Synthesis and application of an polymer auxiliary with silicon

Synthesis and application of an polymer auxiliary with silicon

LUO Jianxun, FENG Yanjuan

（Department of Light Chemistry Engineering，College of Materials and Textile Engineering，Jiaxing University，Jiaxing 314001，China)

Abstract: In order to reduce the apparent density of the finished leather and the amount of fat-liquor during the production of leather-making, an polymer auxiliary with silicon is synthesized by radical co-polymerization of acrylic acid, meth-acrylic acid and polyvinyl silicone oil,etc. The polymers were applied to the re-tanning process of sheepskin. Comparing the viscosity and applied properties of the polymer auxiliary with silicon, the mol ratio of acrylic acid, meth-acrylic acid used was confirmed to be 0.5:0.2, the consumption of polyvinyl silicone oil, ammonium persulfate, the reactive temperature and time is 5%, 1.5%, 80-85°C, 120-180min, respectively. Infrared spectroscopy shows that the structure of the polymer auxiliary contains -Si-O- bond. The thickening rate, softness of the treated leather is 23.1%, 6.0 and the consumption of fat-liquoring agent after re-tanning can be reduced to 4%~8% when the optimum consumption of the an polymer auxiliary is 8%~10%, the retreated leather is fine, soft, hydrophobic and the apparent density is 0.457g/cm^3.

Keywords: Acrylic acid; meth-acrylic acid; Polyvinylsilicone oil; Apparent density; Thickening rate; softness

INTRODUCTION

Leather is one of important products originated from natural resources. Leather industry is one of good example of effectively utilizing natural resources and cutting carbon emission. Owning leather goods has always been the symbol of the owner’s status and position since ancient times because they have good appearance, handle and comfortable[1]. Therefore Leather goods have become one of important components of a better life pursued by the people.

During the process of leather-making, all processes play important roles in the quality of the finished leather. Chrome tannage has been dominant in the tanning field since its application because the chrome-tanned leather has good comprehensive properties[2]. But the shaved wet blue can become the finished leather by the subsequent re-tanning, dyeing and fat-liquoring process. The re-tanning process is one of important processes which can give the leather fullness, relative uniformity etc and is thought as golden touch in modern leather industry[3]. The fat-liquoring process is also one of important processes which can give the leather softness, silk touch, service performance etc. Fat-liquoring materials are the most critical materials in the fat-liquoring process. Traditional fat-liquoring materials include modifiers of natural animal oils, vegetable oils, mineral oils and compound fat-liquoring agents who can lubricate leather fibers and improve the performance of use[3]. But the fat-liquored leather can be easy to have the problem such as strange smell caused by oxidation, greasy spew, etc because the main components of animal oils and vegetable oils are stearic acid glyceride, oleic acid glyceride, erucic acid glyceride, etc. Therefore the quality of the finished leather is directly determined by the quality of fat-liquoring materials. In addition the consumption of fat-liquoring materials is so large that the density of the finished leather is larger than that of microfiber materials. Therefore an new material is needed which can not only have good re-tanning and fat-

liquoring properties and ensure the quality of the finished leather such as good softness, handle, smell or other properties, but also reduce the apparent density of the finished leather, the amount of fat-liquor during the production of leather-making.

However, there is limited research on this type of material. Li Zhengjun synthesized the polymer re-tanning agent WPT-S modified by silicone which can improve the waterproof properties, give the leather softness, silky touch and keep the hygienic property of the leather[4]. Wei Deqing, etc studied and produced FRT polymer series synthesized by meth-acrylic acid and its derivatives who have the re-tanning and fat-liquoring properties and reduce the consumption of the fat-liquoring agents to a certain extent[5]. But the properties of these polymer materials can't completely meet the needs.

The present work focuses on preparing an polymer auxiliary with silicon synthesized by the co-polymerization of acrylic acid, meth-acrylic acid and polyvinyl silicone oil,etc, which can effectively improve reduce the apparent density of the finished leather, the amount of fat-liquor during the production of leather-making. The synthesis, co-monomer ratio, the molecular weight, structure of the polymer auxiliary with silicon has been studied and the application properties are discussed.

