Characterization and Properties of Organic Silicon Modified Amphoteric Fatliquor

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Abstract: The Amphoteric Fatliquor (AF) was prepared by rapeseed oil, 1, 2-ethylenediamine and acrylic acid. An amphoteric fatliquor (SAF) modified with silicon was synthesized by using AF and polyether silicon with stirring and ultrasonic treatment. AF and SAF were measured by Fourier Transform Infrared Spectroscopy (FT-IR), thermogravimetry (TGA), emulsifying capacity, emulsification stability and emulsifying surface tension respectively. The analysis of FT-IR and TG indicated that hydroxy of polyether silicon was polycondensation with carboxylic hyd roxy of AF. The results indicated that the performance of AF could be improved by polyether silicon. The emulsifying surface tension of SAF decreased by 17.0 N/m, compared to 18.2 N/m of AF. SAF was applied in leather fatliquoring process, and was compared with product XQ-F3. The application results indicated that emulsification capacity of SAF was the same as XQ-F3, and the flexibility of SAF was higher than that of XQ-F3. The analysis of fatliquor waste liquid indicated that the absorbing capacity of SAF on leather was better than that of AF.

Keywords: fatliquor; amphoteric; silicon

1 Introduction

Recently, many researchers have paid much attention on the exceptional performance of organic silicon materials [1-3]. Study on organic silicon modified leather chemical has become a hotspot. Organosilicon compounds with lower surface tension and better hydrophobic, can give leather the capability of waterproof, improve the wearable resistance, softness and smoothness of leather [4-6].

Fatliquor is a largest amount of leather-chemistry materials in leather industry, and has extremely important impact on the performance of leather [1-2]. It can penetrate to the collagen fibers, making the leather lubricant and plastic. The fatliquor can make the molecular chain segment easily move, give the leather softness, waterproof, sunproof, moisture and flexibility. There are more than 200 kinds of species of fatliquors, but the amphoteric fatliquors with outstanding performance are few. Amphoteric fatliquors have good emulsifying effect within a wide range of pH values, and can be used with anionic, cationic, nonionic fatliquors. At the same time, amphoteric fatliquors have the capabilities of low toxicity, good biodegradability, excellent resistance to hard water and high concentrations of electrolyte, outstanding softness and smoothness and antistatic properties.

Rapeseed oil is widely used in industry besides direct consumption. Generally, rapeseed oil has a wide range of utility such as machinery, rubber, chemicals, plastics, paints, textiles, soap and medicine. Modified rapeseed oil fatliquor is mainly used in leather application. Through chemical modification methods, introduction of hydrophilic groups to the rapeseed oil molecules, to make it self-emulsification. As the result of lower price of rapeseed oil, in recent years, there are much more researches on the leather fatliquor with modified rapeseed oil [7-8].The typical preparation method of such fatliquor is that making the rapeseed oil and monoethanolamine to amidation reaction, and then esterification with maleic anhydride, finally sulfonation reaction with sulfite. There are lots of reports on the research of such kind

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of composite Fatliquor [9-10]. Jiang Hua et al [8] carried transesterification by using the rapeseed oil and methanol, and grafted them with organic silicon monomer (D4), finally got the silicon-modified rapeseed oil leather fatliquor by further sulfating. The emulsion of fatliquor is stable, contains a variety of activity base, combines well with leather, and has good capability of waterproof at the same time.

In this paper, the amphoteric fatliquor (AF) was prepared by using cheaper rapeseed oil and diethyl amine, then introduction of –COOH through acrylic acid. The organic silicon modified fatliquor (SAF) was prepared by using polyether silicon modified AF fatliquor.

2 Experiment part

2.1 Materials

Rapeseed oil (industrial) was purchased from Nanzheng Country of Hanzhong City, Tiantian Cereals and oil Co, Ltd. Acrylic acid, Aluminiym oxide and Sodium bisulfite used were of analytical grade, which were obtained from Tianjin Chemical Reagent Six Plant. Ethylenediamine was purchased from North Tianjin Fine Chemical Company Ltd. Polyether organic silicon used was of industrial grade, which was obtained from GE Company.

