Synthesis and Application of a Novel Functional Material as Leather Flame Retardant

by

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Abstract

A novel leather flame retardant was successfully synthesized from pentaerythritol, phosphorus oxychloride, melamine and tetrakis-hydroxymethyl phosphonium chloride (THPC) by three steps. Its structures and properties were characterized by FT-IR, elementary analysis, mass spectrometry, DSC and TG. It was applied to the manufacture of flame-retardant leather. The flame-retardant properties were investigated by the Limit Oxygen Index (LOI) test and Vertical Flame test. The effects of the flame retardant on physical-mechanical and handle properties of leather were evaluated at different conditions. The results show that this novel flame-retardant material can effectively inhibit leather burning, increase leather thermal stability and has effective flame retardant property. Furthermore, it has good synergistic effect for improving leather properties like fullness, softness, grain tightness, thus can meet requirements for leather flame-retardant technology.

Introduction

Leather is a kind of materials closely related to people's daily lives and widely used in the manufacture of forest fire prevention equipment, automobiles, home and office furniture where fire prevention is of vital importance. In order to satisfy customers' requirements and government regulations, it is necessary to increase the flame-retardant property of leather. But now, research on high performance, non-toxic, durable flame-retardant materials applied to leather is seldom reported yet. The majority of products presently used in leather industry are derived from the plastic, rubber and textile industries, and these fire retardants can't completely satisfy the requirements for the leather processing.[1] So, it is an urgent problem to study and develop better fire retardants which can be used in leather industry.

The Intumescent Flame Retardant (IFR) has become irresistible focus around the world in recent years owing to its adiabaticity, oxygen-insulation, smoke-restraint and no corrosive gas produced.[2,3] With the development of IFR, the new type of phosphorus-nitrogen (P–N) flame retardant is becoming a research focus[3,4] because of its outstanding properties like good thermal stability, higher limited oxygen index. Applying it to fire prevention of leather industry offers a promising technology for improving the flame retardant performance of leather.[5] However, most of IFRs have some obvious weaknesses such as poor compatibility and low reaction activity with leather fiber, thus affect some properties of leather such as physical-chemical and handle properties. THPX (mainly including THPC and THPS) is a special kind of tetrakis-hydroxymethyl phosphonium salts and has good fire retardancy and tanning properties.[6] Therefore, by introducing THPX into the molecular structure of IFR, it can not only enhance its reaction activity, but also can increase its cross-linking ability with leather fiber,[7] and thus effectively improve its performance in leather application.

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In this paper, an attempt has been made toward the development of a multifunctional material, which can not only meet the requirements for leather flame-retardant technology, and can endue leather with better performance.

EXPERIMENTAL

Materials

All the materials used in this study were commercially available. Pentaerythritol (CP), melamine (AR) and dichloromethane (AR) were all purchased from Kelong Chemical Reagent Factory (Chengdu, China). Phosphorus oxychloride (AR) and tetrakis-hydroxymethyl phosphonium chloride (85%), generally abbreviated as THPC, was supplied by Xiya Chemical Industry Co. Ltd. (Shandong, China). Anhydrous aluminum chloride (AR) was provided by Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). The one millimeter-thick picked pigskins were obtained from Lishen Leather Limited Company (Chengdu, China).

Synthetic Routes of the Compound C

Preparation of Pentaerythritol Phosphonyl Dichloride (A)

Phosphorus oxychloride, pentaerythritol and anhydrous aluminum chloride (as the catalyst) were mixed in a three-neck flask and stirred for 2.5 hours at 75°C. The obtained suspension was filtered after cooled to the room temperature, and then the solid residue of filtered mixture was washed three times by dichloromethane and dried under an infrared lamp. The compound A was obtained.

Preparation of Pentaerythritol Biphosphorate Melamine Salt (B)

Melamine, compound A and distilled water were mixed in a three-neck flask, stirred for 2.5 hours at 80°C. The white suspension was filtered after cooled to the room temperature, and the solid residue was washed by distilled water and then dried under an infrared lamp. The compound B was obtained.

Preparation of THP-Melamine Phosphate Salt (C)

THPC and distilled water were put into a three-neck flask, the pH of the solution was adjusted to 6 with 5% concentration of sodium hydroxide, then the compound B was slowly added into the mixed solution, then heated to the required temperature and stirred for 3.5 hours. The obtained suspension was filtered after cooled to the room temperature, and then the solid residue was washed by distilled water and dried under an infrared lamp. Thus compound C was obtained.

