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Study on a novel multifunctional nanocomposite as flame retardant of leather

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ABSTRACT

The key of leather flame retardant technology is the development of flame retardant materials. A novel intumescent flame retardant (IFR), as the flame-retardant intermediate, was firstly synthesized, then a novel nanocomposite was successfully prepared from the IFR and montmorillonite modified by cetyl trimethyl ammonium bromide (CTAB) and collagen. Its structure and properties were characterized by XRD and FT-IR. The flame retardant was added to leather and its effects on flame-retardant properties of leather were studies by vertical burning test, limiting oxygen index (LOI) test and cone calorimeter test, respectively. The thermal stability and morphology of the flame-retardant leather were characterized by TG and SEM. The results showed that the novel nanocomposite has good flame-retardant properties and can enhance the fire retardancy of leather effectively.

1. Introduction

Leather is widely used in every part of our life, especially in fire prevention manufacturing industry owning to its good air permeability, adiabaticity and abrasion performance. However, leather products could contain some inflammable and harmful organic compounds after tanning, fat liquoring, dyeing and finishing processes [1]. When catching fire, these organic compounds will easily catch fire and release a lot of toxic gases and smoke. On this account, it is very important to improve leather's safety performance of fire prevention. Among the methods used to improve leather flame-retardant property, adding leather flame retardant is the most effective way. However, research on high performance, non-toxic, durable flame-retardant materials suitable for leather is seldom reported yet.

At present, IFR has become a focus around the world owing to its outstanding properties like adiabaticity, oxygen-insulation, smoke-restraint and non-toxicity and so on [2,3]. It will offer a promising technology for improving the flame-retardant performance of leather. However, most IFRs have poor compatibility and low reaction activity with leather fiber, and their application for leather flame retardant are limited to some extent and they are mainly applied to the flame retardant fields of synthetic polymer such as plastic, rubber, chemical fiber.

With the development of IFR technology, Polymer/Layered Silicate (PLS) nanocomposite is considered to be one of the most promising flame retardant materials and gains more and more attention [4]. Montmorillonite (MMT), as natural layered silicate mineral material, due to its special structure, plays a very important role in the preparation of PLS nanocomposite. It can greatly improve IFR materials' heat resistance and flame retardant performance, and have a good synergistic effect for improving polymer mechanical properties and thermal properties [5,6].

In this paper, by combining the advantages of the two kinds of materials (MMT and IFR), an attempt has been made toward developing a novel PLS nanocomposite used for leather flame retardant by the intercalation compounding method.

2. Experimental

2.1. Materials

THPC (tetrakis hydroxymethyl phosphonium chloride) (85%) was supplied by Pengkai Chemical Industry Co. Ltd (Shanghai, China). IFR (Pentaerythritol biphosphate melamine salt) and

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collagen (MW: 1.5–2 kDa) were made in our laboratory. MMT whose CEC (cation exchange capacity) is 145 mmol/100 g was bought from Yiwei Chemical Industry Co. Ltd (Beijing, China). CTAB and Phosphoric acid (85%) were provided by Kelong Chemical Reagent Factory (Chengdu, China). Blue wet pig leather (thickness: 1 mm) was purchased from Sichuan Lishen Leather Co. Ltd (Chengdu, China).

2.2. Preparation of OMMT–IFR nanocomposite

2.2.1. Preparation of IFR materials

The IFR material was prepared from pentaerythritol, phosphorus oxychloride, melamine and THPC according to former studies by our lab [7], and the molecule structure of IFR material is shown in Fig. 1. The IFR is soluble in water, and the solubility improves when the temperature increases.

2.2.2. Preparation of OMMT [8]

A quantitative amount of MMT was swelled in deionized water for half an hour, and then dispersed for 10 min with ultrasound. Quantitative amount of CTAB (equal to the CEC of MMT (145 mmol/100 g)) was added to the mixture to react for 2 h after heated to 80 °C from room temperature, then added collagen to react for another 2 h. After that, the obtained suspension was filtered after cooled to room temperature, and then the solid residue was washed three times with water and absolute ethyl alcohol, respectively. And it was dried under an infrared lamp, then the OMMT was obtained.

