



Modified rapeseed oil/silane coupling agent-montmorillonite nanocomposites prepared by in-situ method: Synthesis and properties



Bin Lyu^{a,b}, Xu-bin Duan^a, Dang-ge Gao^a, Jian-zhong Ma^{a,b,*}, Xue-Yan Hou^a, Jing Zhang^c

^a College of Resources and Environment, Shaanxi University of Science & Technology, Xi'an 710021, PR China

^b Key Scientific Research Group of Shaanxi province, PR China

^c Culture and Communications School, Shaanxi University of Science & Technology, Xi'an 710021, PR China

ARTICLE INFO

Article history:

Received 14 December 2014

Received in revised form 23 February 2015

Accepted 13 March 2015

Available online 28 March 2015

Keywords:

Rapeseed oil
Na-montmorillonite
Silane coupling agent
Leather

ABSTRACT

The environmentally friendly flame retardant fatliquoring agent has aroused the attention of tannery industry. In this study, rapeseed oil and montmorillonite were used to prepare flame retardant fatliquoring agent. Firstly, silane coupling agent modified montmorillonite was prepared from Na-montmorillonite (Na-MMT) and silane coupling agent γ -aminopropyltriethoxysilane. Then the modified rapeseed oil/silane coupling agent modified montmorillonite nanocomposites was obtained by using silane coupling agent modified montmorillonite and rapeseed oil through in-situ method. The as-prepared modified rapeseed oil/silane coupling agent modified montmorillonite was applied in fatliquoring process of goatskin garment leather. Flame retardancy, softness and mechanical properties of the fatliquored leather were tested. Compared with those of the leather fatliquored by modified rapeseed oil (MRO), flame retardancy, softness and tear strength of the leather treated by modified rapeseed oil/silane coupling agent modified montmorillonite were improved. The results of environmental impact assessments indicated that the modified rapeseed oil/silane coupling agent modified montmorillonite nanocomposites did not increase the pollution to the environment.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Rapeseed oil as a kind of renewable material has been applied in leather fatliquoring process. Fatliquoring, which is mainly to add oil (i.e., fatliquoring agent) into crust leather (Zar1ok et al., 2014), is an important process in leather making. It has greatly effects on the softness, fullness and water permeability of leather. Fatliquoring agent prepared from rapeseed oil has been reported in a study (Qiu et al., 2011) which demonstrates that it can endow leather with good fullness and flexibility. However, due to the low combination with leather fibers, fatliquoring agent was easy to migrate to the surface of leather. In this case, adding fatliquoring agent could improve the flammability of leather (Wang et al., 2006).

In recent years, the frequent occurrence of fire accidents brings huge losses to people and their properties. Higher requirements for flame retardancy have been put forward. Especially the issue on

how to improve the flame retardancy of the leather has attracted much attention. In order to meet the market demand for flame resistance of leather, the pace of research needs to be accelerated.

In terms of flame retardant fatliquoring agent, only few researches have been reported. Cao Xiangyu studied the retardant effects of five kinds of fatliquoring agents. The results indicated that phosphate could improve the flame retardancy of the material (Cao and Zhang, 2010). Currently, most flame retardant fatliquoring agents are prepared by using flame retardants. Common flame retardants contain halogen compound and phosphorus compound. However, it is not recommended since many toxic substances will be generated when using this kind of common flame retardants. For leather, once it is on fire, the generated toxic substances are always harmful to human health. For example, some flame retardants containing phosphate could lead to eutrophication. Consequently, the study of environmentally friendly flame retardants has been the objective of many researches (Hu et al., 2011; Wang et al., 2002).

Silicone flame retardant can endow the base material with good flame retardancy, improve the mechanical and heat-resistance properties, and thus, meet the people's requirement for the flame retardant (Kashiwagi et al., 2004). Na-montmorillonite (Na-MMT)

* Corresponding author at: College of Resources and Environment, Shaanxi University of Science & Technology, Xi'an 710021, PR China. Tel.: +86 29 8616 8010; fax: +86 29 86132559.

E-mail address: majz@sust.edu.cn (J.-z. Ma).

of which the length and width are both about 100 nm, is a kind of layer silicate with 2:1 type structure (Alexandre and Dubois, 2000). It has a huge ratio of length to diameter (Du et al., 2011). The introduction of Na-MMT into polymeric material can enhance the properties of the composite such as impact-resistance, fatigue-resistance, dimensional stability and gas barrier properties. In particular, properties of the composite could be improved greatly when MMT was dispersed evenly in the polymer matrix. In other words, it could not only significantly improve hardness and toughness, but also provide excellent flame retardancy to the composite (Huang et al., 2010; Kiliaris and Papaspyrides, 2010; Hao et al., 2006). However, Na-MMT with strong polarity was easy to reunite. In this case, in preparing fatliquoring agents, Na-MMT must be modified in order to ensure its uniform dispersion. Commonly agents used to modified MMT include quaternary ammonium salt (Huang et al., 2012; Wang et al., 2012), fatty acid (Sarier et al., 2010), and so on (Luengo et al., 2011; Zhao et al., 2012). For montmorillonite modifier, silane coupling agent containing silicon element has attracted wide attention in recent years. On the one hand, it can increase the content of silicon element and enhance the thermal stability of organic montmorillonite. On the other hand, the modification of MMT by silane coupling agent can increase the hydrophobicity and lipophilicity of MMT. It is propitious to the dispersion of MMT in polymer matrix (Park et al., 2009). Silva et al. (Silva et al., 2011) prepared modified MMT by *N*-(2-aminoethyl)-3-aminopropyltrimethoxy silane to increase the hydrophobicity of MMT. Thus the reaction between modified MMT and triethylenetetramine could be processed easily.