2.2 Preparation of amphoteric fatliquor (AF)

The rapeseed oil, ethylenediamine and Al_2O_3 were added into 250ml flasks with 3- necked round-bottom. After reaction for certain time at constant temperature, added acrylic acid to system. The mixture was stirred and kept reaction at 60℃ for 5h. Cooled to certain temperature, added saturated sodium bisulfate solution slowly, kept a few time. The pH value was adjusted by using ammonia till the appearance of the reaction was light yellow paste body, adjusted the system concentration using H_2O. The amphoteric fatliquor was obtained.

2.3 Preparation of organic silicon modified fatliquor (SAF)

The reaction was carried out in a three-necked round-bottom flask equipped with stirred and condenser. Amphoteric fatliquor and a certain amount of polyether organic silicone oil were added in flask. The system was stirred by a blender. The mixture was then treated with ultrasound for 20 min. Silicone modified amphoteric fatliquor(SAF) was obtained.

2.4 Application of fatliquor

SAF was applied to the process of goatskin garment leather fatliquoring, comparing with the application performance of industrial XQ-F3 amphoteric fatliquor, the process as follows in table 1.

Tab. 1 Fatliquor process of goatskin garniture

Process	Material	Amount	Temperature	Time	pH value	Remarks
Weight based on the goat blue skin，add 150％as calculation basement						
Weting-back	H_2O DSP-1	300％ 1.5％	Normal	30min		
Fatliquoring	H_2O fatliquor	200% 14%	50℃	60min	6.5±	The fatliquor was emulsified by hotwater at rate of1：4 before adding
Fixing	Formic acid	1.2％	50℃		4.0±	Diluting formicacid by water at the rate of 1：10，adding it for three times
After pH values arriving to 4.0±，wash 15min and take them out of drum						

2.5 Characterization and Measurement

AF and SAF were washed by ethanol and acetone several times respectively. Fourier transform infrared (FTIR) analysis was performed using a FTS-65A Fourier transform infrared spectrometer. Spectra were obtained from powders. Thermogravimetric analyses were carried out using a DSC600 apparatus. The samples were heated from 30 to 1200℃ at a scanning rate of 10℃/min under nitrogen. The microstructure of nanocomposite was observed using transmission electron microscope (TEM) (Japan JEM—10OCXII). The scanning ranges of TEM were X/Y 30×30 mm in the level direction and Z5 μm in the vertical direction.

3 Results and Discussion

3.1 The purification of AF and SAF

Tab. 2 Dissolve capability of reaction material

	Ethanol	Acetone
Acrylic acid	Soluble	Soluble
Ethylenediamine	Soluble	Soluble
Sodium bisulfate	Insoluble	Soluble
Alumina	Insoluble	Soluble
Ammonia	Soluble	Soluble
Rapeseed oil	Soluble	Insoluble
Silicone	Soluble	Soluble

Table 2 shows the solubility of the raw materials which exist in ethanol and acetone in the experiment process. Seen from the table 1, the fatliquor was washed by using ethanol and acetone in the experiment, the unreaction monomer of fatliquor was moved effectively.

2.2 FI-IR analysis

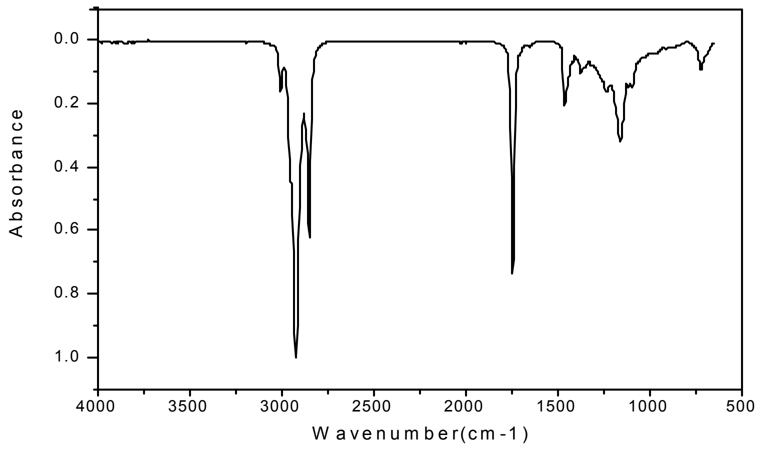


Fig. 1 FT-IR pattern of rapeseed oil

The spectrum of rapeseed oil is showed in Figure 1, 3008cm^{-1} is the stretching vibration peak of =C-H, . 2926 cm-1and 2855cm-1 are the stretching vibration of peak of C-H. The strong peak at 1665 cm-1 correspond to stretching vibration of C=C. The peak at 1746cm-1 causes from C=O stretching vibration.

