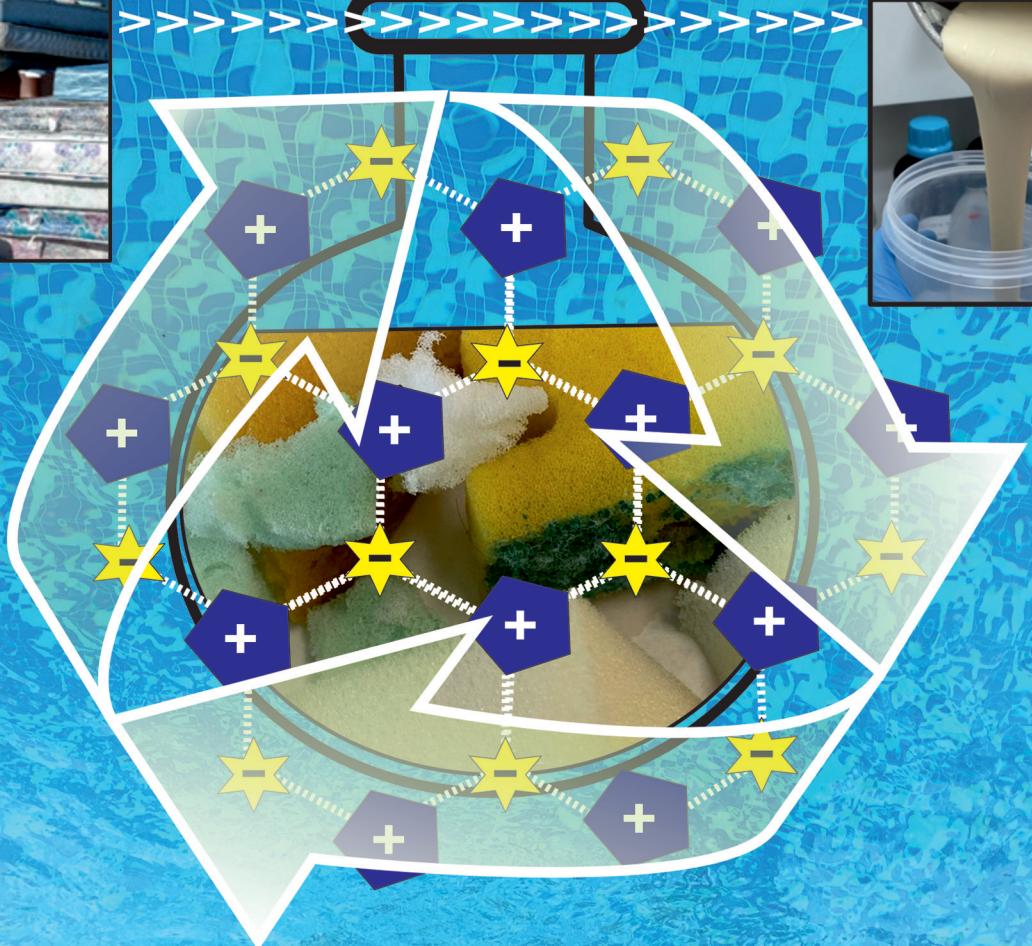


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## Scalable glycolysis-based depolymerization of polyurethane foam waste enabled by ionic liquids

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We report a sustainable and scalable strategy for the chemical depolymerization of polyurethane foam waste (PUFW) by employing the ionic liquids (ILs) 1-*n*-butyl-3-methylimidazolium chloride ([Bmim][Cl]) and 1-*n*-butyl-3-methylimidazolium acetate ([Bmim][OAc]) as dual-function systems that act both as reactive media and efficient catalysts for the selective glycolysis of urethane bonds. Full depolymerization of PUFW is achieved under mild conditions (<100 °C, 1 atm) within 4–5 hours, offering a scalable alternative (up to 100 g of PUFW processing capability) to conventional glycolysis methods that typically require harsh thermal conditions (180–250 °C). The addition of water to the reaction medium enables the direct precipitation of the recycled polyol and allows for the efficient recovery and reuse of the water-miscible ILs [Bmim][Cl] and [Bmim][OAc], enhancing the sustainability of the process. The recycled product is then washed, dried, and analyzed by means of a solubility test in dimethyl sulfoxide (DMSO), the hydroxyl index (iKOH) value, nuclear magnetic resonance (NMR), and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Finally, the obtained recycled polyol is homogenized with the virgin polyol to synthesize new flexible polyurethane foams (FPUFs) that display identical physico-chemical and mechanical properties to the original FPUF. It should be noted that this glycolytic depolymerization process does not generate waste, since the complete mixture of reaction products is suitable for reuse as the starting material in the synthesis of new FPUFs. The active depolymerization medium is completely recoverable and can be reused for up to six operational cycles without any loss of catalytic efficiency, thereby demonstrating the recyclability and promoting the “greenness” of the process. Noteworthily, both the effectiveness and versatility of this process are also extended to the treatment of recalcitrant rigid PUFs (RPUFs), namely polyisocyanurate (PIR), highlighting the versatility of this process, as well as its potential application on an industrial scale.

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### Green foundation

1. A glycolysis-based strategy enables full conversion of polyurethane foam waste (PUFW) into valuable building blocks for new PUFs. Among other genuine properties of ionic liquids (ILs), their negligible vapor pressure enhances safety and allows for their efficient recovery and reuse, fostering a closed-loop recycling system aligned with the Green Chemistry principles.
2. A novel and sustainable PUF depolymerization procedure is reported under mild conditions (<100 °C, 1 atm), using ILs as dual solvent catalysts. Also, their tuneable character promotes the selective urethane bond cleavage while minimizing by-products, achieving >95% yield in 4 h reaction.
3. Future research efforts will extend to other PUFW types and end-of-life foams, aiming to validate the process for real post-consumer waste. The potential for application in mixed plastic streams is particularly relevant for industrial scalability and broader impact.

## 1. Introduction

The global production of plastics is continuously growing and has skyrocketed in recent decades. Only in Europe, the plastic

value chain involved a total of 1.5 million people in 2021, across 52 000 companies with a turnover of more than €400 billion, highlighting the importance of this sector.<sup>1</sup> In fact, by the end of 2023, the production of plastics reached an amount of 413 Mt worldwide, and only less than 10% of them comes from recycled materials.<sup>2</sup>

Among the wide variety of existing plastic materials, polyurethane (PU) is a widely used type of plastic due to its unique versatility and extensive applicability across different sectors, such as automotive, construction, electronics and consumer

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goods.<sup>3</sup> Its entire production of about 25 Mt worldwide places PU as the 6<sup>th</sup> most used synthetic polymer globally,<sup>4</sup> with an estimated annual growth rate of 5.6% over the 2021–2028 forecast period.<sup>5</sup> This polymer has a market presence that extends across flexible and rigid foams, elastomers, adhesives, and coatings, with special interest in thermoset PUFs (both rigid and flexible), whose production exceeds the 65% of PU market share.<sup>6</sup> Despite its multitude and versatile properties, PU exhibits recalcitrant nature that can cause serious environmental damage. In fact, the majority of PUFW is disposed of through landfilling (49%) or incineration (33%).<sup>7</sup>

Furthermore, EUROPUR reported that over 40 million mattresses are discarded every year in the EU, creating a stack that is 904 times the height of Mount Everest.<sup>7</sup> In addition to post-consumer products, it is estimated that up to 15% of PUF production ends up as industrial waste (scraps and cut-outs), worsening this environmental emergency.<sup>8</sup> Hence, the urgent implementation of sustainable technologies for this plastic recycling is required as a solution to this critical environmental situation.

