Preparation of Modified Rapeseed Oil/Organic Montmorillonite Nanocomposite and Its Application as Leather Fatliquoring Agent

LÜ Bin[1] , Gao Jianjing[1] , Ma Jianzhong[1,2] , Xu Qunna[1], Gao Dangge[1] , Han Xuewu[1]*

[1]College of Resources and Environment Shaanxi University of Science & TechnologyXi'an 710021 Shaanxi China;

[2.] Key Laboratory of Ministry of Education on Chemical Science and Technology of Light Chemical Additives, Shaanxi University of Science & TechnologyXi'an 710021Shaanxi, China

Abstract

Montmorillonite was modified by myristic acid via intercalation reaction and organic montmorillonite (OMMT) was obtained. The as-prepared OMMT, rapeseed oil, ethylene diamine, acrylic, and sodium bisulfite were employed to prepare the modified rapeseed oil (MRO) /OMMT nanocomposite (MRO/OMMT) fatliquoring agent. The structures of OMMT and MRO/OMMT were investigated by flourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The stability of MRO/OMMT was determined by dynamic light scattering analyzer (DLS) and emulsion stability tests. MRO/OMMT was applied in the leather fatliquoring process. The physical mechanical properties and flame retardant properties of the crust after fatliquoring were determined. The FT-IR results showed that the MRO/OMMT was successfully prepared. The XRD results indicated that the interlayer spacing of MMT increased from 1.239nm to 1.517nm after modified by myristic acid. The leather samples treated with MRO/OMMT had superior flame retardancy and mechanical properties, to those of leather samples tread with MRO.

Key words: modified rapeseed oil, organic montmorillonite, nanocomposite fatliquoring agent, flame retardancy

1 Introduction

Fatliquoring agent is one of the leather chemicals with the largest use in leather industry, and has extremely important effects on the leather performance. It can penetrate into the skin collagen fibers and play lubricating and plasticizing roles so that the molecular chain segments can easily move. Consequently, fatliquored leather would become soft, waterproof, sunproof and flexible. However, fatliquor could improve the flammability of leather, because the relatively low fastness between fatliquor and the leather fibers lead to fatliquor migrate to the surface of the leather which would flame easily in the heating process.

MMT has become a subject of considerable interest over the past few years because of its lamellar structure, larger surface area, and cationic charge [1-3]. The requirements for high additional environment-friendly flame retardant polymer are rising with the progress of science and technology. MMT can endow the polymer-based hybrid composites with improved mechanical properties, thermal stability, flame retardancy, and barrier properties [4-5] even at very low concentration (usually less than 5%). Since the MMT interlayer has strong polarity, great hydrophilicity and smaller spacing, alkyl chains are very difficult to insert into MMT interlayers. MMT was always modified to enahnce the interlayer spacing of MMT and improve its hydrophobicity. Thus, it can improve the compatibility between MMT and polymer matrix [6]. According to the literatures, there are many kinds of methods regarding the MMT modification [1-7].

In this research, myristic acid was used to modify MMT. Myristic acid is one of natural fatty acid. Fatty acid modified MMT can improve the interlayer spacing and lipophilicity, preferable [8-9]. Modified MMT by myristic acid would have better compatibility with MRO. XRD, FT-IR, and DLS were used to characterize MRO/OMMT. Moreover, effects of usage of OMMT on performances of MRO/OMMT were investigated in this research. To obtain the application performance, the MRO/OMMT nano-composite fatliquor was applied in the leather fatliquoring process, and the physical and mechanical properties, flame retardancy and softness of the crust leather after fatliquoring were measured.

2 Experimental

2.1 Major chemicals

Rapeseed oil of industrial grade was made by Xi'an Aiju grain and oil Co., Ltd., China. Myristic acid was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Na^+-MMT was obtained from Hebei Zhangjiakou City Qinghe Co., Ltd., China. Acrylic acid of analytically pure was manufactured by Tianjing Fuchen Chemical Factory. Ethylene diamine of analytically pure was made by Tianjing Jingbei fine Chemical Co., Ltd., China. Aluminium oxide of analytically pure was purchased from Tianjing Dengfeng chemical plant.

2.2 Preparation of MRO/OMMT

2.2.1 Preparation of OMMT

Heat the system to 50 ℃, the myristic acid and potassium hydroxide solution were added to a three-neck flask with the molar ratio of 1:1. Then stopped heating and the reaction was continued for about 30min. Thus the myristic acid potassium was obtained.

Firstly, 9g of Na+-MMT was added into 75mL of 0.14mol/L sodium dodecyl benzene sulfonate solution and stirred for 1h in 85°C. Then, myristic acid potassium was added and mixture was stirred for 2h. The obtained OMMT was purified by acetone and alcohol for several times separately.

