Study on Leather Modified with Nitrogen-Phosphorus Intumescent Flame Retardant in Fatliquoring Process

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ABSTRACT: *Adding flame retardant into leather is an effective way to improve the flame resistance of leather products. In this paper, a Nitrogen-Phosphorus Intumescent (NPI) flame retardant was synthesized and then added to the fatliquoring process to modify leather. The effect of NPI flame retardant on the flame-retardant properties of leather was investigated using Limiting Oxygen Index (LOI), smoke density, vertical combustion, cone calorimeter tests, and SEM. The results revealed that LOI of leather modified with NPI flame retardant increased with the increase of flame retardant. The flame and flameless combustion time of the modified leather was effectively reduced. Compared with unmodified leather, HRR of the modified leather with 6% NPI flame retardant decreased from 80.32 MJ/m^2 to 63.45 MJ/m^2; the peak HRR dropped from 108.71 MJ/m^2 to 77.23 MJ/m^2. Moreover, the fire growth index of the modified leather with 6% NPI flame retardant is close to half of that of the unmodified sample. The results certified the enhancing effect of NPI flame retardant added in the fatliquoring process on flame retardancy of leather samples.*

KEYWORDS: *Leather modified; Nitrogen-phosphorus; Fatliquoring process; Flame resistance.*

INTRODUCTION

The quality of the leather is affected by animal species, growing environment, and region. From raw leather to finished leather, including a series of processing, the thickness and composition of leather products are also changing, which leads to the change of flame-retardant properties of leather. Fatliquoring is an important process in leather processing, has a significant impact on the handle and mechanical property of leather [1]. Fatliquoring agents mainly include natural fatliquor and synthetic fatliquor. Regrettably, the addition of a fatliquoring agent can significantly reduce the flame-retardant property of leather and limit its practical application [2-10].

Adding flame retardant to leather products is a common and effective method to improve the flame-retardant properties of materials [11-13]. *Li et al.* [14] prepared a nanocomposite from the Intumescent Flame Retardant (IFR) and montmorillonite modified by Cetyl Trimethyl Ammonium Bromide (CTAB) and collagen.

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The results showed that the nanocomposite has good synergistic effect for enhancing the flame retardance of leather. Sanchez-Olivares et al. [15] studied the effect of sodium montmorillonite (Na^+Mt) on thermal, flame retardant and mechanical properties of semi-finished leather added during retaining process. In our previous work, phosphorus flame retardant, nitrogen and phosphorus intumescent flame retardant, nitrogen and phosphorus flame retardant were added in leather retanning process, respectively. Effects of the flame retardants on leathers have been investigated [16]. *Ma et al.* prepared modified zanthoxylum bungeanum Maxim Seed Oil /stearate-layered double hydroxide (MZBMSO/s-LDH) [17] and erucic acid modified montmorillonite/modified rapeseed oil (EA-Mt/MRO) [18] as leather fatliquoring agent. Both kinds of leather treated with MZBMSO/s-LDH and EA-Mt/MRO had improved flame retardancy, respectively [19-28].

In this work, Nitrogen-Phosphorus Intumescent (NPI) flame retardant is synthesized and added in fatliquoring process of leather. The NPI flame retardants are halogen-free, emits very low smoke or toxic gas when burning [29]. The effect of NPI flame retardant on the flame-retardancy of leather samples was investigated in detail using Limiting Oxygen Index (LOI), smoke density, vertical combustion and cone calorimeter tests, and SEM [30-33].

EXPERIMENTAL SECTION

Preparation of NPI flame retardant

The preparation method of Nitrogen-Phosphorus Intumescent (NPI) flame retardant refers to our previous work. The experimental steps are as follows: $(CH_3O)_2POH$ and acrylamide were added into the three bottles respectively. After the acrylamide was completely dissolved, sodium methoxide was added slowly. 3-dimethoxyphosphoryl propionamide was obtained after 3 h reaction. Continue to raise the temperature and adjust to pH 6.5-7.0 with 10% anhydrous sodium carbonate solution. The target product N-hydroxypentyl aldehyde-3-dimethoxyphosphoryl propionamide.

Fatliquoring process

The leather was added to the same mass of water, 11% synthetic fatliquoring agent (Shanghai General Chemical Factory) was added, and the reaction time was retained 40 min at 40 °C. For comparison, 0, 2, 4, 6, and 8% NPI flame retardants were added to the above system respectively. After stirring for 40 minutes, 100% water was added; the reaction was carried out at 50 °C for 60 minutes. Then, 1.5% formic acid was added into the above system (three times with an interval of 10 min) and the reaction was stirred for 10 min. Wash the product leather twice with water, take it out and hang it to dry.