Most recycling methods rely on mechanical and physical processes, which represent the most cost-effective and basic strategy for PUF recycling. These procedures are mainly based on regrinding/powdering techniques and compression molding, which can be implemented.<sup>9</sup> However, the performance of the recycled products is quite low, minimizing their economic value and limiting their application scope.<sup>10</sup> Alternatively, chemical recycling is gaining relevance at laboratory and industrial scales due to the high-quality end-products accomplished.<sup>11</sup>

Investments on these strategies are subject to increase from €2.6 billion in 2025 to €8.0 billion in 2030,<sup>12</sup> driven by policies such as the Directive (EU) 2019/904 that contribute to the achievement of United Nations (UN) Sustainable Development Goal 12 to ensure sustainable consumption and production patterns, entitled in the Agenda 2030.<sup>13</sup> Moreover, these recycling procedures are essential in addressing the critical situation regarding planetary boundaries, at least six of which have already been exceeded due to human activities.<sup>14,15</sup> These recycling processes enable the complete depolymerization of PUFW into its original monomers (*e.g.*, polyols) and/or oligomers through the gradual cleavage of primary (*e.g.*, urethane) and secondary (*i.e.*, biuret, urea, *etc.*) covalent bonds that constitute its molecular network.<sup>16</sup>

The main chemical recycling strategies involve hydrolysis,<sup>17</sup> hydro-glycolysis,<sup>18</sup> aminolysis,<sup>19</sup> glycolysis<sup>20–22</sup> and acidolysis.<sup>23–26</sup> Among all these strategic reactions, glycolysis represents the most widely used chemical recycling method,<sup>27</sup> which enables the development of approaches to achieve high yields and pure final products.<sup>28,29</sup> However, despite the recent advancements in various strategies at both industrial and pilot scales (*i.e.*, Covestro,<sup>30</sup> Rampf® Eco Solutions and Repsol,<sup>31</sup> H&S Anlagentechnik,<sup>32</sup> *etc.*), several challenges remain underdeveloped. These drawbacks include uncontrolled side-reactions due to the harsh reaction conditions (170–250 °C),<sup>33,34</sup> such as the nonselective degradation of urethane linkages, dar-

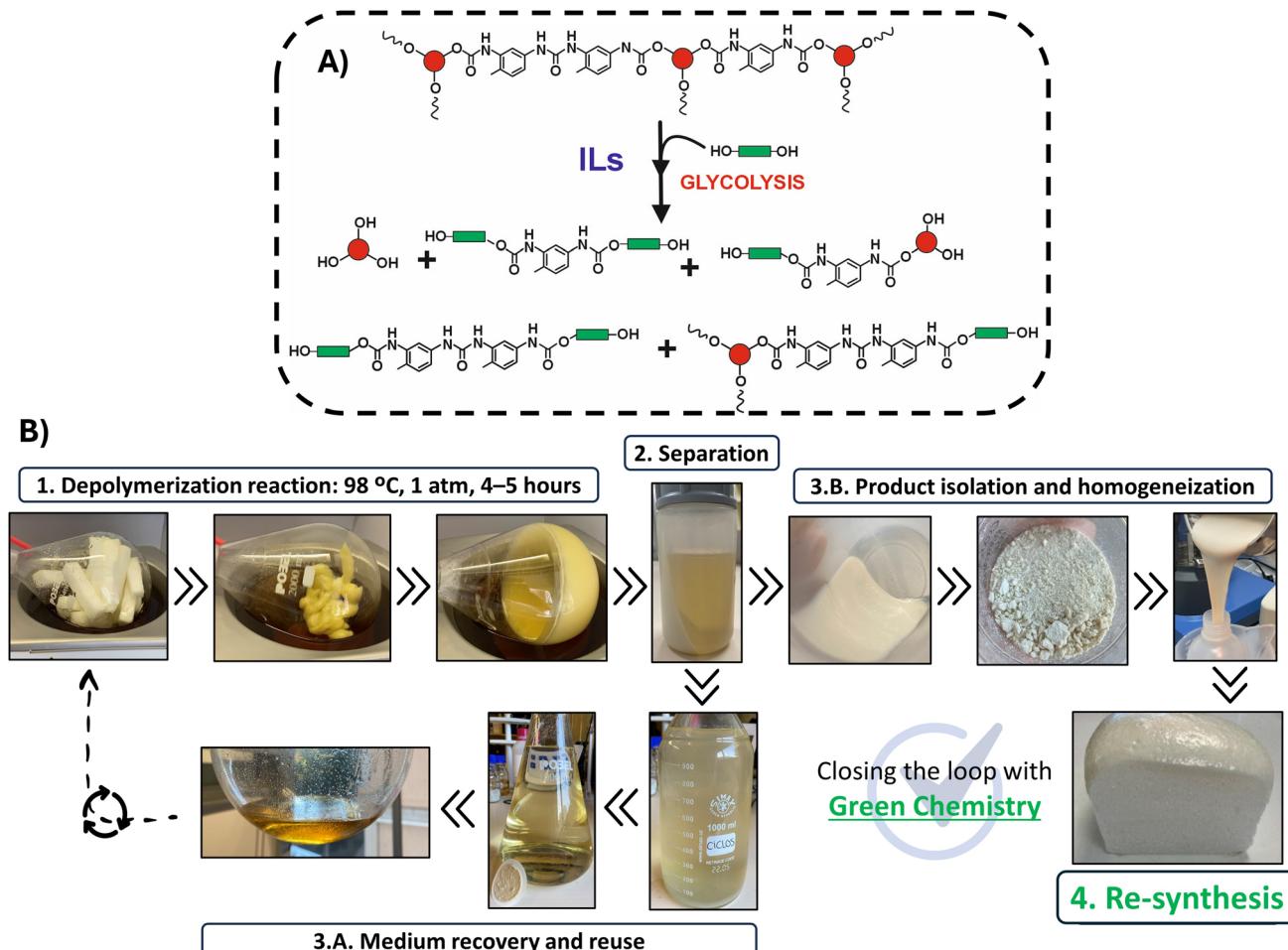
kening of both the mixture and products, and the inadequate phase separation of the resulting components (*i.e.*, recycled polyols, hard-segment oligomers, *etc.*).<sup>35</sup>

