Unprecedently High Dissolution and Depolymerization of Hard to Dissolve Polyurethane in Deep Eutectic Solvents under Low Energy White Light

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Supporting Information

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Annexure S1:

List of merits that our new method/technique for the dissolution of Polyurethane holds over the existing methods reported in literature.

S. No	Merits of our method	Description of Our Method	Description of Reported Methods
1.	Prevention (Less Waste)	**Our method:** Lactic acid-based DESs has been synthesized for the dissolution and degradation of Polyurethane (PU), a form of widely used plastic. The synthesis of DESs and breakdown of PU produces no waste as byproduct. The process of regeneration of dissolved PU from DES is carried by using water, which is again greener in nature, don't produce any waste.	**Reported Methods**: Volatile Organic Solvents (VOSs) used for dissolution of PU involves toxic chemicals, solvents and also produces side products.[1-4] In the mechanical recycling, waste products such as dust and non-recyclable fragments of plastics are formed.[5,6] This process also produces low quality plastic, which tend to be environmentally toxic. In the pyrolysis method, high concentration of acid or alkali are used which again produces greenhouse gases and residues in the environment. [7]
2.	Atom Economy	The synthesis of DES involves the combination of $ZnCl_2$ and Lactic acid, where both these entities gets incorporated in the product and thus offers atom economy. Secondly, the recovery of depolymerized fragments of PU from DESs also adds to atom economy.	The full recovery of VOSs used in dissolution of PU is not possible owing to their high vapor pressure, which hinders the atom economy. VOSs which are involved in catalytic conversion do produce waste at molecular level during their synthesis and also produces side products.[3] Components used in the formation of catalyst for organocatalytic activity on degradation plastic are usually less stable and losses their activity.[4]

3.	Less Hazardous Chemical Syntheses	Both the components of DESs *i.e.* $ZnCl_2$ and Lactic acid are non-toxic if not ingested. Their combination in neat in the absence of organic solvent at optimum temperature conditions gives DESs making the synthesis less-hazardous.	Chemical and catalytic conversion of plastic involves the usage of toxic chemicals, solvents and side products, which are responsible for greenhouse gases.[1,3-4] Besides this, the processing of PU by pyrolysis at high temperatures always poses the risk of accident. Such processing also emits toxic volatile products.[7]
4.	Design for Energy Efficiency (lower energy inputs, temp and pressure)	The DESs has been synthesized at optimum temperature conditions (80 ^oC for 8 hours) at atmospheric pressure. The Dissolution of PU was also carried out optimum temperature condition (60 ^oC) and under white light (40 W). Also, the regeneration process take place by simply adding water at room temperature conditions. The above given premised renders the dissolution and degradation of PU an energy efficient process.	Pyrolysis of plastic is carried out at high temperature and pressure conditions. High capital cost is another disadvantage.[7] In mechanical recycling, recovery costs exceed manufacturing costs.[6] Also, chemical conversion of plastic is energy intensive.[1-2]
5.	Safer Solvents and Auxiliaries	DESs and their components are non-toxic if not ingested. The non-volatility of DESs further makes them safer chemicals. Water was used for regeneration, which is the further addition to sustainability of the process.	Solvents used in various process such as pyrolysis, chemical and catalytic conversion are toxic and volatile.[1-4]

		No heavy equipment's are involved in whole process.	Manufacturing cost is much higher in mechanical recycling. Heavy equipment are required in pyrolysis method, therefore, energy intensive is another disadvantage.[8]
6.	Inherently Safer Chemistry for Accident Prevention (Ease in preparation)	During the preparation of DESs, dissolution of PU and its regeneration, no organic solvents have been used which reduces the risk of fire. Further the relatively low temperature preparation of DESs (80 ^{o}C), dissolution of PU (60 ^{o}C) and its regeneration (25 ^{o}C) using water reduces the risk of any sort of accident.	Solvents used in the degradation of plastics are volatile in nature and less economic.[2,4] Also, the solvents emit volatile compounds in nature, and also forms side-products which may harm the environment.[4,8]
7.	Design for Degradation (Biodegradability)	One of the components used in preparation of DES i.e Lactic Acid is biodegradable in nature. However, the reuse of DES would limit its wastage and leakage into environment.	VOSs and catalysts used in the degradation process non-biodegradable in nature.[9] Mechanical recycling method produces non-recycle fragments of plastic which persists in environment.[6]
8.	Recyclability	The collection of used DESs by simply evaporating water which retains its characteristic structure is expected to offer recyclability to DESs.	Solvents used in pyrolysis, chemical and catalytic conversion methods can't be recycled and reused again.
9.	Reuse	DESs has also been reused without effecting its efficiency to dissolve PU.	The solvents and catalyst used in the degradation process can't be used again.

