Development of Multifunctional Leather via Ionic Liquid-Mediated Polymerisation of Aniline

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ABSTRACT

Integrating electrical conductivity and flame-retardant properties into leather presents a transformative opportunity to broaden its application in advanced functional domains. This study introduces an innovative approach employing ionic liquid (IL)-assisted in-situ polymerization of aniline to fabricate leather with dual functionalities. Imidazolium-based ILs played a crucial role in modulating the size and morphology of polyaniline (PANI) during polymerization, facilitating its deep penetration and uniform distribution across the leather matrix. As a result, the electrical resistance of the leather was significantly reduced from 389.4 MΩ to 1.5 MΩ after three polymerization cycles. Furthermore, the PANI-modified leather exhibited a remarkable 82.8% reduction in flammability, attributed to the nitrogen-rich PANI structure that enhances char formation under combustion. Characterization techniques such as XRD, SEM, and XPS confirmed the uniform deposition and integration of PANI throughout the leather's cross-section. The findings demonstrate that IL-assisted PANI functionalization provides a scalable and cost-effective pathway to engineer multifunctional smart leathers, making them suitable for applications in wearable electronics, defence, automotive interiors, and flame-resistant gear.

Keywords: Polyaniline (PANI); Ionic Liquids (ILs); Electrically Conductive Leather; Flame Retardancy; In-Situ Polymerization

1. Introduction

Leather, a tanned and stabilized form of animal hide, is valued for its durability, comfort, and adaptability in numerous consumer and industrial products (Thomasset & Benayoun 2024). However, with the advent of advanced synthetics offering functionalities like conductivity, heat resistance, and electromagnetic shielding, conventional leather is increasingly challenged in certain markets, such as automotive interiors and wearable tech (Basak et al. 2024; Meyer et al. 2021).

Incorporating functional polymers into leather can bridge this gap. Among conducting polymers, polyaniline is notable for its tunable conductivity, chemical stability, and low production cost (Bhadra et al. 2009; Majeed et al. 2022). In its emeraldine salt form, PANI is conductive, and its nitrogen-rich backbone also contributes to flame-retardant behaviour by releasing non-flammable gases during combustion (Hatchett, Josowicz & Janata 1999). Previous attempts to integrate PANI into leather often suffered from poor penetration into the dense collagen network, leading to surface-only deposition and reduced performance.

Ionic liquids (IL)—salts that are liquid below 100 °C—can address this limitation (Cao, Xia & Chen 2018). Their ability to form ordered molecular assemblies allows them to act as "soft templates," controlling particle size and reducing agglomeration during PANI formation. This study explores IL-assisted in-situ polymerisation of aniline within leather, aiming for uniform PANI distribution and durable multifunctionality.

2. Materials and Methods

Salted sheepskins were processed into chrome-tanned or post-tanned leather substrates. Aniline hydrochloride served as the monomer, ammonium persulfate as the oxidant, and various imidazolium-based ILs as particle size modulators. PANI synthesis was first carried out in aqueous media to screen IL effects, then applied directly to leather in wet-end processing.

For in-situ treatments, leather was immersed in monomer–IL solution, followed by gradual oxidant addition under drum agitation. Trials compared polymerisation before post-tanning (BPT) and after post-tanning (APT), with cycle numbers ranging from one to five. Characterisation methods included standard ISO tests for mechanical properties and flammability tests per ISO 3795. Wastewater from the process was analysed for COD, solids content, and chromium levels.

3. Results and Discussion

3.1 Particle Size Control via Ionic Liquids

In the absence of ILs, PANI particles averaged over a micron in size. Incorporating ILs, particularly hydrogen sulfate-based variants, reduced the mean hydrodynamic diameter to ~100 nm. This fine particle size is essential for penetrating the leather fibre network. FTIR and XRD confirmed that ILs influenced particle size only without altering the chemical structure or crystallinity of PANI. Among the tested ILs, 1-methylimidazolium hydrogensulfate was confirmed to form PANI with the lowest particle size distribution.