2.2.2 Preparation of MRO/OMMT

Firstly, 50g of rapeseed oil was added into a three-neck flask, and various usages of OMMT including 1wt%, 2wt%, 4wt%, 6wt% and 8wt%, were added separately in the mixture followed by stirring for 30min. Ethylene diamine and alumina were added into the three-neck flask and stirred for 2h at 100°C. When the temperature was heated to 110°C, acrylic acid was dropwise added and the reaction was allowed for 1.5h. After the cooling of the mixture, sodium bisulfite solution was dropwise added and the mixture was kept in reaction for 1.5h. Sodium hydroxide was slowly added before the reaction mixture was adjusted to pH of 7.5. Then, water was added to adjust the solid content to 40%. Consequently, the MRO/OMMT was obtained.

2.3 Application experiment

MRO and MRO/OMMT were applied as fatliquoring agents in the fatliquoring process of goatskin garment leather. The fatliquoring process is shown in Table 1.

Table 1 Fatliquoring process of goatskin garment leather

Operation	Chemical	Mass (%)	Temperture (℃)	Time (min)	pH
Fatliquoring	Water	150			
	Fatliquoring agent	14	55	90	
Fixing	Formic acid	2	55	3×20+30	3.8-4.0

2.4 Determination of emulsion properties

2.4.1 Stability of 1:9 (or 1:4) dilution

Firstly, 90mL (or 80mL) hot distilled water was added into a glass-cover measuring cylinder. Then 10mL (or 20mL) samples were added into glass-cover measuring cylinder, after flipped up and down and fully mixing put it under 30°C for 24h. The case of separation of layer and 1:9 (or 1:4) dilution stability of its solution were then observed.

2.4.2 Stability of emulsion

The stability of emulsion was determined by 10% waxberry extract or 10% $KCr(SO_4)_2$ solution or 1mol/L HCl or 1mol/L NH_4OH solution. Firstly, 80mL hot distilled water was added into a 100mL cylinder at 55~60°C. Second, 10mL samples were added into cylinder and fully mixed. Then, 10mL of determined solution was added into cylinder, after flipped up and down and fully mixing, the mixture was kept at 25~35°C for 4h, the case of separation of layer and the stability of solution were observed.

2.5 Characterization

MRO/OMMT was purified by acetone and alcohol, and the purified product was then dried up. The obtained sample was then investigated using X-ray diffraction (XRD) instrument (D/Max2200PC) equipped with Cu-Ka radiation source to identify the d-spacing of MMT. The X-ray generator operated at 40 kV, 40 mV with a scanning speed of 4°/min. Fourier transform infrared (FTIR) analysis was performed using a FTS-65A fourier transforms infrared spectrometer by KBr tableting method. The size distribution of MRO/OMMT particles was measured by a Particle Size Analyzer (Marvin, Nano-ZS) in deionized water (volume fraction of MRO/OMMT particles was 0.1%) after ultrasonic treatment for 15 min to minimize the presence of OMMT aggregates.

Leather samples with an area of 30cm×8cm were cut parallel to the leather backbone before dried up under room temperature. The flame-retardant property of the leather sample was measured by vertical burning method using flame-retardant instrument manufactured by Nanjing Shangyuan Analysis Instrument Co., Ltd. Leather was sampled with the standard mold. After they were fixed on the clamps of GFU55 Functional Materials Examination Machine made by Taiwan High Iron Science and Technology Stock Company, mechanical properties of fatliquored leather samples were determined. The burthen number at break and the highest burthen number were recorded.

3 Results and discussion

3.1 XRD analysis of OMMT

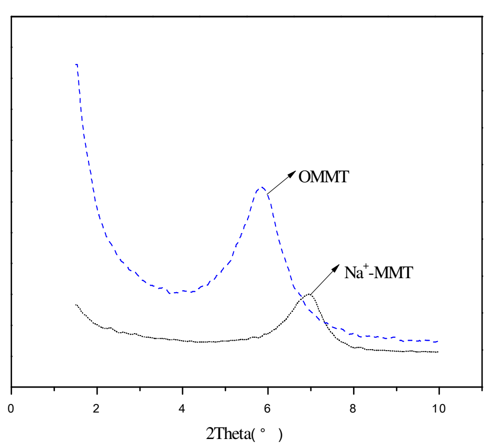

Figure 1 XRD spectra of Na^+-MMT and OMMT

Figure 1 shows XRD patterns of Na^+-MMT and OMMT. The basal spacing of Na^+-MMT was 1.239nm (2θ=6.94°). Compared with the interlayer spacing of Na^+-MMT, the interlayer spacing of MMT modified by myristic acid is 1.517nm (2θ=5.82°) accordind to the determaniton. Consequently, the interlayer spacing of OMMT increased after modification.

