Addressing Multilayer Polymer Complexity in Footwear through a Separation-Led Recycling Strategy

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

Paper reference: TF-87/P

Printed pages: 509–515

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

Addressing Multilayer Polymer Complexity in Footwear through a Separation-Led Recycling Strategy

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Ref. No. TF-87/P

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Abstract

Modern footwear waste is dominated by multilayer polymer assemblies that resist conventional recycling routes due to permanent adhesive bonding and material incompatibility. In this study, a separationled recycling approach is demonstrated for preconsumer footwear waste comprising PU-coated PET fabrics, synthetic leather, and laminated PU foams. Targeted chemical treatment was employed to selectively disrupt interfacial bonding and recover polyurethane-rich fractions, which were subsequently converted into PU oligomers and upcycled into waterborne polyurethane (WPU) emulsions. The proposed strategy prioritises material separation over complete depolymerisation, enabling higher material retention and value recovery. This work highlights a practical and scalable pathway for integrating chemical separation with polymer upcycling in footwear manufacturing waste streams, offering a lowbarrier route toward circularity in the footwear sector.

Keywords : Footwear recycling, Polyurethane recovery, Separation-led recycling, Multilayer polymer systems, Waterborne polyurethane, circular footwear

1. Introduction

Footwear products are inherently complex, comprising multiple polymeric materials such as polyurethane (PU), ethylene vinyl acetate (EVA), polyester (PET),

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thermoplastic polyurethane (TPU) and rubber, which are assembled through lamination, adhesive bonding, and comoulding processes. These multi-material constructions are essential for achieving performance, comfort, and durability, but they pose substantial challenges for endof-life recycling. As a result, the majority of discarded footwear continues to be landfilled or incinerated, with limited material recovery.

Current recycling approaches for footwear waste are dominated by mechanical size-reduction processes, which convert mixed polymer assemblies into heterogeneous granulates suitable only for low-value applications such as mats or fillers1. While chemical recycling has been widely explored for single-polymer streams such as PET packaging or mattress PU foams, its application to footwear waste remains limited due to the presence of laminated structures, mixed polymer chemistries, and filler-rich formulations2.

In contrast, pre-consumer footwear waste generated during manufacturing, including cutting scraps, trimming waste, moulding flash and off-spec components, represents a cleaner and more compositionally defined material stream. These wastes are produced systematically during upper cutting, midsole and outsole moulding, stitching, lasting and final quality control operations. Despite being generated in significant quantities, such wastes are often landfilled due to their high bulk volume and lack of established recycling routes. This practice will become increasingly unsustainable as landfill capacity diminishes.

Addressing this gap, the present work explores a separation-led recycling strategy for pre-consumer

footwear waste, with a focus on polyurethane-containing

multilayer materials3, 4. By prioritising interfacial

separation before polymer recycling, this approach aims

to overcome the intrinsic limitations of mechanical

recycling and enable value-preserving upcycling

pathways relevant to footwear manufacturing.

2. Materials and methods Materials

PU-based footwear upper industrial wastes were collected from a leading footwear manufacturer in India.

Methods

The nature of the material was analysed through an optical microscope and FTIR. The oligomer properties were measured through DSC, TGA, FTIR, and NMR. The molecular weights of the oligomers were determined through size exclusion chromatography (GPC). The waterborne polyurethane emulsions were characterised by analysing their solid content and film-forming ability.

3. Results and Discussion

3.1 Separation of PU from footwear waste

The PU found in the footwear is often bonded to polyester, nylon, or other textiles, complicating direct depolymerisation. Previous studies have explored the direct degradation of complex PU sources; however, achieving polyol recovery with purities exceeding 90% typically requires high temperatures and extensive processing. A more efficient approach involves incorporating a pretreatment step to selectively separate PU from other components before depolymerisation. This strategy enhances process efficiency, improves yield, and enables better reaction control at lower temperatures. In one of our previous studies, polyurethane coatings were successfully extracted intact from PU-coated fabrics (PUCF) using 10 wt.% NaOH at room temperature, preserving PU integrity for subsequent depolymerisation. Applying a similar approach, we investigated the extraction of PU from Elastane PU/PET, a commonly used upholstery/Footwear upper material. Optical microscopy and FTIR analysis confirmed its multilayered structure, comprising a thin elastane layer bonded to a polyester fabric (Fig. 1a). However, alkali treatment (up to 30 wt.% NaOH) failed to induce separation, indicating a stronger bonding mechanism compared to PUCF. Unlike PUCF, where PU adheres via ester- based adhesives or mechanical interlocking, Elastane PU/PET typically employs thermal fusion or highly crosslinked PU layers that resist hydrolysis. Consequently, a solvent-based approach was explored to induce selective swelling of the PU layer, enabling its efficient separation while preserving the integrity

of the textile substrate.