2.2.3. Preparation of OMMT–IFR nanocomposite

A certain amount of OMMT was swelled in deionized water for half an hour, and then IFR-materials were added into the mixture solution to react at different reaction conditions such as reactants ratio, reaction time and temperature. The obtained suspension was filtered and washed with water for three times after cooled to room temperature. The solid was dried at infrared lamp, and the OMMT–IFR nanocomposite was obtained.

2.3. Characterization and performance tests

2.3.1. XRD tests

The XRD experiments were performed on a DX-1000 x-ray diffractometer from Dandong Fangyuan instrument Co. Ltd. (Liaoning, China) using Cu Kα radiation corresponding to a wavelength of 0.1542 nm. The scanning rate of the detector was 1°/min. The interlayer space of montmorillonite in the nanocomposites (d_{001}) could be calculated according to the Bragg equation ($2d \sin\theta = \lambda$).

2.3.2. FT-IR tests

The samples of OMMT and OMMT–IFR were respectively ground with KBr and made into pellets, then scanned with IR detector. The data in the wavelength rage of 400–4000 cm^{-1} were recorded with an FT-IR-670 spectrophotometer from Thermo Nicolet Corporation, USA.

2.3.3. TG tests

The samples were put into Al_2O_3 crucibles respectively and heated up at the speed of 10 °C/min in N_2 atmosphere (the flow rate of N_2: 100 mL/min), the range of temperature was from room temperature to 600 °C. The data of TG were recorded with STA 449C thermal analyzer from Netzsch, Germany.

2.3.4. LOI and vertical burning test

The flame-retardant leathers were produced from pigskin by adding nanocomposite in the tanning process at levels of 0%, 5%, 7% and 9% (relative mass rate of leather weight). The pigskin was treated by the flame retardant according to the processing method given by Li et al. [9]. The leather treated with 0% flame retardant was as a contrastive sample. Several leather samples (140 mm × 52 mm) were taken from flame-retardant leather and were used for parallel tests according to OI standard method ASTM D 2863-77. Other leather samples (317.5 mm × 51 mm) were used for parallel tests according to vertical burning ALCA Method E 50. Data were reported as average values. The LOI values were measured by an oxygen index meter (HC-2) and the UL-94 vertical burning test was conducted by a CZF-3 tester from Shangyuan Analysis Instrument Co. Ltd, China.

2.3.5. Cone calorimeter test

The cone calorimeter test was conducted on a cone calorimeter device (Fire Testing Technology, UK) at an incident heat flux 50 kW/m^2 according to ISO 5660-1 standard. There were two samples studied, blank leather (not treated with the nanocomposite, average thickness: 0.9873 mm) and flame-retardant leather (treated with 10% nanocomposite, average thickness: 0.9863 mm). Both samples were cut into the size of 100 × 100 mm^2.

2.3.6. Scanning electron microscopy

SEM was used to examine the morphology of the residual chars obtained after cone calorimeter test by using an SM-7500F SEM whose accelerating voltage was 15 kV. The surface of char residues was sputter-coated with gold layer before examination.

3. Results and discussion

3.1. The design and preparation mechanism of OMMT–IFR nanocomposite

In order to meet the requirement of Leather Flame Retardant Technology, the nanocomposite should have good compatibility and reaction activity with leather. On that account, the IFR material which has good reaction activity with collagen owning to THPC was firstly designed and synthesized as shown in Fig. 1; on the other hand, how to make IFR and MMT achieve effective composite is one of the key factors for producing the nanocomposite. Therefore, the MMT was modified by CTAB and collagen together to improve the inserting efficiency of IFR in the experiment.

CTAB, as a common modifier, can enter into the MMT layers by cation exchange, but it is not easy to combine with the IFR. What's more, hydroxyls in IFR material are also helpful in the intercalation.

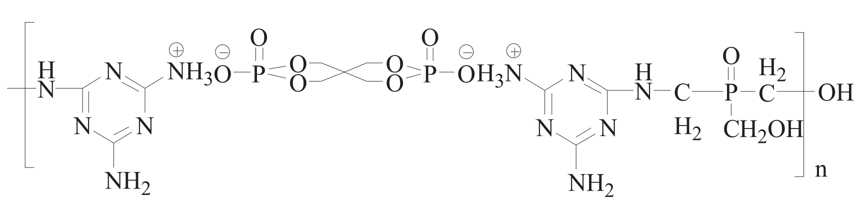

Fig. 1. The molecule structure of IFR material.