EXPERIMENTAL

Materials

Methy-acrylic acid (MAc), Acrylic acid (MAc), sodium dodecyl benzene sulfonate, Peregal O, ammonium persulfate (APS), sodium hydroxide were chemically pure. Polyvinyl silicone oil (commercial grade, content of vinyl group is 22%), Chromium B, Chromopol UFB/W (commercial grade, Mixture of sulfated, sulfonated natural oil and synthetic fatliquor), PAK-N-c (Commercial grade, Mixture of organic salts) were obtained from Jiade polymer s.p.a, Brother S&T s,p.a, TFL (China) Ltd, respectively. TRUPOSOL BCN-60, TRUPONOL SWS were obtained from Trumpler s.p.a. The shaved sheepskin wet blue were purchased from Haining brother tannery, Zhejiang Province.

Preparation of the polymer auxiliary with silicon

The polymer auxiliary was synthesized by free radical copolymerization under the conditions listed in Tables I and II[6]. Firstly, the relevant methyl-acrylic acid, acrylic acid and water were weighed and the mixture in solution was neutralized with 30wt% sodium hydroxide solution. Secondly, the relevant ammonium persulfate solution was prepared. Thirdly, the copolymerization was performed in a stirred 500mL four-neck flask with two feed funnels and a thermometer. At the beginning, the relevant Polyvinyl silicone oil, sodium dodecyl benzene sulfonate, Peregal O were added into the flask, heated to 70°C and stirred for 30 minutes. Then a certain amount of water was added into it and stirred for 30 minutes. The ammonium persulfate solution and the monomer mixture were drip fed in. The rate of addition was controlled in order to be complete within 90 minutes. Then the temperature was regulated to 80-82°C and was kept constant for 180 minutes. At last the flask was cooled to 50°C, adjusted pH to 5.5 with 30wt% sodium hydroxide and formed the polymer auxiliary. The scheme of the reaction is described in Figure 1.

Table I Parameters of orthogonal experiment

Factor	Level 1	Level 2	Level 3
A/acrylic acid/mol	0.5	1.0	1.5
B/methyl-acrylic acid/mol	0	0.2	0.4
C/Polyvinyl silicone oil/wt%	5	10	15

Factor	Level 1	Level 2	Level 3
D/APS/wt%	1.0	1.5	2.0

Table II Formulation of copolymer reaction with acrylic acid, methylacrylic acid, Polyvinyl silicone oil

No	A/acrylic acid/mol	B/methyl-acrylic acid/mol	C/Polyvinyl silicone oil/wt%	D/APS/wt%
1	0.5	0	5	1
2	0.5	0.2	10	1.5
3	0.5	0.4	15	2.0
4	1.0	0	10	2.0
5	1.0	0.2	15	1.0
6	1.0	0.4	5	1.5
7	1.5	0	15	1.5
8	1.5	0.2	5	2
9	1.5	0.4	10	1

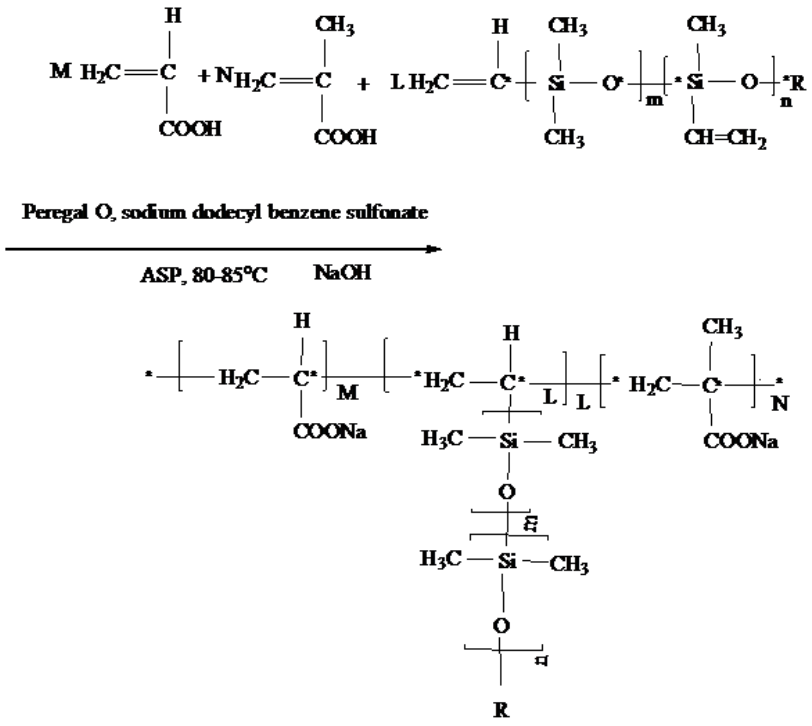


Figure 1. The synthesis of the polymer auxiliary with silicon

Application of series of the copolymers and the selection of the synthetic recipe