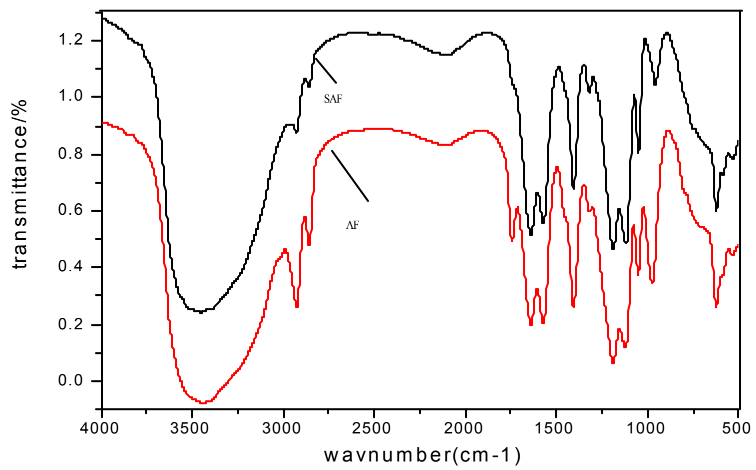


Fig. 2 FT-IR pattern of AF and SAF

Figure 2 shows the FT-IR pattern of AF and SAF comparing with the infrared spectra of rapeseed oil (Figure 1), the wide peak at 3330cm^{-1} correspond to stretching vibration peak of N-H. The strong peak at 1743cm^{-1} is the absorption peak of -C=O from carboxyl. The strong peak at 1690cm^{-1} is the absorption peak of –C=O from amine bond. The strong absorption peak at 1641cm^{-1} is the absorption peak of $–NH_2$. The peak at 2927cm^{-1} and 2856cm^{-1} were corresponding to the symmetric and asymmetric stretching vibration absorption peak of C-H of alkyl chain. The absorption peak at 1190cm^{-1} is the stretching absorption peak of C-N from amide.The absorption peak at 1122cm^{-1} is the absorption peak of C-N from $–CH_2NHCH_2$.

Seen from Ft-IR pattern of SAF, the peak at 3400cm^{-1} is attributed to stretching vibration absorption peak of Si-OH. The peak at 1100cm^{-1} is attributed to absorption peak of Si-O-C. The peak at 1080cm^{-1} is attributed to absorption peak of Si-O-Si. All these peaks are related to coincidence with the peaks of amphoteric fatliquor. Compared with the FT-IR of amphoteric fatliquor, after the amphoteric fatliquor was modified by using polyether silicone, the strong peak at 1743cm^{-1} which is the absorption of –C=O from carboxyl is disappeared. Because of the reaction happened between the –COOH of amphoteric fatliquor and –OH of silicone.