3.2 Emulsion stability

Table 2 Emulsion stability of MRO/ OMMT

MA-MMT (%)	1:9 dilution stability	1:4 dilution stability	10% waxberry extract stability	1mol/L HCl stability	1mol/L NH_4OH stability	10% $KCr(SO_4)_2$ stability
0	√	√	√	×	√	√
1	×	√	√	×	√	√
2	×	√	×	×	√	×
4	√	√	√	×	×	√
6	√	√	√	×	√	√
8	√	√	√	×	√	√

A tick means good stability and a cross means poor stability.

Table 2 shows the emulsion of MRO/OMMT. It is noted that MA-MMT exhibit good stability in 1:9 dilution emulsion stability, 1:4 dilution emulsion stability, 10% waxberry extract stability and 10% $KCr(SO_4)_2$ solution stability. Both EA-MMT and MA-MMT showed poor stability in 1mol/L HCl.

3.3 XRD analysis of MRO/OMMT

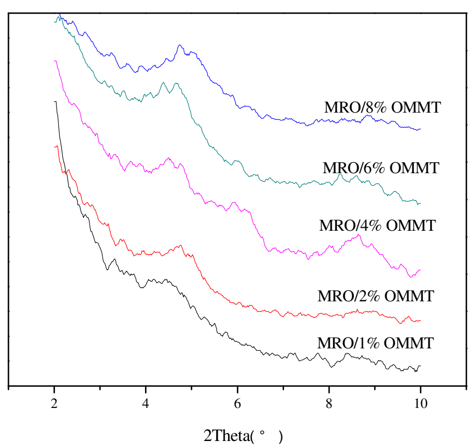

Figure 2 XRD spectra of MRO/OMMT with different amount of OMMT

As Figure 2 shows, all OMMT samples were not exfoliated. One reason is that the interlayer spacing of OMMTs was not large enough; another can be attributed to the difficulty of extending interlayer spacing of OMMTs for its long alkyl chain of MRO. However, the diffraction peaks of MMT decreased with the increase of the amount of OMMT can be seen.

3.4 FT-IR analysis of MRO/OMMT

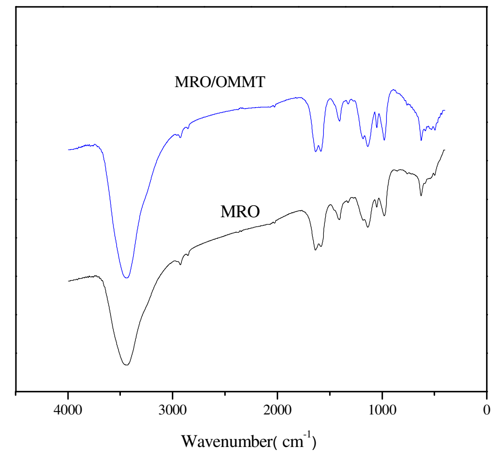

Figure 3 FT-IR spectra of MRO/OMMT

Figure 3 shows the FT-IR spectra of MRO/OMMT. Wide peaks at around 3440cm^{-1} belong to the stretching vibration peaks of –OH. At 2925cm^{-1} the absorption peaks origin from the symmetric and asymmetric stretching vibration absorption peak of -CH_3 of alkyl chain. The strong peaks at 1636cm^{-1} corresponding to the absorption peak of carboxyl can also been seen. Compared with that of MRO, an absorption peak at 1036cm^{-1} corresponding to stretching absorption peak of Si-O of MMT appear on MRO/MMT spectrum. The results proved that MRO/OMMT was succsufully obtained and the structure of MRO did not change the structure of MRO by adding OMMT.

3.5 Particle size analysis of MRO/OMMT

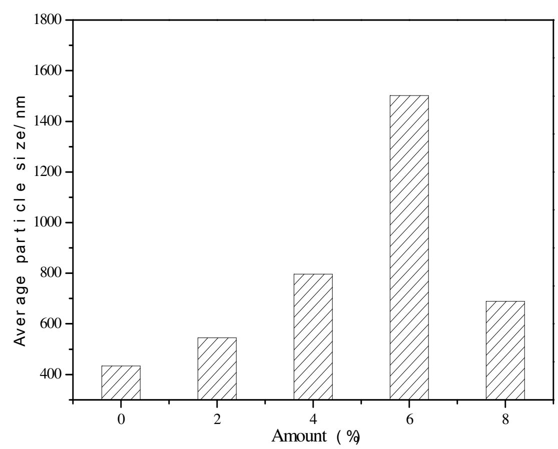

Figure 4 Particle size distribution of MRO/OMMT

The clear regularity in size was shown in Figure 4, the average particle size of MRO/OMMT first increase and then drop with the increase of the OMMT amount. The minimum value of average particle size of MRO/OMMT was obtained when the amount of OMMT was 2%.