Characterization and measurement

Limiting Oxygen Index (LOI) tests were obtained at room temperature according to ASTM D2863-97. The smoke was generated by burning the leather sample in the smoke density box. The measured smoke density was the maximum smoke density within 3 minutes and the time to reach the maximum smoke density. The vertical combustion test was to burn the sample in a 38 mm flame for 12 s, and measure the flame burning time and flameless combustion time after the combustion source is removed. Cone calorimeter test of the sample carried out using a cone calorimeter device CCT (Mo Otis Combustion Technology, China) at an incident heat flux of 50 kW/m^2. The morphology of leather was tested by KYKY3800B Scanning Electron Microscope (SEM, Beijing Zhongke Keyi Co., Ltd).

RESULTS AND DISCUSSION

The data in the Fig. 1 showed that with the increase of flame retardant dosage, the Limiting Oxygen Index (LOI) also increased gradually, indicating efficient flame retardancy [20]. When the amount of flame retardant was 8%, the flame retardant effect was the best, and the oil in leather was relatively less. When leather is burned, the flame retardant releases NH_3 and N_2, which dilutes the oxygen concentration in the surrounding air. At the same time, phosphate ester decomposes into phosphoric acid during combustion, which is dehydrated into metaphosphoric acid. Metaphosphoric acid polymerizes to produce polymetaphosphoric acid (in a viscous liquid film) covering the surface of solid combustible materials. Moreover, both phosphoric acid and polymetaphosphoric acid are strong acids, which can dehydrate and carbonize polymers and form carbon films. The liquid and carbon film can isolate air and improve the LOI of leather [34].

It can be seen from Table 1 that with the increase of NPI flame retardant, the maximum smoke density of the modified leather first increased and then decreased.

Table 1: Smoke density data of leather with different flame retardant dosage.

Amount of flame retardant (%)	0	2	4	6	8
Maximum smoke density (%)	35	38.5	42	36	40
Time to reach maximum smoke density (s)	120	180	180	180	180

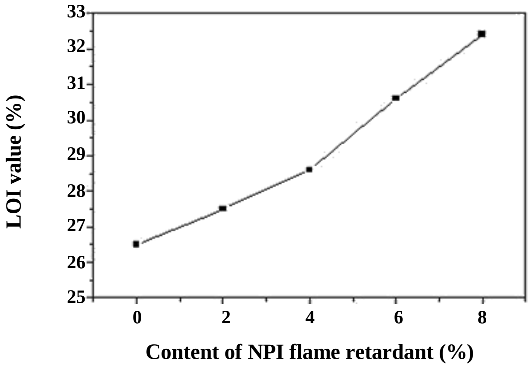

Fig. 1: The LOI values of leather samples.

This is because the intumescent flame retardant released part of the gas during combustion, resulting in an increase of smoke density. When the amount of intumescent flame retardant continues to increase, the compactness of the carbon layer produced by combustion increases, and the smoke emission is difficult, thus reducing the smoke density. Compared with unmodified sample, the time for the modified leather samples to reach the maximum smoke density was effectively prolonged.

Table 2 displays vertical combustion data of leather samples. Compared with the unmodified leather, the flame combustion time of leather modified with NPI flame retardant was effectively reduced. When the amount of flame retardant was 2, 4, 6, and 8%, the flame combustion time of modified leather samples was 5.6, 27.3, 9.1, and 23.1 s, respectively. At the same time, the flameless combustion time of modified leather samples decreased to zero. This is due to the fact that in the process of combustion, NPI flame retardant can carbonize leather to form a thick carbonization layer, which makes it difficult to spread the flame. Generally speaking, flame and flameless combustion time should be considered to evaluate the flame retardant properties of leather samples. The experimental results show that the flame retardant properties of leather samples modified with NPI flame retardant in the fatliquoring process are significantly improved.

The cone calorimeter test data of leather samples are shown in Table 3. Because the test conditions simulate the real fire, the cone calorimeter test can effectively evaluate the flame retardancy of leather samples [35, 36]. The flammability and smoke of the samples were quantitatively analyzed by cone calorimeter test [37, 38].

The cone calorimeter test items of unmodified leather and leather modified with 6% content of NPI flame retardant mainly include ignition time, Heat Release Rate (HRR), peak HRR, total Smoke Production (TSP), char yield, time to peak (t-peak) HRR, Average Effective Heat of Combustion (AEHC), and fire growth index.

It can be seen from Table 3 that the ignition time of leather, with 6% NPI flame retardant is close to that of unmodified leather. After adding NPI flame retardant in fatliquoring process, HRR of the leather decreased from 80.32 to 63.45 MJ/m^2; the peak HRR dropped from 108.71 to 77.23 MJ/m^2; the t-peak HRR increased from 16 s to 24 s. The results show that NPI flame retardant can effectively inhibit the heat release rate of leather and delay the time when the heat release rate reaches the peak value, and it can also reduce the peak value of heat release rate. The total smoke released by modified leather was slightly more than that of unmodified leather, which was beneficial to improve the flame retardancy of leather. In addition, the char yield of the modified leather samples was also greatly improved. The fire growth index of leather modified with 6% NPI flame retardant is close to half of that of unmodified sample, which shows that NPI flame retardant has strong performance of inhibiting leather combustion. AEHC of the modified leather increased from 17.23 to 17.42 MJ/kg. It is concluded that the NPI flame retardant may be used for leather in the form of condensed phase.