2.3 The result and analysis of TGA-DTA-DSC

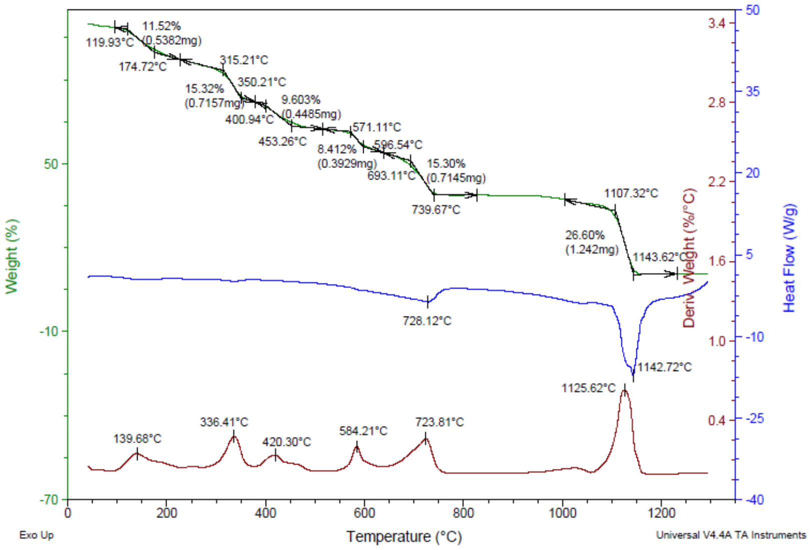


Fig.3 TGA curver of SAF

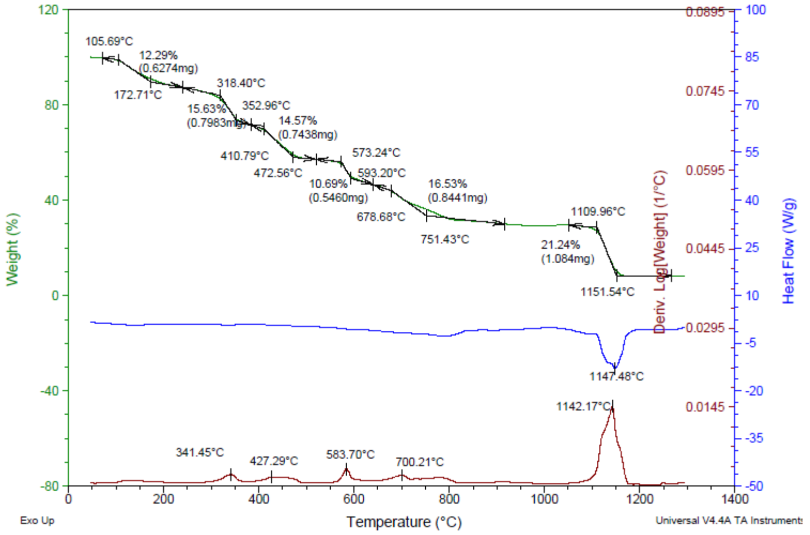


Fig. 4 TGA curver of AF

Tab. 3 TGA results of AF and SAF

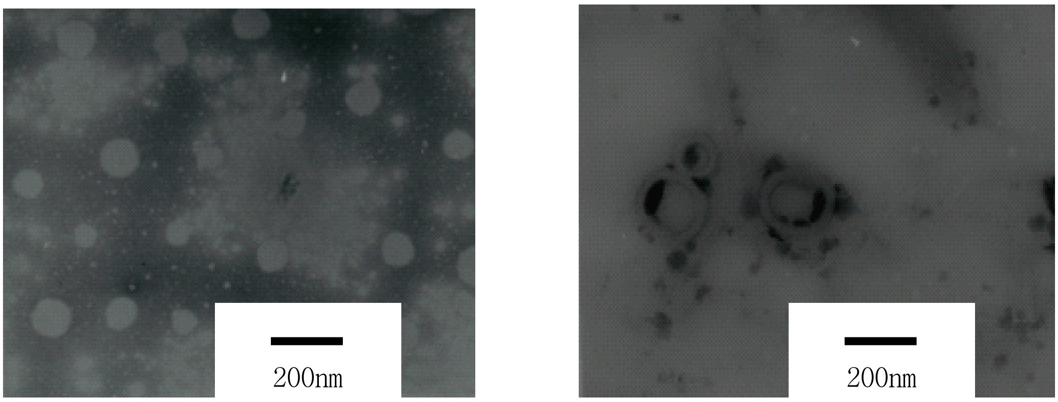
	AF	SAF
weightlessness（%）	90.95	86.75
0-200℃	12.29	11.52
200-1200℃	78.66	75.23

Figure 3, figure 4 and table 3 show the TGA results of SAF and AF. The weightlessness is apparent loss in weight before 120℃. The organic fragments of polymer chain begin to be decomposed after 120℃. Before 200℃, make the temperature of T (weightlessness is 10%) as the initial thermal decomposition temperature of polymer.