A series of these copolymers were applied respectively in the re-tanning and fatliquoring process of the shaved sheepskin wet blue. The re-tanning and fatliquoring process is shown as Table III. The re-tanning properties of these copolymers were investigated using a thickness gage to measure the thickness of the

same part of the leather in the initial and the last stage. The softness of the treated leather were also examined.The optimised synthetic recipe was confirmed according to the data-processing method of the orthogonal experiment. The polymer auxiliary with silicon was synthesized according to the best synthetic recipe.

TABLE III The process of re-tanning and fat-liquoring of the shaved sheepskin wet blue based on the polymer auxiliary with silicon

Process	Chemicals	%	T/^{o}C	t/min	Remarks
Re-wet	Water	200	35		
	BCN-60	0.5			
	Formic acid	0.6		60	pH 3.7
Washing	Water	200		10	drain
Re-chrome	Water	150	40		
	Chrome B	4		90	
	Sodium formate	1		30	
	Sodium bicarbonate	1		3*15	pH 4.0
Washing	Water	200		10	drain
Neutralization	Water	150	35		
	Sodium formate	1		60	
	Sodium bicarbonate	2		3*20	pH6.0
Washing	Water	200		10	drain
Re-tanning and fat-liquoring	Water	200	45		
	The polymer auxiliary with silicon	16		90	
	Formic acid	2		3*15	pH3.6
Washing	Water	200		10	drain
Drying, rewetting, milling, toggle					

Molecular weight of the polymer auxiliary with silicon and its structure determination

The molecular weight of the polymer auxiliary with silicon was investigated by gel permeation chromatograph (Sephadex G-25, using tetrahydrofuran as mobile phase, the flow speed 1.0mL/min, using polyethylene glycol as reference standard). Then the amphoteric polymer auxiliary agent was precipitated with acetone and dried for 6 hours at 80°C in vacuo. The infrared (IR) spectrum was determined with a Nicolet Nexus 470 FTIR spectrophotometer.

Application and the optimum amount of the polymer auxiliary with silicon on shaved sheepskin wet blue

The polymer auxiliary with silicon was respectively applied in the retanning and fatliquoring process of the shaved sheepskin wet blue. The process is the same as in Table III. The amount of the polymer auxiliary with silicon was 4%, 8%, 12%, 16%, 20% respectively. The method of the thickening rate of the leather, the softness and apparent density of the finished leather are consistent with the former. Compared with the thickening rate and the state of the finished leather under the conditions of different amounts of the polymer auxiliary with silicon, the optimal amount of the polymer auxiliary with silicon is determined.

Application of the polymer auxiliary with silicon's Matching with other fat-liquoring on shaved sheepskin wet blue

In order to improve the handle of the leather and ensure the softness of the finished leather, the polymer auxiliary with silicon was matched with the amount of other fat-liquoring agents such as TRUPONOL SWS, UFB/W, etc in the fat-liquoring process of the leather. The amount of TRUPONOL SWS was 0%, 2%, 4%, 6%, 8% respectively when the dosage of the polymer auxiliary with silicon is 10%. The softness and apparent density of the finished leather are examined. Based with the result of the examination, the optimal range of consumption of TRUPONOL SWS is determined.

.

RESULTS AND DISCUSSION

Analysis of the optimised formulation of the copolymer

Table IV shows the thickening rate, softness of the leather treated by different copolymers synthesised by the relevant recipe. Based on the ratio of the monomers and its structure, different copolymers may will show different results in re-tanning and fatliquoring. Based on the thickening rate, softness of the treated leather, the mol ratio of monomers has been optimised. The optimised mole ratio is $C_1B_2D_2A_1$. That is, Polyvinyl silicone oil 5wt%, Methyl-acrylic acid 0.2mol, APS 1.5wt%, Acrylic acid 0.5mol. The reactive temperature and time is 80-85°C, 120-180min, respectively.