3.2 Distribution of PANI in Leather

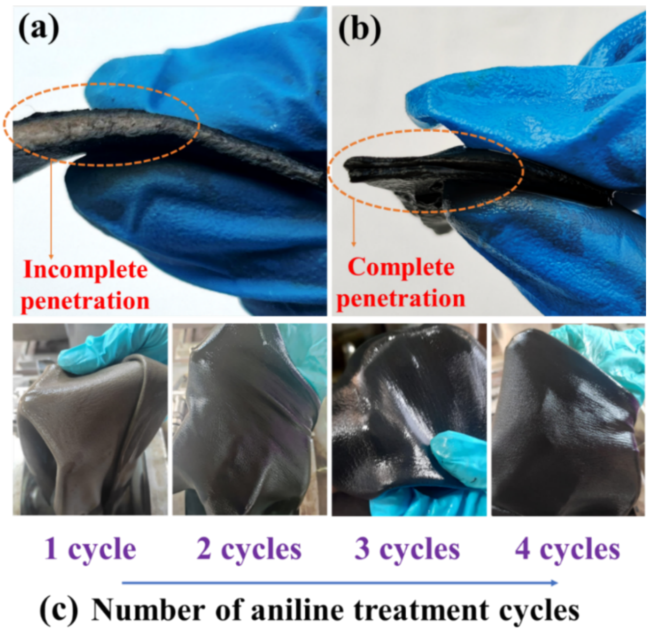

Figure 1. Photographic images (a) cross-section of aniline-treated leather without IL, (b) cross-section of aniline-treated leather with HS-IL and (c) Colouration of leather post-in-situ polymerisation of aniline.

Visual inspection showed that polymerisation without ILs led to uneven distribution, mostly at the grain and flesh surfaces. With IL assistance, colouration and PANI deposition were consistent across the full cross-section. Increasing the number of polymerisation cycles deepened the green hue associated with PANI loading. It was found that with 3 cycles of aniline treatment, the colouration was uniform across the cross-section, confirming the uniform distribution of the PANI across the skin matrix as shown in Figure 1.

3.3 Conductivity Performance

Electrical resistance decreased sharply with additional polymerization cycles. For BPT-treated leathers, resistance fell from hundreds of megaohms to 1.5 MΩ after five cycles. APT-treated leathers reached even lower values (~20 kΩ) but suffered from reduced color fastness due to surface-heavy deposition. BPT samples treated for two or three cycles offered the best balance between conductivity and wear resistance.

3.4 Physical and Organoleptic Properties

While tensile strength and softness remained within acceptable ranges, tear strength and grain crack load declined slightly after multiple treatments, likely due to the acidity of the polymerisation bath, since the oxidant addition makes the process liquor more acidic. PANI-treated leathers were heavier, indicating greater filling of the fibre structure. Visual evaluation confirmed even colouration, smooth grain texture, and—most notably—successful operation of capacitive touchscreens.

3.5 Flame Retardancy

Flammability testing revealed significant improvement in fire resistance. Three-cycle BPT-treated leathers self-extinguished after ignition, reducing the flammability degree by 82.8% compared to control leather. This performance stems from the release of nitrogenous gases and the formation of protective char during combustion.

3.6 Wastewater Evaluation

Effluent from the PANI process contained higher COD, TDS, and TSS than controls, reflecting the presence of residual polymer and byproducts. Notably, hexavalent chromium appeared in the wastewater owing to the oxidative nature of ammonium persulfate despite being absent in the leather itself; it was effectively neutralised using sodium metabisulfite. These findings suggest that integration into industrial operations is feasible with minor adjustments to wastewater treatment.

4. Conclusion

Through IL-assisted in-situ polymerisation, PANI can be uniformly integrated into leather, imparting both high electrical conductivity and substantial flame resistance while preserving core mechanical and aesthetic qualities. This approach minimises the limitations of earlier PANI-leather methods by achieving deep fibre penetration via nanoscale particle control. With manageable environmental impacts, the technology presents a practical path toward high-performance leathers for electronics, safety apparel, and specialised interiors.

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6. References

1. Thomasset A., Benayoun S., Review: Leather sustainability, an industrial ecology in process, J. of Industrial Ecology, 28, 1842-1856, 2024.
2. Basak S., Shakyawar D.B., Samanta K.K., Kumar N., Bhowmick M., Ghosh S., A review on natural fibre-based engineered flexible composite: a futuristic development as leather alternative, J. of The Textile Institute, 1-18, 2024.
3. Meyer M., Dietrich S., Schulz H., Mondschein A., Comparison of the Technical Performance of Leather, Artificial Leather, and Trendy Alternatives, Coatings, 11, 226, 2021.
4. Bhadra S., Khastgir D., Singha N.K., Lee J.H., Progress in preparation, processing and applications of polyaniline, Prog. in Polymer Science, 34, 783-810, 2009.
5. Majeed A.H., Mohammed L.A., Hammoodi O.G., Sehgal S., Alheety M.A., Saxena K.K., Dadoosh S.A., Mohammed I.K., Jasim M.M., Salmaan N.U., A Review on Polyaniline:

Synthesis, Properties, Nanocomposites, and Electrochemical Applications, Int. J. of Polymer Science, 2022, 9047554, 2022.

6. Hatchett D.W., Josowicz M., Janata J., Acid Doping of Polyaniline: Spectroscopic and Electrochemical Studies, J. of Physical Chemistry B, 103, 10992-10998, 1999.
7. Cao Z., Xia Y., Chen C., Fabrication of novel ionic liquids-doped polyaniline as lubricant additive for anti-corrosion and tribological properties, Tribology International, 120, 446-454, 2018.