In general, ILs serve as tunable, fully recoverable, and reusable media that can also function as catalysts. They regulate the miscibility of reactants and products, control species' lifetimes, and stabilize both ionic and radical intermediates. Such properties enhance their capacity to govern catalytic processes, including biomass conversion and plastic recycling.<sup>36,37</sup> Hence, in the case of depolymerization processes, these unconventional solvents are not only used for polymer deconstruction, but can also serve as reaction media. For instance, [Bmim][Cl] and [Bmim][OAc] were the first ILs reported to be able to solubilize chitin.<sup>38</sup> On the other hand, the depolymerization of polylactic acid (PLA) was achieved for the first time using [Bmim][OAc] and 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ([SPmim][HSO<sub>4</sub>]) as catalysts, reaching conversion up to 92% after 3 hours at 115 °C.<sup>39</sup> Nakasu *et al.* pretreated *sugarcane bagasse* with monoethanolammonium acetate ([MEA][OAc]) at 150 °C for 2 hours, achieving up to 60 wt% lignin solubilization without carbohydrate losses.<sup>40</sup> In another example, the depolymerization of poly(bisphenol A carbonate) (PC) was carried out using a reaction system of [Bmim][OAc] as the catalyst and methanol as the breaking agent, resulting in a bisphenol A (BPA) yield of up to 95% after 2.5 hours at 90 °C. Moreover, the IL could be reused up to 6 times with no apparent decrease in PC conversion and yield.<sup>41</sup> Hence, this "green" pivotal tool offers feasible solutions to address many limitations of the current traditional chemical recycling methods.<sup>37,42,43</sup>

Herein, it is demonstrated for the first time a below-100 °C glycolysis-based recycling strategy for the complete depolymerization of thermoset PUFs, both rigid and flexible (Fig. 1A), leveraging the distinctive physicochemical properties of ILs.<sup>44</sup> These non-innocent sustainable solvents exhibit tunable properties, very low vapor pressure, high thermal and chemical stability as well as high capacity to dissolve several natural and artificial polymers such as cellulose and polyethylene terephthalate (PET), respectively.<sup>45–47</sup>

This innovative process exploits the synergetic effect observed when combining ILs and basic media reactions to achieve the efficient depolymerization of recalcitrant polymeric materials, such as thermoset PUFs.<sup>48,49</sup> In this context, the combination of water-miscible ILs, [Bmim][Cl] and [Bmim][OAc] (70/30, w/w), provides an extremely active medium which facilitates the deconstruction and subsequent depolymerization of both FPUF and RPUF. The acetate-based anion of the IL-[Bmim][OAc] provides the alkaline-catalytic character required to enable the nucleophilic attack of the corresponding glycol to the urethane group, facilitating the complete depolymerization of PUFW by means of a transcarbamoylation reaction. During this single-phase glycolysis strategy, the PUFW is first deformed due to the solvent capacity of the ILs, leading to a homogenous reaction medium that minimizes mass transfer limitations while enhancing reaction kinetics.





**Fig. 1** (A) Scheme of the depolymerization reaction of thermoset PUF through glycolysis to obtain the recycled polyol and rigid segments (urethane/urea oligomers). (B) Complete scheme of the overall depolymerization process. (1) Glycolysis of the PUFW using an IL mixture and EG as the rupture agent. (2) Washing–centrifugation cycles for product isolation from the depolymerization medium. (3.A) Filtration and concentration of the depolymerization medium. (3.B) Product drying and subsequent homogenization with Alcupol F-4811®. (4) Re-synthesis of PUF. See the SI for further details.

This innovative work describes a sustainable glycolytic process for PUF depolymerization conducted at temperatures below 100 °C and at atmospheric pressure, achieving yields of up to 95% in only four hours. After the glycolysis step, a straightforward separation protocol is carried out to achieve the isolation of the recycled polyol as a semi-solid phase (Fig. 1B), suitable for the synthesis of a new PUF. Also, the IL reaction medium can easily be recovered after four water washing–centrifugation cycles and then reused in further depolymerization reactions.

## 2. Results and discussion

### 2.1. Glycolysis-based depolymerization strategy and product isolation

Ethylene glycol (EG) was chosen as the nucleophile due to its cost-effective, low molecular weight and relatively low viscosity

compared to other glycols.<sup>30</sup> The depolymerization reaction was carried out with a mixture of [Bmim][Cl], [Bmim][OAc], and EG in a 65 : 28 : 7% (w/w) ratio. The EG and the ILs form a homogenous and relatively low viscosity liquid phase. These properties enabled a reduced glycol-to-PUFW ratio, still promoting efficient mass transfer within the reaction system. To establish an EG mass of half the PUFW, the milliequivalents of carbamate groups per gram of PUF were estimated (see the SI). PUFW was added at a 7.5 : 1 weight ratio relative to the depolymerization media. The reaction mixture was maintained at 98 °C under continuous stirring until complete dissolution of the PUFW was achieved, which occurred after 4 h.

To demonstrate the effectiveness of the strategy and both the quality and the potential applicability of the resulting recycled product, the following analysis was conducted: (i) a solubility test of the recycled product in DMSO, (ii) iKOH determination, (iii) NMR, (iv) ATR FT-IR, (v) elemental analysis (EA) and (vi) PUF re-synthesis. Prior to the overall analysis, an easy

separation protocol must be performed to efficiently recover the resulting recycled polyol and the depolymerization medium that contains both water-miscible ILs.

This protocol consists of consecutive washing-centrifugation cycles, in which the IL mixture based on [Bmim][Cl] and [Bmim][OAc]-ILs and a slight excess of glycol move towards the aqueous phase, effectively separating the depolymerization medium from the semi-solid polyol product. In this context, two critical parameters must be considered: the amount of water required per cycle and the number of cycles necessary to fully recover both ILs, ensuring that energy consumption is justified.

Therefore, owing to the high viscosity of the reaction mixture at the end of the depolymerization reaction, an excess of water by twice the total reaction mass is required to achieve two well-distinguished phases after the first washing step (see the SI for conditions). This leads to the recovery of most of the IL mixture, reducing the required amount of water by half in the second cycle and onwards. The influence of the washing water cycles was then evaluated based on two analyses: (i) the residual IL in the recycled polyol, determined by  $^1\text{H-NMR}$  analysis (Fig. S5), and (ii) the glycol traces present in the solid product, assessed by the iKOH value.

Table 1 showcases the influence of washing cycles on the residual IL and the iKOH value of the recycled polyol. As expected, the substantial reduction of IL content was observed, with a 60.6% IL content in the polyol after the first cycle (see entry 1), followed by a gradual decline with additional washes (entries 2–4). The iKOH values also decreased gradually because of the washing of the EG excess retained to the recycled polyol network. Notably, after the fourth washing cycle, no significant differences were observed among the final products, establishing four washing-centrifugation steps as the optimal conditions (see entries 4 and 5). These assays evaluating the effectiveness of the number of washing cycles were conducted using 140 g of IL and 20 g of PUFW. Consequently, the residual IL values, approximately 3%, refer to the total mass of the recycled product recovered (>19 g), which corresponds to an overall IL recovery efficiency exceeding 99%. Following the washing steps, the aqueous fraction was filtered using a Büchner flask and then concentrated under vacuum for subsequent reuse. Finally, the recovered solid polyol was recombined with the wet solid product prior to the drying step (Fig. 1).