Table IV Results of $L_9(3^4)$ copolymer reaction and application

No	A/Acrylic acid/mol	B/Methyl-acrylic acid/mol	C/Polyvinyl silicone oil/wt%	D/APS/wt%	Thickening rate of the treated leather/%	Softness of the treated leather
1	0.5	0	5	1	23.2	3
2	0.5	0.2	10	1.5	20.8	4
3	0.5	0.4	15	2.0	18.6	5.5
4	1.0	0	10	2.0	21.3	3.5
5	1.0	0.2	15	1.0	18.3	6
6	1.0	0.4	5	1.5	21.8	4
7	1.5	0	15	1.5	19.4	3
8	1.5	0.2	5	2	22.9	4
9	1.5	0.4	10	1	18.1	4

Analysis of the molecular weight and the structure optimised formulation of the copolymer and its characteristics

As shown in Figure 2, the molecular weight and the distribution index (M_w/M_n) of the polymer auxiliary with silicon are 61187 and 1.83 respectively, which indicates that the copolymer may have good re-tanning and filling properties.

Figure 3 show the FTIR spectra of the polymer auxiliary with silicon. The relation between the bands are shown as Table V. The chemical structure is confirmed by FTIR[7].

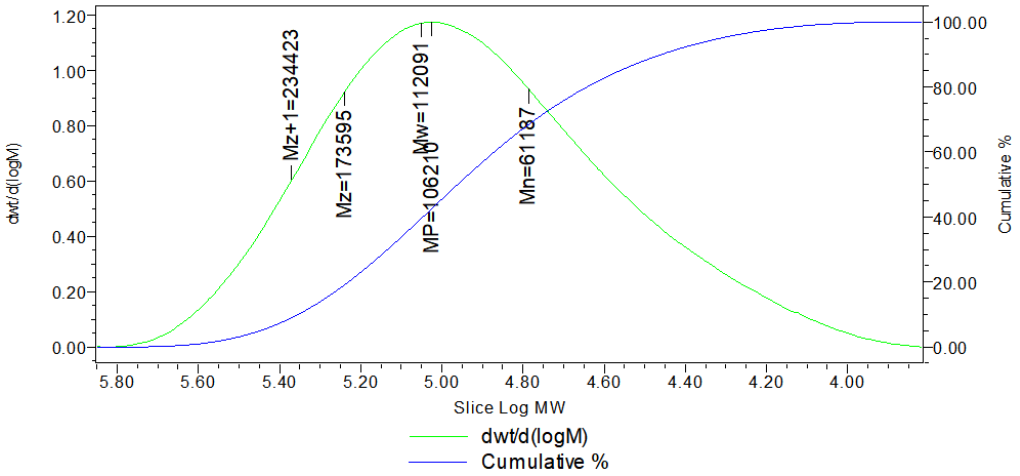
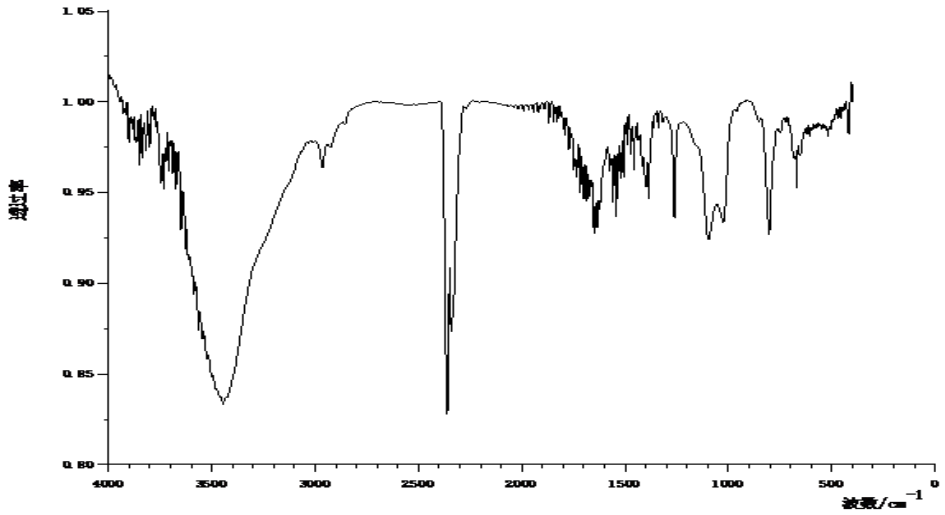


