Development of Bromine-Free Aluminum-Carboxymethyl Melamine MOFs As Hybrid Flame Retardants for Leather Application

Conference: 13th AICLST, Kolkata, 6–8 March 2026

Paper reference: TI-57/O

Printed pages: 182–184

Source: *Leather 2050: Challenges & Opportunities*, ILTA (2026)

Development of Bromine-Free Aluminum-Carboxymethyl Melamine

MOFs As Hybrid Flame Retardants for Leather Application

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Ref. No. TI-57/O

Abstract

The increasing restrictions on halogenated flame retardants, particularly brominated compounds, have created an urgent need for environmentally benign and high-performance alternatives in leather manufacturing. This study presents the development of a bromine-free aluminum–carboxymethyl melamine (Al-CMM) Metal–Organic Framework (MOF) as a hybrid flame-retardant system specifically engineered for leather applications. The nitrogen-rich carboxymethyl melamine ligand was synthesized and complexed with Al^{3+} ions under aqueous conditions to obtain a thermally stable MOF with high charforming capability. To enhance its processability and distribution, the MOF was wet-milled to sub-micron sizes and subsequently introduced into the leather matrix during the rechroming stage, ensuring uniform penetration across collagen fibrils.

The treated leathers were evaluated using horizontal flammability testing, revealing a maximum reduction of 18.2% in flammability at a 9% MOF offer level, without compromising the structural integrity of the leather. SEM–EDS mapping confirmed homogeneous MOF deposition throughout the cross-section, while ICP-OES studies demonstrated efficient exhaustion behaviour. Importantly, the physical and organoleptic properties of the treated leathers - softness, fullness, tensile strength, and grain smoothness - remained comparable to conventional chrome-retanned controls, indicating that the MOF does not adversely interfere with downstream post-tanning processes.

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The Al-CMM MOF system thus offers a sustainable, metal–organic route to flame-retardant leather manufacture, eliminating the environmental and toxicological concerns associated with halogen-based retardants. This work contributes a viable materialschemistry–driven solution for enhancing fire safety in automotive, upholstery, and speciality leather sectors, aligning with global sustainability mandates.

Keywords: Flame retardant, MOFs, Aluminum-CMM, Leather, Bromine-free, Fire safety.

1. Introduction

Leather is widely used in various applications, including automotive upholstery, furniture, footwear, and protective garments, where flame resistance is often a critical safety requirement1,2. Conventional flame-retardant treatments for leather predominantly rely on halogenated compounds3, particularly brominated additives, due to their high flame suppression efficiency. However, these materials pose significant drawbacks, including the release of toxic gases during combustion, environmental persistence, and adverse health effects on humans. Regulatory frameworks worldwide are increasingly restricting or banning brominated flame retardants, driving the search for safer and more sustainable alternatives.

Metal–organic frameworks (MOFs) have emerged as a versatile class of porous coordination polymers offering tunable chemistry, high thermal stability, and multifunctionality. Their potential in flame retardancy lies in their ability to combine metal centers with nitrogen-

rich organic ligands, enabling condensed-phase char formation and heat insulation mechanisms4,5. Despite extensive studies on MOFs in catalysis and gas storage, their application as flame retardants in leather processing remains underexplored.

This work addresses this gap by developing a brominefree aluminum-based MOF derived from carboxymethyl melamine (CMM), a nitrogen-rich ligand known for its inherent flame-retardant characteristics. The study focuses on the synthesis, characterization, leather application, and performance evaluation of the Al-CMM MOF, with an emphasis on sustainability, industrial compatibility without affecting the leather quality.

2. Methodology

2.1 Materials

Melamine, chloroacetic acid, aluminum salts, and standard leather processing chemicals were used as received. Chrome-tanned leathers were selected as the substrate for flame-retardant application to evaluate compatibility with existing industrial processes.