Characterization and Performance Tests

FT-IR Test

The samples from compound A, B, C were respectively ground with KBr and made into pellets, then scanned with IR detector. The data in the wavelength range of 400-4000 cm^{-1} were recorded from a FT-IR-670 spectrophotometer from Thermo Nicolet Corporation, USA.

MS and Elemental Analysis Tests

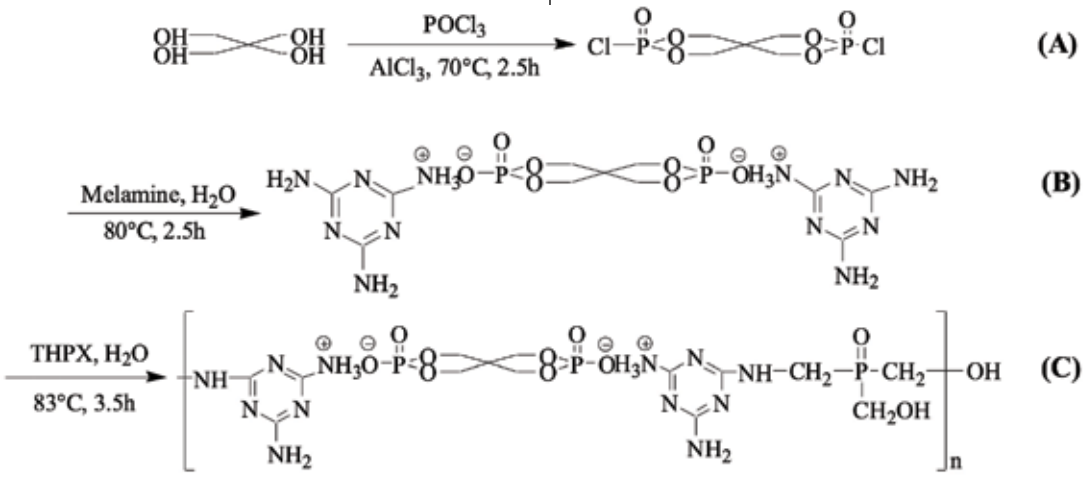
Mass analysis was carried out using a GCMS-QP 2010 instrument produced by Shimadzu Corporation (Japan) with ESI source and mass range of m/z 100-1500. The samples were dissolved in a mixture of methanol and acetonitrile solution. Elemental analysis was performed on EURO EA 3000 from Euro vector S.P.A, USA.

TG and DSC Tests

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

LOI and Vertical Combustion Tests

The flame-retardant leathers were produced from pigskin treated by compound C at levels of 0%, 5%, 8% and 10% (relative mass of skin weight). The pigskin was treated by the flame retardant according to the processing method given by Jing Li *et al*.[8] The leather treated with 0% flame retardant was



Scheme 1. The synthetic routes of the compound C.

used as a contrastive sample (blank sample). Five leather samples (140 × 52 mm) were taken from flame-retardant leather and were used for parallel tests according to OI standard method ASTM D 2863-77. Five leather samples (317.5 × 51 mm) were used for parallel tests according to vertical combustion 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 combustion test was conducted by a CZF-3 tester from Shangyuan Analysis Instrument Co. Ltd, China.

Measurement of Leather Softness

Softness measurement of leather was carried out using a GT-303 leather softness tester. Samples were conditioned at 20 ± 2°C and relative humidity of 65 ± 2% over a period of 48 hours before tested. Measurements were carried out at 5 locations within the sampling area and reported as average values with the higher value indicating higher softness.

Evaluation of Physical-mechanical and Handle Properties of Leather

Samples for various physical tests from experimental leathers were obtained as a standard method from QB/T 2710-2005. Samples were conditioned at 20 ± 2°C and relative humidity of 65 ± 2% over a period of 48 hours before test. Physical properties such as tensile strength, tear strength, elongation at break were examined. The evaluation of organoleptic property (handle and visual examination) was carried out according to softness, fullness, grain tightness. Samples were rated by experienced tanners on a scale of 1-10 for each functional property. Higher value indicates better property.