Figure 2. Curve of GPC of the polymer auxiliary with silicon



Transmittance/%

Wave numbers/cm^{-1}

Figure 3. IR Spectrum of the polymer auxiliary with silicon

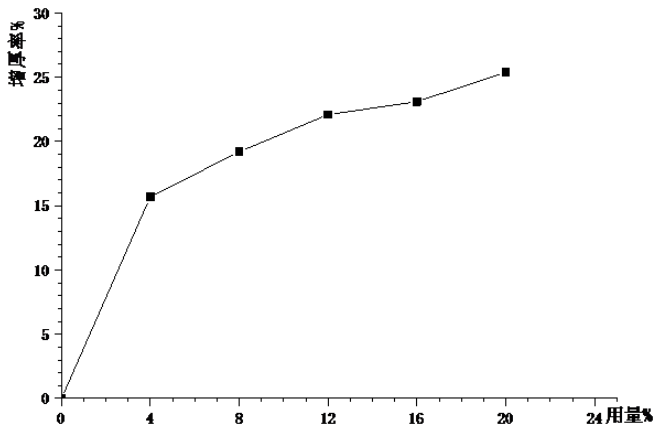
TABLE VI Relation between the band and the relevant group of the polymer auxiliary with silicon

No	Wave numbers/cm^{-1}	Group
1	3440	-OH(-COOH)

No	Wave numbers/cm^{-1}	Group
2	2950	C-H(CH_3)
3	2350, 2390	-CH=CH-
4	1700	-COO-
5	1090-920	-Si-O-
6	840-670	-Si-C-

Results of application of the polymer auxiliary with silicon on shaved sheepskin wet blue

Figure 4, Table VII show the relation between the thickening rate, softness and apparent density of the treated leather and the consumption of the polymer auxiliary with silicon. The thickening rate and softness of the treated leather increases with the increase of dosage of the co-polymer, which show that the polymer auxiliary with silicon has good re-tanning and filling properties. When the dosage of the co-polymer exceeds 8%, the trend of increasing of the thickening rate and softness slows down. In addition excessive consumption of the polymer auxiliary with silicon cause the finished leather has slightly tight grain and plastic feeling. The apparent density of the treated leather is the range of 0.46 and 0.48 g/cm^3, which is close to that of the synthetic leather and is less than that of the leather. Reasons for the decrease in the apparent density of the leather is that the polymer has the structure of -Si-O- bond who can increase the flexibility of polymer chains and lubricate the fibers of the leather so as to improve the softness and apparent density of the finished leather. Therefore the optimal range of the consumption of the polymer auxiliary with silicon is 8% and 10% based on the weight of the shaved sheepskin wet blue. The treated leather is full, soft and light.



Thickening rate/%

Rate/%

Consumption of the polymer auxiliary with silicon/%

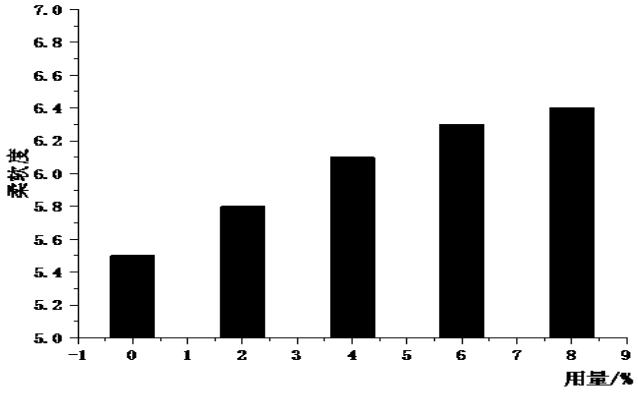
Figure 4. Relation between the thickening rate of the treated leather and the consumption of the polymer auxiliary with silicon

