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EFFECT OF PHYTIC ACID ON ANTI-FLAMMABILITY IN LEATHER PRODUCTION

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Abstract: *Anti-flammability properties are increasingly demanded in leathers used for upholstery applications in a variety of industries, including furniture, aerospace, automotive and motorcycles. Traditionally, halogen-based compounds have been widely used in the commercial leather industry to impart flame retardant properties. However, due to increasing environmental regulations and the unfavorable environmental and health effects of halogen-based products, bio-based flame-retardant alternatives have attracted great interest in recent years. Considering this, the present study aims to evaluate the efficiency of phytic acid-based retanning agents in enhancing the flame-retardant properties of leather. To investigate the influence of phytic acid on leather flammability, five novel retanning agents were synthesized through various combinations of phytic acid with pentaerythritol, 1,2,3,4-butanetetracarboxylic acid (BTCA), citric acid, and glycerol. These synthesized compounds were applied during the retanning stage of chrome-tanned leather at concentrations of 5% and 10%, calculated based on leather weight. Laboratory analyses conducted on the treated leathers revealed that, with the exception of the formulation containing phytic acid, glycerol, and citric acid, all synthesized phytic acid-based retanning agents contributed to improved flame retardancy and enhanced hydrothermal stability. These findings suggest the potential of phytic acid-based systems as environmentally friendly alternatives for producing flame-retardant leather materials.*

Key words: *phytic acid, anti-flammability, flame retardancy, retannage, leather*

1. INTRODUCTION

Upholstery leathers are used in areas like furniture, aviation, automotive, and motorcycles, where properties such as light fastness, abrasion resistance, and flame retardancy are required [1]. Leather is preferred for its durability, breathability, and abrasion resistance [2]. However, despite its strengths, leather remains flammable due to its natural polymeric structure containing carbon, nitrogen, oxygen, and sulfur [3]. Additionally, chemicals used in tanning, retanning, dyeing, fatliquoring, and finishing can increase its flammability [2].

To expand leather's use in technical fields such as maritime, aviation, and automotive, it must meet certain flame retardancy levels [4]. The automotive industry enforces special flame resistance standards [3]. However, current flame-retardant methods in leather production are limited. These methods typically fall into three categories: halogenated compounds (e.g., chlorinated, brominated), halogen-free options (e.g., ammonium phosphate, organophosphorus), and nanocomposites/minerals [1].

Halogenated flame retardants are cost-effective but have been banned in textiles due to environmental and health risks [5]. As a result, industries are shifting toward safer alternatives. In leather, research has focused on phosphorus-nitrogen compounds, nanocomposites, fullerenes [6], and mineral-based flame retardants—all showing promising results. These compounds are mostly applied during retanning and finishing, and occasionally during fatliquoring.

Bio-based, renewable substances are also gaining attention. Natural materials like chitosan, lignin, tannic acid, deribonucleic acid, and phytic acid are being explored for flame retardancy in textiles and polymers. Phytic acid, derived from beans, grains, and oilseeds, contains negatively charged phosphate groups that interact well with metal ions and positive compounds [7]. It has shown positive flame-retardant effects in protein-based fibers like wool and silk [5].

Though not previously used in leather, which also has a protein structure, phytic acid is expected to bond strongly with leather's NH_3^+ groups. This study builds on prior research where phytic acid-based esters improved flame retardancy in wool [5]. The goal was to synthesize flame retardants from phytic acid combined with pentaerythritol, BTCA, glycerol, and citric acid, and evaluate their effects on the flame resistance and properties of chrome-tanned leather.

2. MATERIAL AND METHODS

2.1. Materials

Within the context of this study, phytic acid (50% aqueous solution, MW 660 g/mol), pentaerythritol (conc. 99%, MW 136.15 g/mol) and 1,2,3,4-butanetetracarboxylic acid (BTCA) (conc. 99%, MW 234.16 g/mol) were used in the synthesis of flame retardant retannage agents. Also, citric acid (conc. 99%, MW 192.124 g/mol) and glycerol (conc. 90%, MW 92.1 g/mol) were used in the synthesis process with these substances. To occur a comparison group in leather applications, a commercial flame retardant was used as blind. Six wet-blue sheepskins used in the application of the synthesized chemicals were supplied by Akaylar Deri Inc.

2.2. Methods

2.2.1. Synthesis of Flame Retardant Retanning Agents

The synthesis process of the flame-retardant retanning agents is shown in Table 1. It was conducted using a single-neck flask connected to a cooler and heated with a magnetic stirrer. Glycerin, used to achieve the high temperatures required for esterification, filled the pot in which the reaction flask was placed.