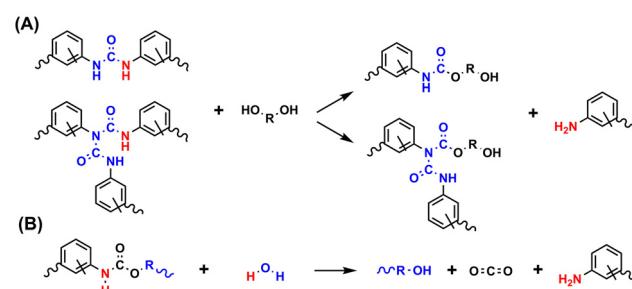
**Table 1** Influence of the number of washing cycles on the recovery of ILs and the iKOH of the recycled polyol

Entry	Wash cycles <sup>a</sup>	Residual IL <sup>b</sup> (%)	iKOH (mg KOH per g)
1	1	60.6	—
2	2	19.8	144 ± 10
3	3	13.6	133 ± 5
4	4	3.4	119 ± 3
5	5	3.0	114 ± 8

<sup>a</sup> Number of washing-centrifugation cycles performed. <sup>b</sup> Residual IL mass percentage present in the recycled polyol, confirmed by  $^1\text{H-NMR}$  (see Fig. S5). iKOH determination was carried out in duplicate.

Notably, the structural complexity of PUFW can induce multiple side reactions: urea and Biuret transcarbamoylation, leading to urethane, allophanate and monomeric aromatic (di) amines, or hydrolysis of urethane groups because of the residual water within the reaction system (Fig. 2A and B, respectively).<sup>9</sup> This underscores the importance of developing a selective process capable of effectively controlling the depolymerization reaction.

In our case, this control is achieved through an optimal combination of water-miscible ILs with EG, acting as a nucleophilic agent. [Bmim][Cl] was selected for its previously reported exceptional ability to dissolve recalcitrant polymers, including cellulose,<sup>50</sup> and [Bmim][OAc] owing to the basic nucleophilic character of its acetate anion, which has also been shown to solubilize synthetic polymers like PET.<sup>51</sup> This efficient catalysis when both ILs are combined in an optimal mass ratio 70/30 ([Bmim][Cl]/[Bmim][OAc]) can be attributed to the complementary roles of their respective anions.<sup>52</sup> Specifically, [Bmim][Cl] contributes primarily through its solvation capacity, which facilitates the partial dissolution and physical swelling of the polyurethane matrix—an effect analogous to its known interaction with polysaccharides such as cellulose.<sup>53</sup> This disruption of the polymer structure enables better diffusion of the reagents into the bulk material. On the other hand, [Bmim][OAc] provides a basic acetate anion that acts as a catalytic species, promoting the nucleophilic attack of the glycol on the urethane bonds. The acetate anion facilitates a transcarbamoylation reaction, leading to efficient urethane bond cleavage. Collectively, the 70/30 mass combination results in a homogeneous single-phase medium that improves mass transfer and reaction kinetics, enabling complete depolymerization with high efficiency. Notably, the performance of [Bmim][Cl] and [Bmim][OAc] with each of the neat ILs was evaluated in this depolymerization process (see Fig. S14). The use of [Bmim][Cl] alone does not induce glycolysis or depolymerization of polyurethane foam (see Fig. S14). In contrast, neat [Bmim][OAc] not only dissolves the foam, but also affords a dark-coloured solution, which can be attributed to the enhanced release of aromatic amines followed by their oxidation. This could arise from the higher basicity of the acetate



**Fig. 2** Uncontrolled side-reactions that may occur due to harsh conditions and long operation times. (A) Urea and Biuret transcarbamoylation, leading to urethane and allophanate groups along with monomeric aromatic diamines. (B) Hydrolysis of carbamate bonds due to the presence of residual water within the reaction system.<sup>9</sup>



anion, which together with residual water in the IL medium, undergoes the reaction pathway from glycolysis to hydrolysis, thereby promoting amine liberation and solution darkening. In the mixed  $[\text{Bmim}][\text{Cl}]/[\text{Bmim}][\text{OAc}]$  system, such undesirable coloration is absent, owing to the proper combination of both ILs that modulates the basicity of the medium, thus enabling controlled depolymerization *via* glycolysis.

## 2.2. Product characterization and analysis

While thermoset polymers such as PUF are entirely insoluble in most conventional organic solvents, including DMSO or tetrahydrofuran (THF), the recycled polyol generated through the depolymerization process exhibits solubility in a range of solvents.<sup>48</sup> Hence, the progress of depolymerization can be monitored by measuring the percentage of the dried product that is soluble in DMSO at different reaction times. During glycolysis, the transcarbamoylation of carbamate bonds with glycols leads to the formation of lower-molecular-weight carbamate/urea soluble oligomers (rigid segments) and the recovery of the virgin polyol originally used in the synthesis of the treated PUFW. These depolymerization products are soluble in DMSO, and the extent of this solubility provides a direct measure of depolymerization yield (conversion). Solubility was determined using a standardized assay with a fixed ratio of 100 mg sample per mL of DMSO (see the SI). Noteworthily, up to 700 mg of the recycled product could be resuspended in 1 mL of DMSO while reaching solubilities over 90% (see Fig. S6).

Furthermore, a molecular-level comparison between the original polyol used in the synthesis of the PUF and the resulting recycled polyol obtained is crucial to demonstrate the potential applicability of this new technology. The virgin polyols employed are Alcupol F-4811® and Alcupol P-3041®, which are commercially available and whose properties are described in the polyols catalogue of Repsol.<sup>54</sup>

In this sense, the structural characterization of Alcupol F-4811® by NMR spectroscopy has been previously reported (see Fig. S3 and S4).<sup>55</sup> By comparing the standard polyols with the recycled product obtained after the depolymerization process, it was concluded that both virgin polyols and rigid segments were successfully recovered, as a result of the transcarbamoylation reaction occurring during glycolysis.

Fig. 3 depicts the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of the product obtained after the depolymerization process. The region between 7.0–8.4 ppm in the  $^1\text{H}$ -NMR and 120–160 ppm in the  $^{13}\text{C}$ -NMR corresponds to aromatic oligomer compounds (rigid segments). In contrast, the aliphatic protons associated with the rigid segments appear between 2.0–2.3 ppm in the  $^1\text{H}$ -NMR and 16–22 ppm in the  $^{13}\text{C}$ -NMR. The signals corresponding to the recycled polyol are indicated in Fig. 3(1.D and 2.C).