The first one of the largest thermal decomposition rate of organic silicone modified amphoteric fatliquor is corresponding to T_{max} which is 139.66℃. It is may be caused by the decomposition of silicone segment. Organic silicone in composite fatliquor caused the phase separation of polymer. It is caused by the segment gathering of silicon and oxygen. At different temperatures, the largest rate of thermal decomposition of which is corresponding to T_{max} changes. It is because Si-O chains of system increased, Si-O-Si belong to inorganic structure, the energy of Si-O chain is 462kJ/mol, which is much higher than the bond energy of C-C and C-O. Therefore they make an impact on the decomposition of organic segment.

Seen from table 3, after being modified by using organic silicone, the weightlessness of amphoteric fatliquor decreased from 78.66% to 75.23%. It may be due to the introduction of more silicone segment to complex fatliquor. The SiO2 which is generated after the silicone is thermal decomposed covered on the surface of copolymer. It seems to the layer of protective coating to prevent the internal organic matters from being oxidated and decomposed. It can also be thought that the flame-retardant properties of copolymer can be improved.

2.4 TEM analysis



a) AF **b) SAF**

Fig. 5 Transmission electron microscope (TEM) photographs

Figure 5 shows the TEM image of amphoteric fatliquor and silicone modified amphoteric fatliquor. Seen from figure 5a, the gray spherical particles is the emulsion of amphoteric fatliquor, particle size is 80~100nm. After being modified by organic silicone, the surface of emulsion particle is covered in a circle by silicone, and the diameter of particle increased by about 20nm.

Combination of TEM and FT-IR, results show that the amphoteric fatliquor is successfully modified by organic silicone. Combination of TEM and TGA results, silicone formed on the surface of a layer which is similar to protective layer to prevent the internal decomposition of organic matter.

2.4 Surface tension analysisi

Tab. 4 Physical and chemical results of AF and KRF

	AF	SAF

Surface tension of 1:4 dilution （Nm^{-1}）	18.2	17.0

As shown in table 4, the surface tension of amphoteric fatliquor is 18.2 Nm^{-1}. After AF modified by organic silicone, the surface tension is 17.0Nm^{-1}.It indicates that emulsion ability of SAF is easier than AF.

2.5 Analysis of application

Tab. 5 Results of leather sample's tensile strength and elongation

Product name	Tensile strength P/(N/mm^2)	Elongation at break （%）	Tear strength P/(N/mm)
SAF fatliquor	20.36	110.22	77.66
XQ-F3 amphoteric fatliquor	20.25	118.56	77.37

Tensile strength is the value of load the sample cross-section can bear when loaded by the axial load, and it is related with the leather sample state of collagen fiber bundles weaving, weaving point of view, loose, lubrication, fastness of bundles of collagen fibers. Therefore, the tensile strength can characterize the flexibility of fibers besides for the strength of collagen fibers.

Flexibility [9] is one of the most important properties of leather given from fatliquor. By the addition of fatliquor, covering a grease layer on the surface of leather fibers is in order to reduce friction between the fibers and make the purpose of soft leather. The softness of fibers given by fatliquor is mainly related to the nature of raw oil and the type and quantity of combination groups introduced at oil molecule. The elongation at break can characterize the softness, flexibility, strength and toughness of leather billet.

As shown in table 5, there are the mechanical property results of leather which are with the application by silicone-modified fatliquor and XQ-F3 amphoteric fatliquor respectively. The physical and mechanical properties of leather are equivalent when fatliquored by KRF fatliquor and XQ-F3 amphoteric fatliquor.

4 Conclusions

Amphoteric fatliquor was prepared by using rapeseed oil, diethylamine and acrylic acid. Organic silicone modified amphoteric fatliquor was prepared by using amphoteric fatliquor and polyether organic silicone. AF and SAF were characterized by FT-IR, TGA and TEM. The results show that the polyether silicone successfully modified the amphoteric fatliquor by the ultrasonic treatment. The polycondensation occurred between the surface hydroxyl of polyether silicone and the hydroxyl-carboxy of amphoteric fatliquor. Compared to AF, the surface tension of the SAF emulsion is decreased from 18.2Nm^{-1} to 17.0Nm^{-1}.The application results show that the physical mechanical properties of leather fatliquored by SAF is equivalent to the leather fatliquored by industrial XQ-F3 amphoteric fatliquor.

Acknowledgments

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