2.2 Synthesis of Carboxymethyl Melamine (CMM)

Carboxymethyl melamine was synthesized via controlled carboxymethylation of melamine using chloroacetic acid under aqueous conditions. The reaction introduced carboxyl functionalities while preserving the nitrogen-rich triazine backbone, enabling coordination with aluminum ions.

2.3 Synthesis of Al-CMM MOF

The Al-CMM MOF was prepared by reacting the synthesized CMM ligand with aluminum ions under controlled conditions in aqueous medium to form a stable coordination framework. The resulting MOF was separated by centrifugation, washed, and dried for further use.

2.4 Particle Size Reduction by Wet Milling

To improve penetration and uniform distribution within the leather matrix, the synthesized Al-CMM MOF was subjected to wet milling. A reduction in particle size was

achieved with increasing milling time, thereby optimizing the material for leather processing applications.

2.5 Leather Application Trials

The Al-CMM MOF was incorporated into leather during the rechroming stage, ensuring effective diffusion into the collagen fiber network. Different offer levels (up to 9% on shaved weight) were evaluated. Post-tanning operations were subsequently carried out using standard industrial recipes.

2.6 Flame Retardancy and Leather Property Evaluation

Flame retardancy was assessed using a horizontal flammability tester, measuring flame spread characteristics. Physical properties such as tensile strength, tear strength, softness, and fullness were evaluated using standard leather testing methods to ensure no deterioration in quality.

3. Results and Discussion

3.1 Characterization of CMM Ligand and Al-CMM MOF

Spectroscopic analyses confirmed successful carboxymethylation of melamine and coordination with aluminum ions. FTIR spectra showed characteristic shifts corresponding to metal–ligand bonding, while PXRD patterns confirmed the formation of a crystalline MOF structure. Thermal analysis revealed enhanced thermal stability, a critical requirement for flame-retardant performance.

3.2 Effect of Milling on Particle Size

Wet milling significantly reduced the particle size of the Al-CMM MOF below 500 nm, resulting in improved dispersion and penetration into the leather matrix. Finer particles facilitated uniform distribution, minimizing surface aggregation and enhancing functional efficiency.

3.3 Uptake and Distribution in Leather

Elemental mapping and cross-sectional analyses demonstrated effective uptake and homogeneous distribution of the Al-CMM MOF throughout the leather structure. Exhaustion studies using ICP-OES indicated efficient uptake of the flame retardant during processing, reducing chemical loss to wastewater.

3.4 Flame Retardant Performance

Flammability testing showed a progressive reduction in flame spread with increasing MOF concentration. At an optimal offer level of 9%, the Al-CMM MOF-treated leather exhibited a maximum reduction of 18.2% in flammability compared to untreated control leather. The flame-retardant action is attributed to the synergistic effect of aluminum ions promoting char formation and the nitrogen-rich melamine ligand releasing inert gases that dilute combustible volatiles.

3.5 Physical and Organoleptic Properties

The incorporation of Al-CMM MOF did not adversely affect the mechanical or aesthetic properties of leather. Treated leathers retained their tensile strength, softness, and fullness, comparable to the control samples, demonstrating that functional enhancement was achieved without compromising material quality.

3.6 Sustainability and Ethical Considerations

The developed system is free from halogens, particularly bromine, addressing major environmental and health concerns associated with conventional flame retardants. The aqueous synthesis route, efficient exhaustion, and compatibility with existing leather processing operations further enhance the sustainability profile of the technology.

4. Conclusion

A novel bromine-free aluminium–carboxymethyl melamine MOF was successfully developed and applied as a hybrid flame retardant for leather. The material demonstrated

effective flame retardancy, with up to an 18.2% reduction in flammability, while preserving essential physical and organoleptic properties. The use of a nitrogen-rich ligand and a non-toxic metal center provides an environmentally benign alternative to halogenated flame retardants. Importantly, the process is compatible with conventional leather manufacturing practices, ensuring ease of industrial adoption. This study highlights the potential of MOF-based systems as sustainable, ethical, and highperformance solutions for advanced functional leathers.

5. Reference

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