The iKOH values were determined using a standard titration method (ASTM D-4274-16)<sup>56</sup> to assess the cross-linking properties of the depolymerization product, specifically by quantifying the hydroxyl functional groups present per gram of sample. This value is a key parameter to determine the type of foam in which the polyol can be used. Therefore, achieving values between 50 and 250 mg KOH per g sample is crucial to enable the resynthesis of PUF, primarily for applications in the comfort sector (*i.e.*, mattresses, vehicle seats, *etc.*).<sup>26,54</sup>

Finally, the elemental analysis of both the recycled product and PUFW was performed. Since the glycolysis reaction involves transcarbamoylation of the carbamate bonds, the obtained results are very similar, as only incorporation of EG into the urethane oligomers should occur (see the SI).

## 2.3. Optimization of the PUFW depolymerization process

As previously mentioned, both mass transfer and reaction kinetics are key parameters to consider in the development of a process with significant industrial relevance. Noteworthily,

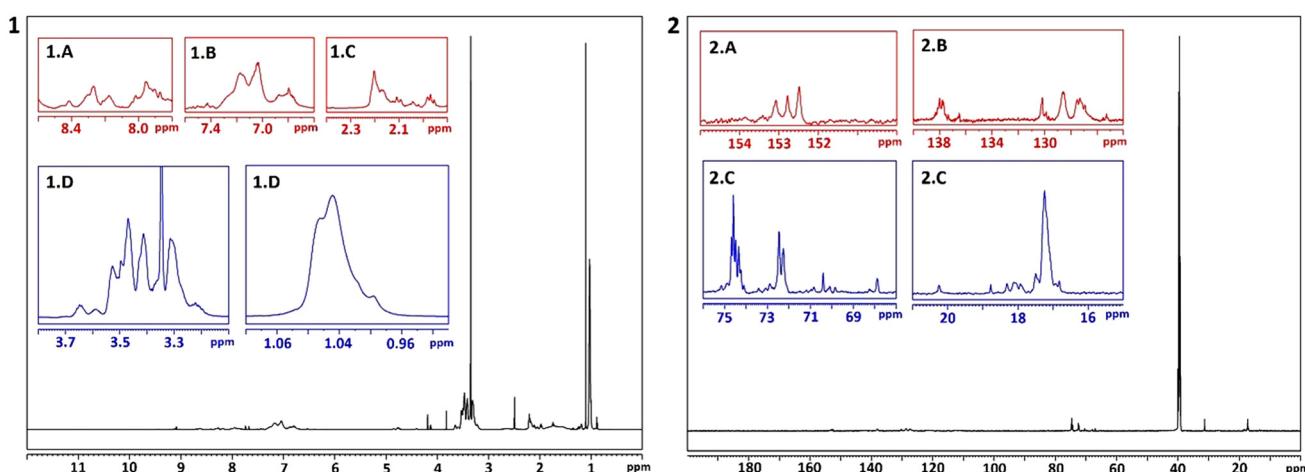


Fig. 3  $^1\text{H}$  (1) and  $^{13}\text{C}$ -NMR (2) spectra of the recycled product obtained after the depolymerization process. Signals assigned as (1.A and 1.B) aromatic protons of rigid segments; (1.C) aliphatic protons of rigid segments; (1.D) protons of recycled polyol (Alcupol F-4811 and Alcupol P-3041); (2.A) carbamate/urea carbonyls of rigid segments; (2.B) aromatic carbons of rigid segments; (2.C) carbons of recycled polyol and aliphatic rigid segments. See the SI for further details.



optimizing the reaction conditions involves more than just minimizing the reaction time or reducing the amount of the depolymerization medium. It is also crucial to consider factors such as reactor loading duration and the overall viscosity of the reaction mixture, as these significantly impact the operational efficiency and equipment requirements. Additionally, controlling side reactions and by-products formation is key to ensure the process efficiency and to avoid potential contamination of the final product or the depolymerization medium (e.g., carcinogenic monomeric aromatic amines).<sup>57</sup> Consequently, both the kinetics profile and the ILs : PUFW (w/w) ratio were evaluated (see the SI for details).

Fig. 4A depicts the time-course profile of the depolymerization of PUFW, measured from the solubility of the recycled product in DMSO at 1 hour intervals over a total of 8 hours, achieving the maximum solubility (ranging between 92–95%) after 3 hours. These solubility values confirm that the depolymerization process was complete at this point. However, the solid product obtained after 3 hours still exhibited a significantly larger particle size compared to the product obtained after longer reaction times (see Fig. S7). This particle size hinders subsequent washing and centrifugation steps and the final homogenization with the virgin polyol (e.g., Alcupol F-4811®).

Fig. 4B showcases how the iKOH value remains practically unchanged over time, further confirming that the depolymerization reaction was complete after 3 hours. The differences in iKOH values between the virgin polyol and the recycled polyol result from the transcarbamoylation reaction of the urethane group, leading to the formation of both the recycled polyol and carbamate oligomers with hydroxyl functionalities. However, <sup>1</sup>H-NMR analysis revealed that a longer reaction time (up to 8 hours) resulted in an increased release of free aromatic amines, attributed to the presence of residual water that promotes hydrolytic reactions (see Fig. S8). Based on

these results, the optimal reaction time was determined to be 4 hours.

Regarding the IL : PUFW ratio, different assays were performed in which the amount of [Bmim][Cl] and [Bmim][OAc] was reduced proportionally, from a total IL mass of 14 g to 5.6 g (see Table S1). Firstly, a total amount of 14 g of ILs was fixed, with a 30/70 (w/w) of [Bmim][OAc]/[Bmim][Cl] and a PUFW processing capacity of 2 g per reaction. Considering the milliequivalents of carbamate groups previously mentioned, the EG : PUFW mass ratio of 1 : 2 remained constant. As previously stated, the 70/30 [Cl]/[OAc] mass ratio was chosen experimentally to balance polymer swelling and dissolution ([Cl]) with catalytic activity ([OAc]), while maintaining manageable viscosity and good miscibility. This efficient combination involving chloride/acetate imidazolium ILs has been reported for biomass deconstruction.<sup>47,58</sup>

On the other hand, while concerns have been raised regarding the toxicity of ILs, it is important to note that, for most imidazolium-based ILs, significant toxicity is typically associated only with those containing long *N*-alkyl side chains ( $\geq C_{10}$ ), which tend to exhibit higher hydrophobicity and bioaccumulation potential. In contrast, commonly used [Bmim]-based ILs (with  $C_4$  side chains) generally present moderate to low toxicity, particularly toward aquatic organisms, and their environmental fate is influenced by both the nature of the anion and the biodegradability of the cationic core. Furthermore, [Bmim]-based ILs are typically used in closed-loop processes where their recovery and reuse are integral to the operational design, significantly reducing potential environmental release. These ILs have been shown to be recyclable over multiple cycles without loss of performance, aligning with the principles of green chemistry and minimizing their environmental footprint.<sup>59–61</sup>

As expected, the overall IL mass reduction resulted in a progressive increase of the reaction viscosity, hindering the overall