Table 1. *Synthesis process of flame-retardant retanning agents*

	Mol	**Weight (g)**	**Temperature (C°)**	**Time (s)**
PAno1				
Phytic Acid	0.01	13.2	130	
Pentaerythritol	0.03	4.08	130	120
BTCA	0.03	7.02	130	30
PAno2				
Phytic Acid	0.02	26.4	130	
Pentaerythritol	0.06	8.16	130	120
Waiting 24 hours in the room temperature (23° C)				
BTCA	0.06	14.04	130	40

PAno3				
Phytic Acid	0.02	26.4	130	
Pentaerythritol	0.06	8.16	130	120
Waiting 24 hours in the room temperature (23° C)				
Citric acid	0.06	11.5	130	40
PAno4				
Phytic Acid	0.02	26.4	130	
Glycerol	0.06	6.1	130	120
Waiting 24 hours in the room temperature (23° C)				
BTCA	0.06	11.5	130	40
PAno5				
Phytic Acid	0.02	26.4	130	
Glycerol	0.06	6.1	130	120
Waiting 24 hours in the room temperature (23° C)				
Citric acid	0.06	11.5	130	40

After each reaction, the pH was adjusted to 4.5–5 with NaOH to make the products suitable for retanning.

2.2.2. Material Characterization Analysis

The quantity of solid substances of the synthesized products was determined by the Shimadzu MOC63 Moisture Analyzer.

Perkin Elmer brand Spectrum-100 model FT-IR+ATR spectrometer device was used in the structural determination of the synthesized flame retardants. IR spectra of the samples obtained in dried solid form were obtained after 4 scans using 2 cm^{-1} resolution power at 4500 - 600 cm^{-1} wavelength.

Differential Scanning Calorimetry (DSC) analysis was performed by Shimadzu DSC-60 Plus on the synthesized substances to examine the changes in their structures when they exposed to heat.

2.2.3. Retanning Processes with Flame Retardants

The PAno1 sample was excluded from retanning due to its unsuitable form, while the other four synthesized samples were used in the retanning of wet-blue leathers at the rates of 5% and 10% based on the leather weight from trial 1 to trial 8, respectively. Similarly, commercial flame retardant was used at the rates of 5% and 10% for trial 9 and 10. In the blank trial, the process was continued without using flame retardant as trial 11. The coding of leather trials can also be seen in Table 2.

2.2.4. Horizontal Flammability Test

The horizontal flammability test was carried out in accordance with ISO 3795 standard in SL-S33 Horizontal Burning Testing Device with the support of Sun Tekstil Inc.. In this test, the burning distance (mm) and burning seconds (min) are obtained and the burning speed rate (mm/min) is obtained.

2.2.5. Vertical Flammability Test

The vertical flammability test was carried out in accordance with the ISO 15025 standard on the SL-S18T Vertical Combustion Test Device with the support of TDU Defense and Trade Inc.

3. RESULTS AND DISCUSSION

3.1. Results of Solid Substances Determination

Five flame retardant synthesis samples were conducted, yielding light brown liquids as a result of the processes in Table 1. Water solubility was tested, as it's essential for wet finishing. PAno1 was eliminated due to poor solubility, and the remaining four samples were used for leather production trials. The results of the solid substances determination of the flame retardants PAno 2, PAno 3, PAno 4 and PAno 5 were found 70.1%, 69.4%, 71.4% and 70.8% respectively.

3.2. Results of Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR transmittance–wavenumber graph for pentaerythritol, BTCA, citric acid, and the 4 flame retardants is shown in Figure 1. The synthesized substances showed similar profiles to the analytes, with abundant C–O bonds, indicating their strong potential to bind effectively to leather.

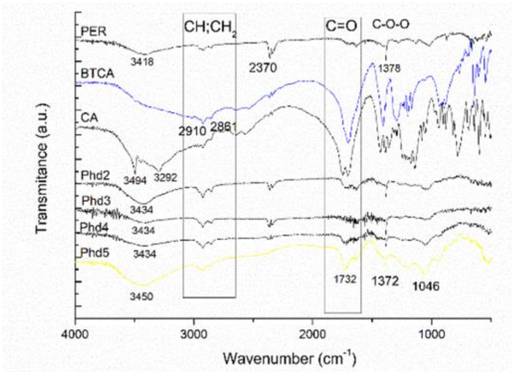

Fig. 1. *FTIR (transmittance-wavenumber) analysis graphic*

3.3. Results of (Differential Scanning Calorimeter) DSC Analysis

DSC analysis results are shown in Figure 2 as thermograms of phytic acid, pentaerythritol, citric acid, and the four synthesized substances. The synthesized flame retardants showed no broad endothermic transitions below 150 °C. Their decomposition temperatures ranged from 130–140 °C, indicating thermal stability and suitability for leather applications.