Table VII Relation between the softness, apparent density of the treated leather and the consumption of the polymer auxiliary with silicon

No	Consumption of the polymer auxiliary with silicon/%	Softness of the treated leather	Apparent density of the treated leather/g/cm^3
1	0	3.0	0.46
2	4	4.2	0.46
3	8	5.5	0.48
4	12	5.5	0.48
5	16	5.6	0.48
6	20	5.8	0.48

Results of Application of the polymer auxiliary with silicon's Matching with other fat-liquoring on shaved sheepskin wet blue

In order to improve the slightly tight grain and plastic feeling of the leather treated single by the polymer auxiliary with silicon, a certain amount of TRUPONOL SWS is applied in the fat-liquoring process of the leather. Figure 5 shows the relation between the softness of the finished leather and the consumption of TRUPONOL SWS. As the dosage of TRUPONOL SWS increases, the softness of the leather is softer than before. When the consumption of TRUPONOL SWS exceeds 4%, the softness of the leather achieves over 6.0. Therefore the optimal range of the consumption of TRUPONOL SWS is 4% and 8%, the apparent density of the finished leather is 0.49g/cm^3. In order to further improve the feeling of the leather, other fat-liquoring materials such as UFB/W, TRUPONOL DB, etc can be used for replacement of part of TRUPONOL SWS.



Consumption of TRUPONOL SWS/%

Softness

Figure 5. Relation between the softness of the treated leather and the consumption of TRUPONOL SWS

Conclusion

The results of preparation and application of the polymer auxiliary with silicon, show that acrylic acid, methyl-acrylic acid, polyvinyl silicone oil were used in a free radical copolymerization using ammonium persulfate at 80-85°C for 120-180 minutes, with the optimal mole ratio of acrylic acid, methyl-acrylic acid being 0.5,0.2, the consumption of polyvinyl silicone oil and ammonium persulfate is 5%, 1.5% respectively.

The structure of the polymer auxiliary with silicon was characterised by FTIR. The results of the applied the polymer auxiliary with silicon on the re-tanning and fat-liquoring process of shaved sheepskin wet blue show that it has good re-tanning and filling properties. The optimal range of the consumption of the polymer auxiliary with silicon is 8% and 10%, the thickening rate, softness and apparent density of the treated leather can obtain 20% or so and the softness, apparent density of the treated leather is 5.5, the range of 0.46 and 0.48 g/cm^3. Matching 4-8% TRUPONOL SWS can further improve the quality of the finished leather whose apparent density is 0.49g/cm^3, which is close to that of the synthetic leather(0.3~0.5g/cm^3)and is less than that of the leather(0.6~0.8g/cm^3).

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support of Science Technology Department of Zhejiang Province (Project number: LGG22ZE030016), Science and Technology Bureau, Jiaxing City, Zhejiang Province (Project number:00321102AL), the help of Zhejiang Fubang Leather, co.,Ltd, Zhejiang Province.

References

1.Luo Jianxun and Feng Yanjuan, Cleaner processing of bovine wet white: synthesis and application of a novel chrome-free tanning agent based on an amphoteric organic compound. J. Soc. Leather. Technol. Chem., 2015, 99(4), 190.

2.Luo Jianxun and Feng Yanjuan, Cleaner Chrome Tanning – Technology of Chrome-reduced Tanning Without Salt, Pickling and Short Procedure. J. Soc. Leather. Technol. Chem., 2019, 103(9), 289.

3.Shan Zhihua, Chen Hui, Luo Jianxun, etc. Chemistry and technology of leather manufacture, Beijing: Chemical Industry Press, (2017).

4.Li Zhengjun, Luo Yonge, Liu Liangjun, etc. Study on the applied technology of fat-liquoring and re-tanning agent WPT-S.China Leather, 1995,24(10):31-34.

5.Wei Deqing, Study on FRT Fatliquor re-tanning agent.China Leather, 1998,27(1):9-11.

6.Yang, De, Design of Experiments and Analysis, Beijing: Chemical Industry Press, (1999).

7.Ning Yongcheng. Structure Identification of Organic Compounds and Organic Spectroscopy. Beijing: Science Press,(2002).