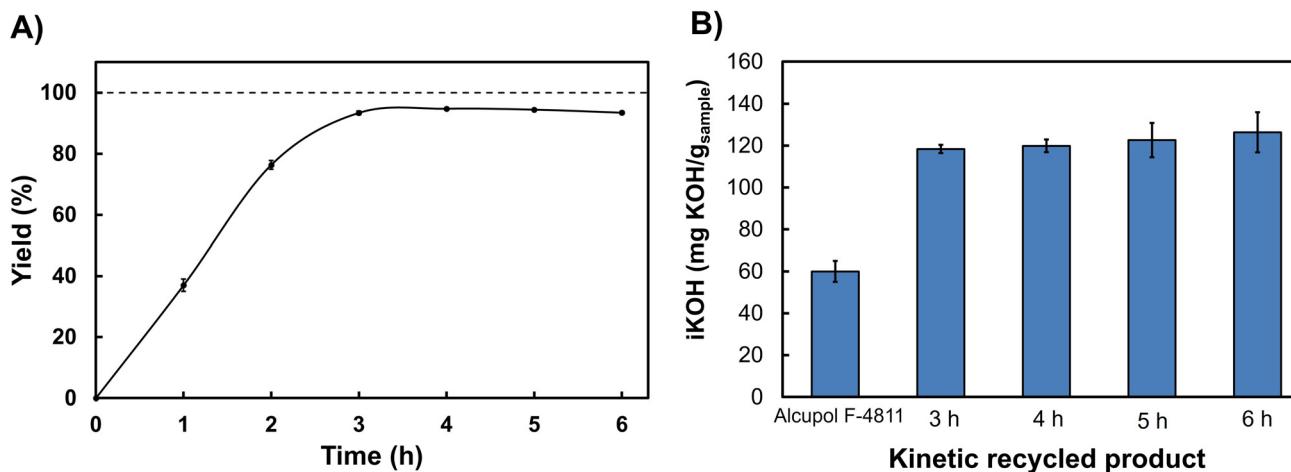


Fig. 4 (A) Time-course profile for the PUFW depolymerization process by glycolysis reaction with EG. (B) iKOH value of the virgin polyol (Alcupol F-4811) compared to the depolymerization product at hours 3 to 6. Experiments were carried out in duplicate. Conditions: 6.9 g [Bmim][Cl], 2.6 g [Bmim][OAc]; 1 g EG; 2 g PUFW, 98 °C, 6 h.



mass transfer and slowing the reaction kinetics. Hence, the optimal IL mass was established at 9.8 g, corresponding to an ILs : PUFW ratio of 4.9 : 1 (w/w), to ensure the efficiency of the depolymerization process and both the suitable product isolation and the medium recovery. Notably, the mass proportion of ILs within the depolymerization system is essential for achieving an ionic-based mixture rather than an ion-based dissolution.<sup>45,49</sup> This significantly influences cation–anion interactions during the reaction, which is a critical factor for the success of the strategy.<sup>62</sup>

#### 2.4. Rigid polyurethane foam and mixed waste stream depolymerization

After the evaluation of glycolysis-based depolymerization of FPUF, the present technology was tested with RPUF, concretely polyisocyanurates (PIR), commonly used as thermal insulation panels in the construction sector.<sup>3,10,25</sup> This type of thermoset plastic is synthesized with highly functionalized polyols, characterized by higher iKOH values and lower molecular weights (see the SI). These properties increase the crosslinking degree and reduce the average pore size of the final material.<sup>63,64</sup> Additionally, metals can be incorporated during its synthesis,<sup>6</sup> enhancing the density while reducing the open cell content, parameters correlated with thermal conductivity and heat transport phenomena.<sup>65</sup>

These physicochemical properties make this material a more resilient and recalcitrant plastic than FPUF, requiring the development of adjusted approaches to achieve a complete and efficient depolymerization. As can be seen in Fig. 5A, the PIR is first mechanically processed to facilitate homogeniz-

ation within the catalytic medium (e.g., IL mixture and EG) and to increase the specific area, thereby favouring the mass transfer of the reaction mixture. Then, depolymerization *via* glycolysis is successfully performed and scaled up at 115 °C for 7 hours (Fig. 5B and the SI for further details). Finally, the same protocol described above is carried out to separate the recycled product from the depolymerization medium. After the overall process, 95% yield was confirmed by dissolving 100 mg of the isolated and dried product in 1 mL of DMSO. The iKOH value was  $530 \pm 30$  mg KOH per g of sample, which is within the expected range (e.g. 300–800 mg KOH per g) according to the data provided by CETEM. Finally, <sup>1</sup>H-NMR analysis confirmed the presence of aromatic protons in the recycled polyol structure, as aromatic polyester polyols are key components in PIR formulations (see Fig. S9).<sup>64,65</sup>

Additionally, the robustness, versatility and potential scalability of this technology in realistic waste scenarios were also tested (see Fig. S15). Thus, a preliminary assay using a representative mixed waste stream composed of different PUF post-consumer products (*i.e.* discarded domestic mattress, scouring pads, seats of office chairs, and post-production residues containing impurities) was conducted for depolymerization (see section S1.6 for further details). The depolymerization reaction yielded a recycled product that, after washing and drying, resulted in the same amount as that obtained from standard PUF. This new recovered polyol exhibited a solubility of 93% in DMSO, which corresponds to the previously defined depolymerization yield. Also, the FTIR spectrum of the resulting polyol from this PUFW stream is essentially identical to that obtained from a standard PUF (Fig. S16), proving that the strategy is not limited to laboratory-grade PUF samples.

#### 2.5. Scale-up of the depolymerization process

To evaluate the industrial application of the proposed process, the strategy was scaled up to 50 times, depolymerizing up to 100 g of PUFW. The reaction mixture was incubated at 98 °C for 4 hours, reaching a white solid product after the previously described isolation protocol. Then, the recycled product was subsequently homogenized with Alcupol F-4811® in a 33 : 67 (w/w) ratio (see the SI). Fig. 6 presents the process flow diagram of the overall strategy at the industrial level (1) and the different stages of the process using up to 100 g of PUFW (2). The selectivity of the process leads to negligible monomeric aromatic (di)amine content (0.05 w%), preventing the implementation of further purification steps (see Fig. S11). This minimum content is compared with the H&S Anlagentechnik depolymerization technology, proving the industrial potential of this approach.<sup>50,66</sup>

#### 2.6. Operational stability of the depolymerization medium

The traditional linear economic model, strongly established in the society, is based on the non-renewable raw material extraction for its further manufacture and subsequent deposition. In contrast, this depolymerization strategy promotes a closed-loop model in which the whole system can be fully recovered and reused in consecutive cycles, proving the “greenness” of