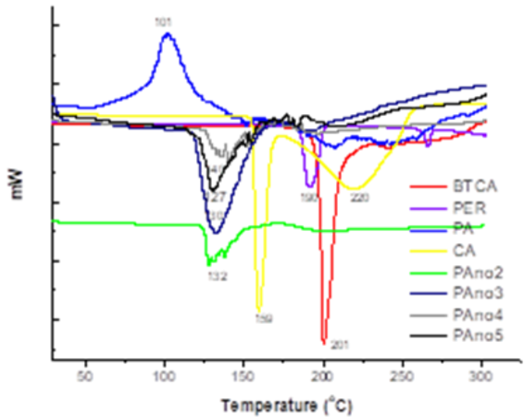

Fig. 2. *DSC (Differential Scanning Calorimeter) analysis graphic*

3.4. Horizontal Flame Retardancy Test Results

Burn tests showed all leather samples resisted flame, with none reaching the textile reference point—thus considered non-burning by standard. The blind trial (Leather 11) burned more than others. Leathers with commercial flame retardants (9 and 10) showed better resistance, especially at 10%. PAno2 samples (1 and 2) had similar performance, with better resistance at 10%. PAno3 leather at 5% (3) matched commercial flame retardants, but at 10% (4), it resembled the blind. PAno4 samples (5 and 6) showed the best performance, comparable to commercial flame retardants at both concentrations. PAno5 samples (7 and 8) performed better than the blind at 5% but worse than commercial; the 10% sample was closest to the blind. Overall, flame retardant samples approached the performance of commercial ones, though leather thickness and raw material properties also influenced burning behavior.

3.5. Vertical Flame Retardancy Test Results

The test showed no significant differences on the grain side of all leather samples. Only trails 7 and 8 burned through to the flesh side, likely due to their raw material properties, as also noted in the horizontal flammability test.

3.6. Shrinkage Temperature

The shrinkage temperatures of all the produced leathers are presented in Table 2, which reflects their hydrothermal stability. Upon examination of Table 2, it is evident that, with the exception of the leathers treated with the flame retardant from PAno5, the remaining samples exhibited significantly higher hydrothermal stability compared to the blind leather trial. Leathers numbered 7 and 8 demonstrated poorer hydrothermal stability than the blind leather, consistent with the results from the horizontal and vertical flame retardancy tests.

Table 2. *Shrinkage temperatures of leather trials*

Leather Trials	Shrinkage Temperature (C°)
Leather 1 (%5 PAno 2 sample)	138
Leather 2 (%10 PAno 2 sample)	136
Leather 3 (%5 PAno 3 sample)	134
Leather 4 (%10 PAno 3 sample)	133
Leather 5 (%5 PAno 4 sample)	135
Leather 6 (%10 PAno 4 sample)	135
Leather 7 (%5 PAno 5sample)	130
Leather 8 (%10 PAno 5 sample)	130
Leather 9 (%5 the commercial sample)	137
Leather 10 (%10 the commercial sample)	136
Leather 11 (blind)	132

4. CONCLUSIONS

Upon examination of the results obtained from the horizontal burning test, vertical flame retardancy test, and shrinkage temperature analysis, it was determined that the leather samples treated with the synthesized flame retardants designated as PAno 2, PAno 3, and PAno 4 exhibited fire retardancy behavior comparable to that of leathers treated with conventional commercial flame retardants. In contrast, the leather sample treated with the PAno 5 formulation demonstrated thermal and flammability characteristics more closely aligned with those of the untreated control (blind test) leather sample. Further evaluation of the physical properties revealed no significant variations attributable to the type or presence of flame retardants applied. This finding indicates that the incorporation of the synthesized flame retardants did not adversely impact the mechanical integrity or sensory quality of the finished leather.

In conclusion, the experimental flame retardants, synthesized through varying formulations involving phytic acid—a naturally derived, bio-based compound known for its efficacy in enhancing the flame resistance of protein-based and cellulosic substrates—demonstrated a favorable influence on both the flame retardancy and hydrothermal stability of chrome-tanned leathers. These results suggest that phytic acid-based formulations can serve as sustainable and effective alternatives to conventional flame retardants, offering environmental and performance-related benefits without compromising the essential qualities of leather materials.

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