$ was grafted onto the C=C group of maleate by addition reaction. After adding water to adjust solids content, organic silicon (hydroxy-terminated silicone oil) modified palm oil fatliquor was prepared; quality indicators of the final product was shown in Table 4.

Application Test of Fatliquoring

In accordance with general fatliquoring technology of pigskin suede garment leather and goatskin garment leather, the final resultant of optimization synthesis condition, the organic silicon modified palm oil fatliquor, was tested. Application results are shown in Table 5.

The results showed that the prepared organic silicon modified palm oil fatliquor agent has good permeability, high combined oil in leather, little fatliquor agent residue in the fatliquoring liquor, and excellent fatliquoring properties which meet the requirements of garment leather.

CONCLUSIONS

Synthetic procedures of organic silicon modified palm oil fatliquor were investigated and were found to be a more

TABLE 5

**Fatliquoring Properties of Organic
Silicone Modified Palm Oil Fatliquoring**

Fatliquoring properties	Performance		
	Good	Very good	Very good
The absorption (exhaustion) of fatliquoring	Good	Very good	Very good
Waste liquor	Muddy	Clear	Clear
Oil feeling (hands) of leather	Poor	Good	Greasy
Softness of leather	Medium	Good	Moderate

efficient method for obtaining fatliquor with excellent properties. Although silicon-containing fatliquor has been applied for a long time, the present results confirmed a new method for synthesis of hydroxy-terminated silicone oil modified palm oil fatliquor.

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