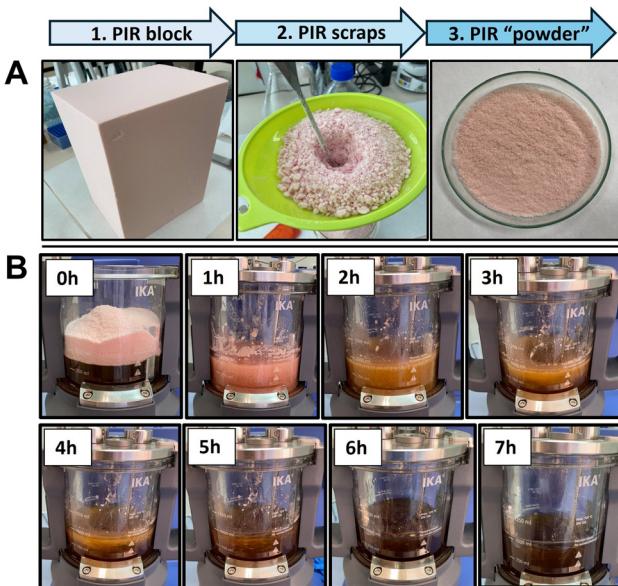
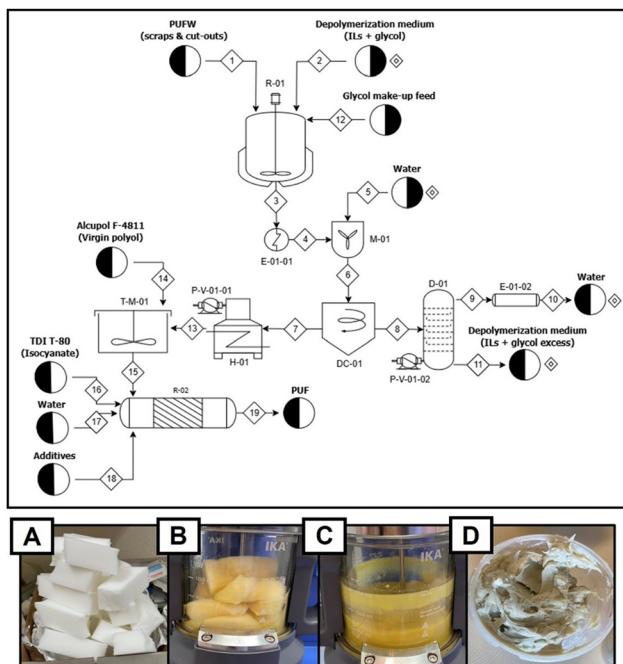


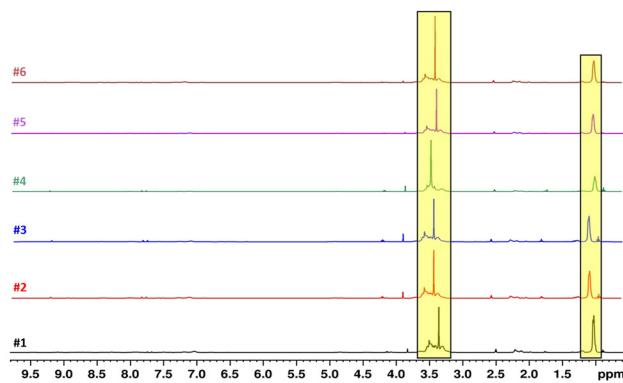
Fig. 5 (A) Mechanical pretreatment of PIR; (B) scale-up PIR depolymerization process after each hour of reaction, until reaching a homogeneous overall medium. Conditions: 400 g of [Bmim][Cl] (2.29 mol), 300 g of [Bmim][OAc] (1.51 mol), 100 g of ethylene glycol (1.61 mol) and 50 g of PIR, 115 °C, 7 h, 100 rpm.





**Fig. 6** Process flow diagram described in the SI (see Tables S3 and S4) (top). PUFW cut-outs before starting the process (A); PUFW homogenized with the IL mixture and EG after 30 minutes (B); overall reaction medium after 4 hours (C); dry recycled polyol (D) (bottom). Conditions: 343 g of  $[\text{Bmim}]\text{Cl}$  (1.96 mol), 147 g of  $[\text{Bmim}]\text{OAc}$  (0.74 mol), 50 g of EG (0.81 mol) and 100 g of PUFW, 98 °C, 4 h and 100 rpm.

the process. Fig. 7 shows the identical  $^1\text{H-NMR}$  spectra of the obtained recycled product after 6 consecutive cycles. To verify the stability and integrity of the recovered ILs,  $^1\text{H-NMR}$  analyses were performed after each depolymerization cycle, revealing identical signal protons (Fig. S10). Additionally, to further confirm the glycolysis reaction of PUFW, the recycled products obtained after each cycle were analysed using ATR-FTIR (see Fig. S12). The spectra consistently showed the presence of car-



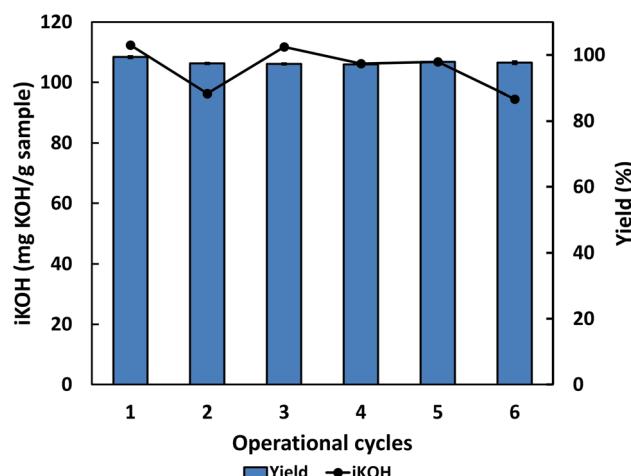
**Fig. 7** Comparison of  $^1\text{H-NMR}$  spectra of the obtained recycled polyol after 6 consecutive depolymerization cycles. Conditions: 98 g of  $[\text{Bmim}]\text{Cl}$  (0.56 mol), 42 g of  $[\text{Bmim}]\text{OAc}$  (0.21 mol), 10 g of EG (0.16 mol) and 20 g of PUFW, 98 °C for 4–5 h and 100 rpm.

bamate bonds, indicated by the characteristic carbonyl band around 1700–1740  $\text{cm}^{-1}$  in all cycles.

There are several factors that can limit the system efficiency, namely (i) loss of the depolymerization medium due to recipient changes during washing–centrifugation cycles; (ii) IL traces adhere to the polyol surface after the isolation protocol; and (iii) release of monomeric aromatic amines during the depolymerization process.<sup>57</sup> To overcome the mass loss issue, the depolymerization reaction and subsequent system concentration were carried out within the same set-up. Additionally, IL recovery optimization was deeply studied during this assay, as previously described. As expected, both the mild reaction conditions and short reaction times allow selective cleavage of the urethane bonds, avoiding uncontrolled side reactions that can negatively affect the catalytic system (0.05 w% monomeric aromatic (di)amine content).