RESULTS AND DISCUSSION

FT-IR Analysis of Compound A

Figure 1 shows the main absorption peaks of compound A: the peak at 1310 cm^{-1} is the stretching vibration of P=O, P–O–C stretching vibration band is observed at 1028 cm^{-1}, the absorption peak at 550 cm^{-1} corresponds to the bond of P–Cl. The characteristic absorption peaks shown in the above spectrum are identical with the other reports[9] and the results indicate that compound A has been synthesized successfully as expected.

FT-IR Analysis of Compound B

By comparing Figure 2 with Figure 1, it can be seen that the absorption peak at 550 cm^{-1} from the P–Cl has disappeared while the –C=N characteristic peak of melamine appears at 1691 cm^{-1}. The absorption peaks at 3300~3500 cm^{-1} correspond to the characteristic peaks of $–NH_2$ and the stretching vibration peaks of $–NH_3^+$ are observed at 3000~3300 cm^{-1} which is coincident with the other reports.[10] The results indicate that compound B has been synthesized successfully as expected.

FT-IR Analysis of Compound C

As shown in Figure 3, it can be seen that the characteristic peak of P–O–C stretching vibration (1026.65 cm^{-1}) and the –C=N characteristic peak of melamine (1667.40 cm^{-1}) exist at the spectrum above, while the absorption peaks of $–NH_2$ and $–NH_3^+$ (3000~3500 cm^{-1}) turn into two broad peaks which are attributed to overlap effect of –OH, $–NH_2$, $–NH_3^+$ each other. Besides, the P–C stretching vibration band (1386.53 cm^{-1}) is observed. The above results indicate that THPC and compound B are successfully combined as expected.

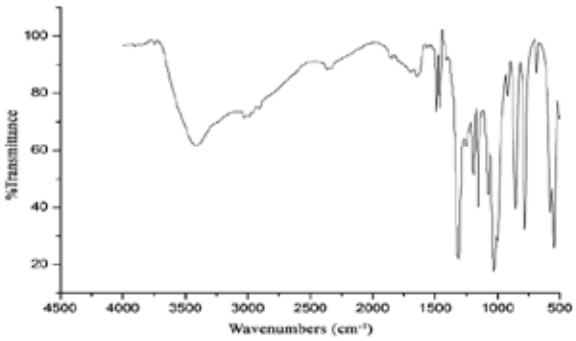


Figure 1. The FT-IR spectrum of compound A.

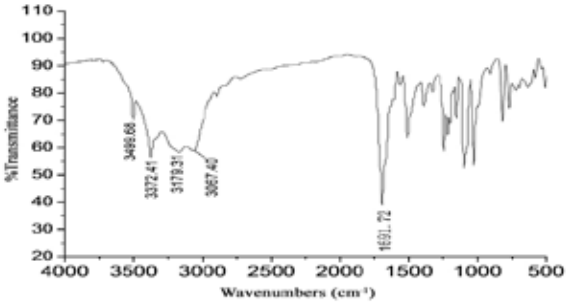


Figure 2. The FT-IR spectrum of compound B.

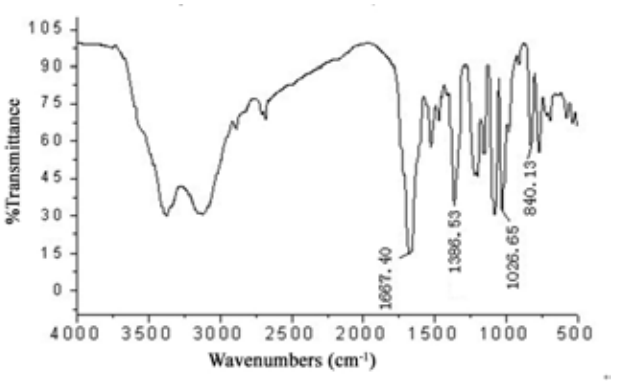


Figure 3. The FT-IR spectrum of the compound C.

MS and Elementary Analysis of the Compound C

From Figure 4, it can be inferred that the m/z = 636.86 is the molecular ion peak $[M+H]^+$ of compound C which is resulted from dehydration reaction between compound B and THPC. Its main fragment ion peaks such as m/z = 513.10 (compound B), 127.37 (melamine) and 387.04 are observed at the spectrum. The m/z = 387.04 corresponds to ion peak of the molecule fragment obtained by compound B losing a molecule of melamine. The results of elementary analysis of compound C are as follows: C 26.52% (26.75%), H 6.41% (6.21%), N 26.31% (26.75%). Values in brackets are theoretical calculation results. Based on the above analysis, it further indicates that the compound C has been synthesized successfully as expected.