Two solvent-based approaches were evaluated for elastane recovery from polyester fabrics. In the first approach, soaking in DMF induced rapid swelling and delamination of the elastane layer within 15 min, followed by Soxhlet extraction that achieved 99.3% elastane recovery. However, DMF is classified as a substance of very great concern under REACH, limiting its practical applicability. As a safer alternative, the same protocol was assessed using dimethyl sulfoxide (DMSO). Elastane swelling and partial delamination occurred within 20 min, yielding ~80% recovery. Complete extraction required refluxing in DMSO at 120 °C, resulting in an overall recovery of ~93%. Thus, while DMF enabled faster and more efficient recovery, DMSO offered a less hazardous alternative at slightly reduced efficiency. (Fig 1b -1e)

Fig 1: (a) Optical microscopy images of Elastane PU/PET, PU-coated fabric, and Laminated foam (top to bottom). (b) Separation of the elastane layer from the fabric (c) SEM images of PU foam after delamination under different concentrations of alkali (d) Optimization of elastane recovery through Soxhlet extraction

(e) Time taken vs % recovery for PU foam

3.2 Controlled depolymerization of polyurethane to derive functional oligomers

Subsequently, polyurethane (PU) foam separation from multilayer laminated foams (LF), commonly used in footwear sock liners and furniture upholstery, was investigated. Optical microscopy confirmed that the PU foam was sandwiched between polyester fabric layers, necessitating chemical delamination. LF samples were treated with aqueous NaOH solutions (1–40 wt.%) at room temperature. Intact separation of PU foam was achieved within 90 and 45 minutes using 1 wt.% and 5 wt.% NaOH, respectively. Increasing the concentration to 10 wt.% reduced the separation time to 30 min but induced partial structural disintegration of the foam. At 40 wt.% NaOH, severe degradation and alkali deposition were observed, preventing recovery of intact foam.

Given the highly crosslinked nature of PU foams, which typically require temperatures above 180 °C for effective depolymerisation, the partial disruption observed during alkali treatment was leveraged as a pre-treatment strategy5. Controlled NaOH exposure was found to

induce partial cell opening, improving reagent accessibility for subsequent aminolysis while avoiding complete structural collapse. Based on this balance, a treatment condition of 10 wt.% NaOH for 30 min was selected as the optimal pre-treatment, sufficiently weakening the foam network to enhance downstream depolymerisation into functional oligomers.

The organic phase oligomers were selected for functional upcycling into waterborne polyurethanes (WPU) due to their balanced hydroxyl functionality and molecular weight. These oligomers, containing terminal hydroxyl and urea groups, react with isocyanate- terminated prepolymers to form urethane linkages and hydrogen-bonded networks, enabling crosslinked WPU formation. In contrast, the aqueous phase oligomers exhibited exceptionally high hydroxyl values, which could result in overly rigid or unstable emulsions if directly used in WPU synthesis. The FTIR spectra of the organic phase oligomers from PU coatings (PUCO), PU foam (PUFO), and PU elastomers (PUEO) exhibit a broad N–H stretching band between 3400–3300 cm^{-1}, indicative of hydrogen bonding. In PUCO, this peak appears at 3300 cm^{-1}, likely due to the

higher proportion of hard segments in the oligomer (Fig. 2b).

Since PU coatings inherently contain harder segments, depolymerization generates a greater number of urea groups, which form strong hydrogen bonds, resulting in this peak shift. In contrast, PUFO is predominantly composed of soft segments, and its partial depolymerization does not produce a significant amount of urea linkages in the organic phase. Similarly, PUEO exhibits a phaseseparated morphology, where soft segments dominate, leading to weaker hydrogen bonding and a higher N–H

Fig 2: (a) Reaction setup of controlled depolymerization reaction of industrial PU materials (b) Reaction scheme of separating the oligomers. (c) FTIR spectra of the organic phase oligomers

(d) DSC thermogram of the organic phase oligomers

3.3 Synthesis of waterborne polyurethane

The organic phase oligomers were upcycled into waterborne polyurethanes (WPU), a sustainable alternative to solvent-based systems. WPU's are increasingly used in textile coatings, synthetic leather, and adhesives due to their low VOCs, flexibility, and filmforming ability. This approach supports circularity while

stretching peak near 3400 cm^{-1}. Additionally, PUFO and PUEO show two distinct C=O stretching bands at 1730 cm^{-1} and 1650 cm^{-1}, confirming their phase- separated structure, where 1730 cm^{-1} corresponds to free C=O groups in soft segments and 1650 cm^{-1} to hydrogenbonded C=O in hard segments. In PUCO, this phase separation is less evident due to the dominance of hard segments, resulting in a more uniform hydrogenbonding environment. Furthermore, all three oligomers exhibit a C–O–C stretching band at 1100 cm^{-1}, characteristic of urethane linkages.