Following the first cycle, a gravimetric analysis revealed that approximately 8% residual water remained attached to the ionic network of the depolymerization medium. This residual moisture could reduce both the nucleophilic character of EG and the catalytic efficiency of  $[\text{Bmim}]\text{OAc}$ . To compensate for this effect, the reaction time was adjusted to 4 hours in the first cycle and extended to 5 hours in the subsequent operational cycles. Furthermore, additionally, 5 g of EG were added after each cycle as make-up feed, to ensure an excess of glycol during the reaction. Fig. 8 depicts the yield and the iKOH value of the final recycled polyol after each cycle performed. Notably, the mass recovery of the recycled product remained unchanged in all cycles, consistently exceeding 95%.

To further emphasize the mild reaction conditions and recyclability of the present technology, Table 2 provides a brief comparison summarizing previous glycolysis approaches reported in the literature. As previously described, most reported glycolytic methods not only require high reaction



**Fig. 8** Operational stability of the active depolymerization medium confirmed by means of the iKOH determination as well as the yield of the recycled product. Conditions: 98 g of  $[\text{Bmim}]\text{Cl}$  (0.56 mol), 42 g of  $[\text{Bmim}]\text{OAc}$  (0.21 mol), 10 g of EG (0.16 mol) and 20 g of PUFW. Each depolymerization cycle was performed at 98 °C for 4–5 h and 100 rpm.



Table 2 Comparison of glycolysis approaches reported in the literature with the present work

Catalyst	Conditions	Steps	Ref.
2-Pyrrolidone, bismuth(II) neodecanoate	200 °C 3 h	(1) Split-phase glycolysis (2) Hydrolysis of the bottom phase	67
KOH	200 °C 5 h	(1) One-phase glycolysis (2) Deamination protocol	68
CsOH and KOH	170 °C 2.5 h	One-phase glycolysis (rigid PUF)	69
1,4-Diazabicyclo octane	200 °C 3 h	(1) Split-phase glycolysis (2) Upper phase purification	70
NaOH	210 °C 1 h	One-phase glycolysis (rigid PUF)	71
[Bmim][Cl]/[Bmim][OAc] (recoverable and reusable)	98 °C 4 h	One phase glycolysis	This work

temperatures (*i.e.*, 170–210 °C), but also multi-step protocols, often including phase separation, hydrolysis, or purification steps.<sup>67–71</sup> In contrast, the present method employs fully recoverable and reusable ILs at a significantly lower temperature (<100 °C) in a single-step process.

## 2.7. Resynthesis of new PUF

Finally, the quality of the recycled product was assessed by synthesizing new PUF and evaluating the chemical, physico-chemical and mechanical properties (*i.e.* Differential Scanning Calorimetry (DSC) resilience, tensile strength, compressive strength, *etc.*) of the resulting material (see Fig. S13 and Table S2). As shown in Fig. 9A, the PUF synthesized from the recycled polyol obtained through the present technology yielded a soft foam with appropriate foaming properties. Notably, the PUF obtained from virgin polyol (E1) exhibits similar properties compared to that obtained from a mixture containing 30 w% of the previously homogenized recycled polyol (E2). As expected, when 50 w% of the recycled mixture was used (E3), slight limitations in the foaming process were observed mainly attributed to an imbalance between expansion (gasification) and polymerization (gelation) reactions.

Nevertheless, the resulting foam's appearance and texture were more suitable for direct application in the polymer industry, underscoring the effectiveness and superior quality of the

polyol recovered mixture by this method. Fig. 9B presents the optical microscopy images of the re-synthesized PUF, confirming the consistency of its structure. DSC analysis reveals no significant differences in the glass transition temperature ( $T_g$ ) between the reference foam and the one containing 30 w% recycled polyol (Fig. S13). The slight increase in  $T_g$  could indicate reduced mobility of the polymer's soft phase.

## 3. Conclusions

A scalable glycolysis-based depolymerization process for PUFW (up to 100 g of PUFW processing capability) has been successfully developed and optimized by leveraging the unique tunable properties of ILs. This innovative and robust technology represents the first reported transcarbamoylation approach for PUFW that operates entirely on a highly active IL based-medium, employing [Bmim][Cl] and [Bmim][OAc] as both the reaction medium and catalyst. The process operates under mild conditions, enabling selective cleavage and subsequent exchange of carbamate bonds. As a result, the residual aromatic (di)amine content remains at 0.05 w%, avoiding the need for additional purification steps that make industrial implementation difficult. The recyclability of the [Bmim][Cl]/[Bmim][OAc]/EG system was demonstrated by successfully reusing it for six consecutive glycolysis depolymerization cycles, confirming its stability and effectiveness. Although the use of ILs may involve additional costs, increasing regulatory demands on polymer recycling could justify their application, making the process both technically feasible and practically relevant. Overall, ongoing advances in large-scale synthesis, bio-derived feedstocks, and recyclability are steadily reducing the cost of ILs, reinforcing their viability as sustainable alternatives to conventional solvents.<sup>72</sup> The apparent short-term economic costs of implementing sustainable technologies pale in comparison to the long-term catastrophic destruction already caused by climate change.<sup>15</sup>

To conclude, this technology clearly highlights the potential of IL-based approaches for the sustainable depolymerization of recalcitrant polymers such as PUFW at temperatures below 100 °C, proving a straightforward strategy for polyol recovery. Furthermore, the versatility, scalability and robustness of this

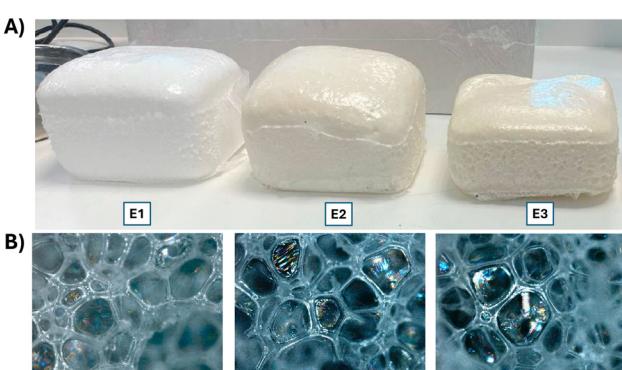


Fig. 9 (A) Re-synthesized PUF prepared from virgin polyol (E1), using 30% and 50% of recycled polyol mixture (E2 and E3, respectively.). (B) Optical microscopy images in reflection mode.



method have been successfully extended to other types of PU wastes, such as PIR, reinforcing its relevance for industrial application. Finally, the re-synthesized PUF, incorporating up to 50 w% of the recycled polyol produced using the current technology, demonstrates the suitability of the final product for direct application in the synthesis of new PUFs with identical chemical, physicochemical and mechanical properties, supporting the advancement of circular chemistry.

## Author contributions

F. V. methodology, investigation, data curation, and writing first drafts; R. S. methodology, investigation, and data curation; N. A.: methodology, investigation, and data curation; J. D. and E. G. V.: investigation, supervision, writing review and editing; R. V. investigation, supervision, writing and editing, project administration and resources; P. L.: conceptualization, investigation, supervision, writing review and editing, project administration resources, and funding acquisition.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

All data, methodologies and any other experimental details necessary to reproduce this work, mainly with regards the depolymerization of different PU and analysis of the resulting recycled product, can be found in the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5gc03643g>.

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