DSC Analysis of Compound C

As shown in Figure 5, the DSC curve of compound C has three endothermic peaks: the first peak which appears at about 100°C may be the endothermic process from its surface water volatilization. The second peak appears at about 326°C, in this process, the compound C may be decomposed into compound B and hydroxymethyl-phosphonium (THP). The last peak is at about 466°C, in this stage, the compound B is further decomposed into phosphorous compounds and nitrogen compounds (melamine) . The phosphorous compounds have a catalytic dehydration and charring effect,[11] while the melamine mainly plays a producing gas role at higher temperature and the noncombustible gases such as NH_3, N_2 and H_2O may be released out.[12,13] The above analysis reveals the compound C with P–N structure has a good synergistic effect on improving flame retardant function.

TG Analysis of Leather and Flame Retardant Leather

As shown in Figure 6 and Table I, compared with the untreated leather at each stage ($T_{5\%}$, $T_{10\%}$, $T_{50\%}$ and T_{max}), the degradation temperatures of flame-retardant leather have obviously increased, the temperature of maximum weight loss rate increases from 350°C to 400°C, while the residual mass rate of flame-retardant leather under 700°C increases from 29.3% to 41.2%. The results indicate that the fire-retardant material can effectively inhibit the leather burning and reduce its mass loss, therefore effectively improve leather thermal stability and flame-retardant effect.

Results of LOI Test from Flame-retardant Leather

As seen from the results of Table II, the LOI of leather samples treated with compound C all increase with increasing content from 5% to 8% and 10%, and the highest LOI reaches 32.9%. The results show that the compound C can satisfy the requirements for flame-retardant leather.

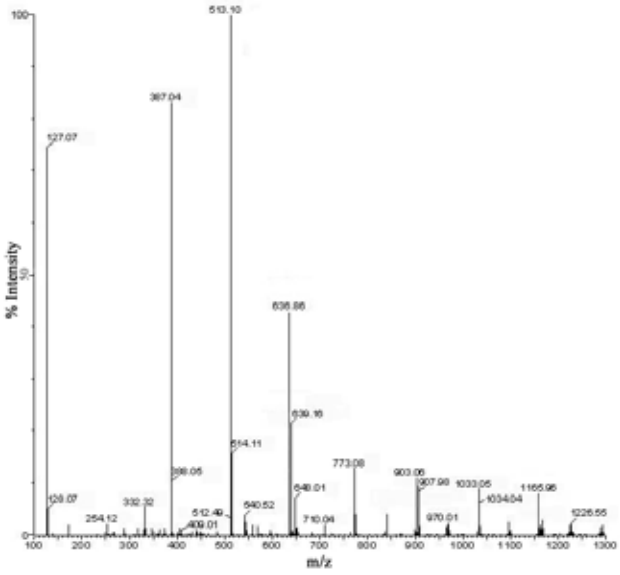


Figure 4. The MS spectrum of the compound C.

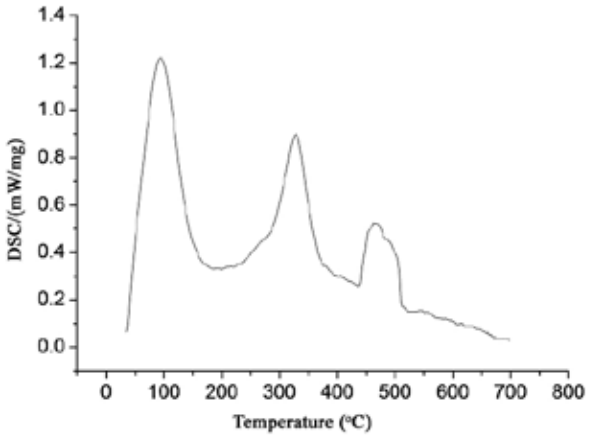


Figure 5. The DSC curve of compound C.