Modified rapeseed oil/Na-MMT nanocomposite was prepared through introducing MMT (with flame retardant properties) into modified rapeseed oil in a previous study of our group (Lv et al., 2011). The dispersion of MMT in modified rapeseed oil was quite poor owing to the strong hydrophilicity of MMT, which led to the reduction of stability of nanocomposite. This study is launched on the basis of our previous research. Silane coupling agent modified montmorillonite was prepared from MMT and silane coupling agent γ -aminopropyltriethoxysilane. Thus the lipophilicity of MMT was enhanced. Then silane coupling agent modified montmorillonite was introduced into modified rapeseed oil via in-situ method. Finally, a flame retardant composite was obtained and applied in the fatliquoring process of goatskin garment.

2. Material and methods

2.1. Materials

Silane coupling agent γ -Aminopropyltriethoxysilane (commercial product) was obtained from Nanjing Jingtianwei Chemical Co., Ltd., MMT (commercial product) was obtained from Qinghe Chemical Factory. Ethylenediamine (analytically pure) was purchased from Tianjin Jinbei Fine Chemical Co., Ltd., Acrylic acid (analytically pure) was purchased from Tianjin Fuchen Chemical Reagent Factory. Aluminum oxide (analytically pure) was purchased from Tianjin Dengfeng Chemical Reagent Factory. Sodium bisulfite (analytically pure) was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd.

2.2. Preparation of silane coupling agent-montmorillonite

A certain amount of methanol and distilled water was added into a 250 mL three-neck flask and then the pH of the system was adjusted to 5.5 with acetic acid after the addition of KH551. The temperature was controlled at 56 °C for 1.5 h. Then Na-MMT was added into the system after the temperature was elevated to 85 °C. The system was maintained for 2 h, and cooled to room

temperature. Then the product was washed with methanol, precipitated and centrifugally separated 3 times and then dried 24 h at 90 °C. Finally, silane coupling agent modified montmorillonite was obtained.

2.3. Preparation of modified rapeseed oil/silane coupling agent modified montmorillonite

Firstly, a certain amount of rapeseed oil and silane coupling agent modified montmorillonite (0, 2%, 4%, 6%, or 8%, according to solid content) were added into a three-neck flask. The system was maintained at 100 °C for 30 min with a rotation rate of 350 r/min. Secondly, the system was maintained for 2 h after the addition of aluminum oxide and ethylenediamine. Thirdly, acrylic acid was added into the system and the system was maintained for 4 h at 120 °C. Fourthly, sodium bisulfite solution was added into the system at 80 °C for 2 h. Then, 40% sodium hydroxide solution was used to adjust the pH to 7.5 and maintained at 75 °C for 1.5 h. Finally, modified rapeseed oil/silane coupling agent modified montmorillonite was obtained after solid content was adjusted to 40% with hot water and maintained for 30 min.

2.4. Determination of emulsifying stability of modified rapeseed oil/silane coupling agent modified montmorillonite and modified rapeseed oil

(1) Determination of stability after 1:9 dilutions or 1:4 dilutions

About 90 mL (or 80 mL) hot distilled water and 10 mL (or 20 mL) sample at 55–60 °C were placed in a 100 mL cylinder. With the cylinder corked, it was turned up and down for 1 min (about 30 times) and placed for 24 h (or 8 h) at 25–35 °C. Then the state of oil slick and stratification was observed to investigate 1:9 dilutions (or 1:4 dilutions) stability.

(2) Determination of stability in 10% chromium potassium sulphate solution, 10% HCl solution, 1 mol/L NH₄-OH solution or saturated sodium chloride solution

About 80 mL hot distilled water and 10 mL sample at 55–60 °C was placed in a 100 mL cylinder with a stopper. Then 10 mL chromium potassium sulphate solution (100 g/L), 10 mL HCl solution (1 mol/L), 10 mL NH₄-OH solution (1 mol/L) or 10 mL saturated sodium chloride solution were added. The cylinder was turned up and down for 1 min (about 30 times) and placed for 4 h at 25–35 °C. Then the state of the oil slick and stratification was observed to investigate the stability.

2.5. Application process

The goat skin wet-blue was made in the beam-house operation as usual. The thickness of leather samples was about 1 mm. The weight of wet-blues was recorded. The leathers were put into drums retanning by 5% chrome containing tannin for 60 min and followed retanning by 2% chrome for 180 min. The wet-blue was kept in the bath overnight before being washed with 300% water for 15 min on the next day. When the water drained away, 200% water was added to the drum. About 2% sodium formate and 1–1.5% sodium-bicarbonate were used to neutralize the bath pH value to 5.5–5.8. The temperature was controlled at 55 °C for 120 min. The wet-blue was washed with 300% water for 15 min. After the water drained away, 150% water and 10% fatliquoring agent were put into the drum and the temperature of the bath was controlled at 55 °C for 90 min. Finally, 2% Formic acid was added to beam-house up to pH of 3.8–4.0 for 90 min, and then the skin was washed for 15 min. During the fatliquoring process, the weight of wet-blues was used as a measurement basis of chemicals.

Download English Version:

<https://daneshyari.com/en/article/4512860>

Download Persian Version:

<https://daneshyari.com/article/4512860>

[Daneshyari.com](https://daneshyari.com)