Fig. 2 (a and b) shows SEM of unmodified leather after combustion at 200 °C and 300 °C, respectively. When the temperature increased from 200 °C to 300 °C, the adhesion between the fibers of the unmodified leather sample was enhanced and a large amount of carbon was formed on the surface. Fig. 1 (c and d) shows SEM of leather modified with 6% NPIFR after combustion at 200 °C and 300 °C,

Table 2: Vertical combustion data of leather samples.

Amount of flame retardant (%)	0	2	4	6	8
Flame combustion time (s)	35.7	5.6	27.3	9.1	23.1
Flameless combustion time (s)	84.6	0	0	0	0

Table 3: The cone calorimeter test data.

Properties	Ignition time (s)	HRR (MJ/m^2)	Peak HRR (MJ/m^2)	TSP (m^2)	Char yield (%)	t-peak HRR (s)	AEHC (MJ/kg)	Fire growth index ($MJ/m^2.S$)
unmodified leather	77	80.32	108.71	12.3	15.23	16	17.23	6.79
modified leather	78	63.45	77.23	13.4	27.32	24	17.42	3.22

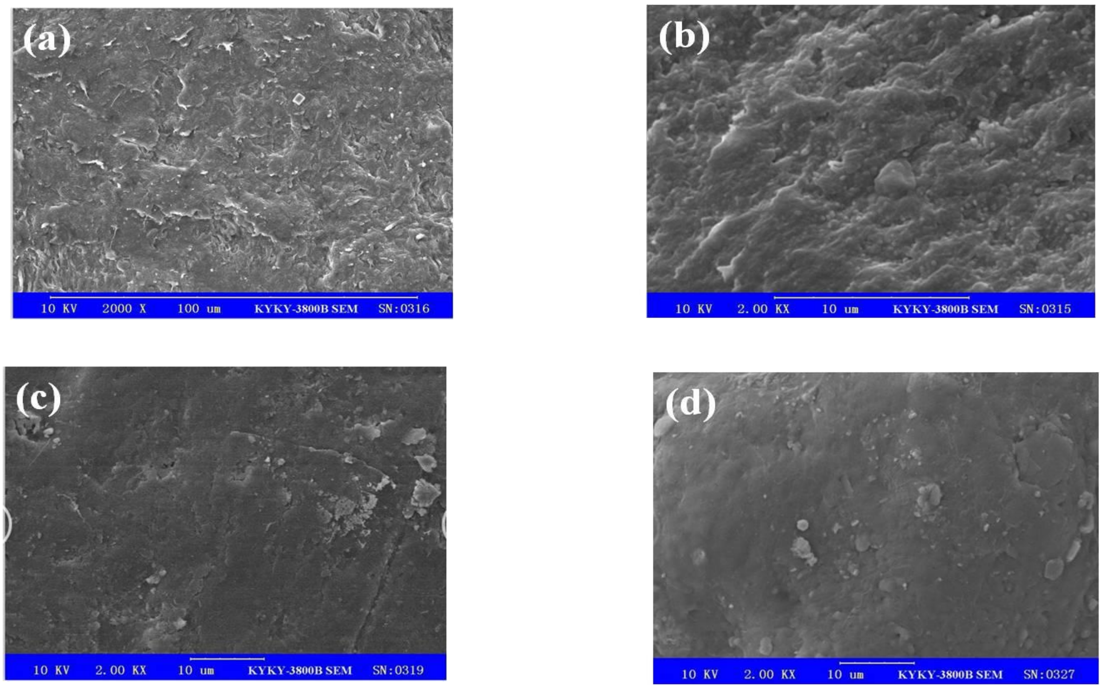

Fig. 2: SEM of leather samples after combustion at 200 and 300 °C.

respectively. It can be seen that from 200 °C to 300 °C, the carbon produced on the leather surface modified with NPIFR increases greatly, and the carbon forming density is enhanced. This is due to the fact that NPIFR is applied in fatliquoring process, which not only does not reduce the absorption of fatliquoring agent for leather samples, but also makes the fatliquor disperse evenly. The carbon amount and carbon layer on the surface of the sample are denser after combustion. The density of carbon content will enhance the flame retardancy of the material [39-47].

CONCLUSIONS

In order to improve the flame retardant property of leather, NPI flame retardant was synthesized and then applied to the fatliquoring process. The flame-retardant properties of the leathers with and without NPI flame retardant were investigated. Through LOI, smoke density, vertical combustion, cone calorimeter test, and SEM, it can be concluded that leather modified with NPI flame retardant in fatliquoring process displays high flame retardancy.

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