3.6 Mechanical analysis of fatliquored leather

Table 3 Mechanical properties of leather samples fatliquored by MRO/OMMT

The amount of OMMT (%)	Tensile strength (N/mm^2)	Elongation at break (%)	Tear strength (N/mm)
0	22.66	63.39	66.28
1	21.76	103.54	77.10
2	17.76	86.05	67.97
4	15.28	117.95	67.87
6	24.11	70.97	78.54
8	24.08	93.74	71.03

Table 3 shows that the tear strength of leather fatliquored by MRO/OMMT was better than those fatliquored by MRO. However, the changes in tensile strength and elongation at break were not obvious. Because of the nano-level of modified MMT, OMMT could penetrate among collagen fibers, thus improve the tear strength of leather. Besides, tensile strength and elongation at break of the leather fatliquored by MRO/OMMT reached the leather industrial standards.

3.7 Leather flame retardant analysis

Table 4 Fire resistance of the leather sample fatliquored by MRO/OMMT

The amount of OMMT (%)	After flame time /s	After glow time/s	LOI (%)	Burning rate (mm/s)
0	72.0	122.0	23.7	0.5773
1	73.3	430.3	26.0	0.0876
2	58.5	637.7	26.5	0.0945
4	67.3	455.5	26.5	0.0913
6	58.5	698.6	26.7	0.0834
8	50.5	721.3	27.0	0.0851

Table 4 shows fire resistance of the leather samples fatliquored by MRO/OMMT. The flame retardancy of the leather fatliquored by MRO/OMMT increased to different degree. The after flame time and after glow time showed no regularity with the increase of the OMMT amount. However, the burning rate of MRO/OMMT decreased and the limited oxygen index (LOI) value of MRO/OMMT increased with the increase of OMMT amount. The reason for this result was that OMMT could form char with nano-structure. The nano-structure of char could: ① improve the barrier performance, ② strengthen the stability of char to make it dense and hard ③ form ceramic with porous after thermal oxidation under high temperature and protect matrix from flaming. Therefore, the flame retardancy of MRO was improved by adding OMMT.

4 Conclusions

A simple route to prepare MRO/OMMT with myristic acid was proposed in this study. The interlayer spacing of MMT was increased by adding myristic acid. Compared with those of MRO, the mechanical properties of leather fatliquored by MRO/OMMT reached a higher level. The flame retardancy of leather fatliquored by MRO/OMMT obviously increased with the increase of OMMT amount.

Acknowledgements

This work was financially supported by Pre-Research of National Program on Key Basic Research Project of China (973 Program) (No.: 2011CB612309), Scientific Research Program of Key Laboratory for light industry and chemical additives of chemistry and technology, Ministry of education (No.:2011szs007), and National Natural Science Foundation of China (No.:21104042).

References

[1] Changqing Fang, Ruien Yu, Ying Zhang, etal., 2012, Combined modication of asphalt with polyethylene packaging waste and organophilic montmorillonite, Polymer Testing, 31, 276-281p．

[2] Shou Zhao, Chenghong Feng, Xangning Huang, etal., 2012, Role of uniform pore structure and high positive charges in the arsenate adsorption performance of 13Al-modified montmorillonit, Journal of Hazardous Materials, 203(204), 317-326p．

[3] Daimei Chen, Jian Chen, Xinlong Luan, etal., 2011, Characterization of anion–cationic surfactants modified montmorillonite and its application for the removal of methyl orange, Chemical Engineering Journal, 171, 1150-1158p．

[4] Bin Lü, Jianzhong Ma, Dangge Gao, etal., 2011, Synthesis and properties of modified rapeseed oil/montmorillonite nanocomposite fatliquoring agent, Journal of Composite Materials, 45(24), 2573–2578p.

[5] Marcos R. Guilherme, Luiz H.C. Mattoso, Nathalie Gontard, etal., 2010, Synthesis of nanocomposite films from wheat gluten matrix and MMT intercalated with different quaternary ammonium salts by way of hydroalcoholic solvent casting, Composites: Part A, (41),375-382p．

[6] Henglong Zhang, Jianying Yu, Shaopeng Wu., 2012, Effect of montmorillonite organic modification on ultraviolet aging properties of SBS modified bitumen, Construction and Building Materials, 27, 553-559p .

[7] Chi-Nhan Ha Thuc, Anne-Cécile Grillet, Laurence Reinert, etal., 2010, Separation and purification of montmorillonite and polyethylene oxide modified montmorillonite from Vietnam- ese bentonites, Applied Clay Science, 49, 229-228p.

[8] Zhong Li, Shaoming Yu., 2005, Prepared of fatty acid/MMT composite materials for energy storage, Hefei University of Technology, 1-50p .

[9] Nihal Sarier, Emel Onder, Sabri Ersoy., 2010, The modification of Na-montmorillonite by salts of fatty acids: An easy intercalation process, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 371, 40-49p.