addressing industry demand for eco-friendly materials in apparel and upholstery applications. As a reference, a Model WPU (WPUM) was synthesised with NCO: OH, equivalents as 1.2:1 and optimised for soft, flexible coating applications. This model WPU served as a benchmark for assessing the properties of WPU derived from oligomers. To ensure consistency and industrial relevance, the PTMEG-to- oligomer ratio was fixed at 1:1, allowing

for the replacement of 50% of virgin polyol with a recycled counterpart—a key consideration for practical implementation (Fig 3). This standardised ratio enabled a direct comparison between the synthesised oligomerbased WPU (WPUO) and a reference formulation using

Fig 3: Reaction scheme of the synthesis of WPU emulsion by incorporating the organic phase oligomer

The hydroxyl value (OHV) of the organic-phase oligomers was used to determine the appropriate PTMEG-tooligomer ratio in the WPU formulations, ensuring balanced hydroxyl functionality for efficient prepolymer formation.

commercial PTMEG-based polyol (WPUM). Accordingly, three distinct WPU formulations were prepared based on the recovered oligomers: WPUF (from foam-derived oligomer), WPUC (from coating-derived oligomer), and WPUE (from elastane-derived oligomer).

Waterborne polyurethanes were synthesised via the acetone process using DMPA as an internal emulsifier and 1,4butanediol as a chain extender. The model WPU (WPUM) formed a milky white emulsion, whereas ;

Sample Mn (g mol-1) Mw (g mol-1) PDI Hydroxyl value

PUEO 3800 7068 1.86 112

PUCO 1440 3302 2.29 95.7

PUFO 4618 14369 3.11 62.8

PUEA 514 576 1.12 122.2

PUCA 471 709 1.50 110.6

PUFA 2112 4108 1.94 98.3

Table 1: Properties of the organic and aqueous phase oligomers on performing

controlled depolymerisation at 130ÚC, 4 hours.

oligomer-containing WPUs exhibited a paler appearance due to the inherent colour of the recovered oligomers (Fig. S37). Owing to the presence of reactive hydroxyl and urea/urethane end groups, the recovered oligomers were directly incorporated as polyol substitutes and chain extenders during prepolymer synthesis, contributing to molecular growth and internal hydrogen bonding within the WPU network.

Emulsion stability was evaluated based on phase continuity

Sample Mna (Kg mol-1)

Mwa (Kg mol-1) PDIa Appearance Storage stability (months)

WPUM 10.4 15.8 1.56 Milky white >6 months 31.2 264 Yes WPUE 12.8 20.73 1.73 Dirty white > 6 months 33.9 359 Yes WPUC 11.4 19.26 1.69 Dirty white > 6 months 36.2 372 Yes WPUF 10.7 20.97 1.89 Creamy

white

Table 2: Mass ratio of the starting materials used in the synthesis of WPU

4. Conclusion This study demonstrates that a separation-led recycling strategy offers an effective pathway for addressing the intrinsic complexity of multilayer footwear waste. By selectively separating polyurethane from PU-coated textiles, synthetic leather, and laminated foams and

(mg KOH/g)

and resistance to sedimentation over time. All WPU formulations formed stable, single-phase dispersions and exhibited shelf- life stability exceeding six months. The incorporation of oligomers resulted in higher solid content compared to the model WPU, consistent with increased molecular weight. A progressive increase in viscosity was also observed, with WPUF showing the highest viscosity (432 mPa·s), attributed to its larger particle size (~400 nm), which enhanced interparticle interactions and restricted flow within the dispersion (Table 2).

Solid content

Viscosity

Film- forming

[mPa.s]

(%)

ability

> 6 months 42.7 432 Yes

subsequently converting it into functional oligomers for upcycling into stable waterborne polyurethane systems, the approach moves beyond conventional size-reduction and downcycling routes. The results highlight that prioritizing interfacial separation and controlled chemical transformation enables higher material value retention

while remaining compatible with footwear manufacturing waste streams. Importantly, the strategy leverages clean pre-consumer waste, reducing landfill burden and facilitating scalable implementation. Collectively, this work underscores the potential of integrating selective pretreatment with polymer-specific upcycling to advance circular material flows in the footwear sector.

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