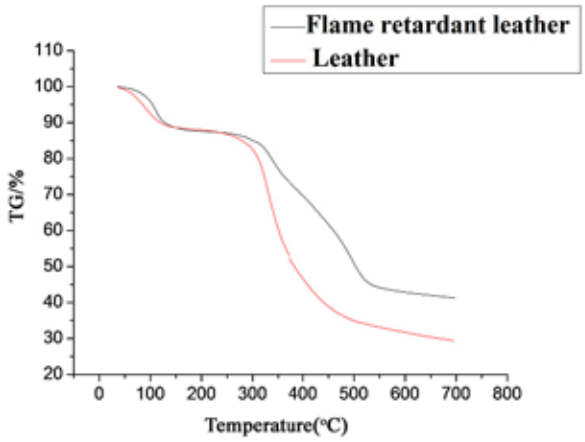


Figure 6. TG curves of leather and flame- retardant leather.

TABLE I
TG results of leather and flame-retardant leather.

Sample	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	T_{max} (°C)	W_{700} (%)
Untreated leather	80.3	110.3	380.3	350	29.3
Flame-retardant leather	100.7	120.7	500.7	400	41.2

***Note:** $T_{5\%}$, $T_{10\%}$, $T_{50\%}$ represent the weight loss temperature of samples where the percentage weight loss is 5%, 10%, 50%, respectively. T_{max} is the temperature of the maximum weight loss rate. W_{700} is the residual mass rate at 700°C.

TABLE II
The results of LOI test.

Content of compound C	OI(%)
0%	26.1
5%	29.5
8%	31.3
10%	32.9

Results of Vertical Combustion Test from Flame-retardant Leather

Significant results can be observed from Table III, after the flame retardant was added into leather, the flame combustion time, the flameless combustion time, the length of carbonation and the mass loss rate all decrease obviously with increasing content of compound C. When adding 10%, these data will achieve the lowest value. The results show compound C can obviously increase non-flammability of leather.

Results of Physical and Organoleptic Properties of Flame-retardant Leather

The results of physical property of leather treated with compound C are shown in Table IV, while organoleptic properties are presented in Table V. From Tables IV and V, it can be seen that the physical strength and thickness of leather increased with increasing amount of compound C, while the elongation rate at break decreased slightly. Because it has better compatibility and higher reaction activity with leather fiber, it takes a positive role in improving the leather properties such as fullness, grain tightness and grain smoothness. On the other hand, from Tables IV, it can be seen that it has a little effect on softness when the addition amount is less than 8%, the treated leathers can still maintain softness, fullness properties. It has been found from our study that compared with THPC, the compound C will not release free formaldehyde, thus has better environmental benefits in leather processing.

CONCLUSION

The results of FT-IR show that the main characteristic absorption peaks of compound C appear at the relevant positions in spectrum. Combining with the MS and elementary analysis, it was proved that compound C has been synthesized successfully as expected. The novel material with P–N–C structure was used to produce flame-retardant leather; it can effectively improve non-flammability of leather and has good flame resistance effect. At the same time, because it has a more environmentally friendly characteristics and higher reaction activity with leather fiber, the material also has a good synergistic effect on improving the comprehensive performance of leather such as physical-mechanical and handle properties, etc. Therefore, as a kind of non-toxic, durable, multifunctional flame retardant, it can completely meet the technical requirements of flame retardant for leather.

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TABLE III
Vertical flammability test data for the flame-retardant leather.

Content of C (%)	Flame combustion time (s)	Flameless combustion time (s)	The length of carbonation (cm)	Mass loss rate (%)
0	35	60	7.5	6.8
5	15	30	4.8	4.4
8	10	21	3.5	3.1
10	4.2	6	2.1	1.3

TABLE IV
Physical properties of leather treated with compound C.

Content of C(%)	Tensile strength (N/mm^2)	Tear strength (N/mm)	Elongation at break (%)	Softness (mm)
0	14.20	32.00	65.22	5.82
5	15.10	33.70	64.52	5.76
8	15.78	34.62	64.15	5.70
10	15.91	34.92	63.55	5.37

TABLE V
Organoleptic properties of leather treated with compound C.

Content of C (%)	Thickness increment (%)	Fullness	Grain tightness	Grain smoothness
0	0	5	5	5
5	5.21	6	6	6
8	7.34	7	7	7
10	7.55	8	7	7

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