Annexure S2:

2. Experimental

2.1. Materials

Metal based DESs comprising $ZnCl_2$ as *H*-bond acceptor (HBA) and lactic acid (LA) as H-bond donor (HBD) (LA:$ZnCl_2$) in molar ratio of 1:1 and 4:1 have been taken from the lot reported previously.23 Karl-Fischer titration analysis using an automated Methochm 831 KF Coulometer demonstrates that the used DESs are hygroscopic in nature and saturate at $ZnCl_2$:H_2O = 1:1 in both DESs. Polyurethane (PU) Selectophore and dimethyl sulphoxide-d_6 (DMSO-d6) (>99.9%) were purchased from Sigma Aldrich. The weighing of different chemicals was performed on an analytical weighing balance (Precisia) with a precision of 0.0001 g, and the dissolved PU was regenerated using degassed Millipore grade water.

2.2. Dissolution and Regeneration of Polyurethane in DESs

A given amount of PU was put into a glass vial having 4 g of respective DES pre-heated at 60 ^{o}C in the presence of white light (40 W LED) at atmospheric pressure and stirred at 200 rpm after having an approximate idea about the extent of dissolution by adding PU in a stepwise manner (200 mg per lot). The appearance of a yellowish color marked the onset of dissolution, which eventually turns blackish and relatively viscous with the gradual dissolution of PU. The monitoring of dissolution was also made via optical microscopy, where the appearance of solid particles, even after prolonged stirring (24 h), marked the saturation of dissolution. Viscosity of DES with dissolved PU was measured using Anton Paar MCR-92, Modular compact rheometer 159 000 Model using cone plate geometry (CP 25 mm). The dissolved PU was regenerated using water as anti-solvent, and the precipitated product was subsequently separated using centrifugation at 6000 rpm for 15 minutes. Following the separation of regenerated material, the aqueous layer having respective DES was vacuum dried and DES was recovered.

2.3. Characterization of Regenerated Material

Fourier Transform-Infrared Spectroscopy (FTIR) measurements were performed using Agilent Cary 630 FTIR instrument in the range of 500–4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) measurements of native PU and regenerated material were performed on a Thermo-Scientific NEXSA spectrometer employing a monochromatic Al Kα X-ray source with magnetic focusing and a charge neutralizer operated at 1486.6 eV. Data analysis and data processing were done on Thermo Avantage v5.9925 software and Thermo Avantage v5.9921 software, respectively. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements of regenerated material in DMSO-d_6 were performed on a JEOL, ECZR 600 MHz NMR spectrometer. Powder X-ray diffraction (XRD) measurements were performed on a

SHIMADZU MAXIMA 70000 instruments in the 2θ range of 5–80°. Thermogravimetric analysis (TGA) was done on a HITACHI STA7200 thermal analysis system under an N_2 atmosphere in the temperature range of 25 to 1000 °C at a heating rate of 10 °C min^{-1}. The METTLER TOLEDO Differential Scanning Calorimeter, DSC 3, which has a strong and adaptable DSC sensor with 56 thermocouples, has been used to perform differential scanning calorimetry (DSC) at a rate of 2 °C min^{-1} under N_2 atmosphere. Atomic force microscopy (AFM) was performed on Anton Parr Tosca Series 400 AFM in tapping mode. Transmission electron microscopy (TEM) was performed on JEOL JEM-2100 electron microscope, operating at 200 kV. The ethanolic solution of the regenerated material was drop casted on mica sheets for AFM measurements and 300 mesh carbon coated TEM grid for TEM imaging, followed by drying at room temperature. Zeta-potential (ζ-Pot) and hydrodynamic radius (Dh) measurements were performed using a Malvern Nano-Series ZS light scattering instrument at 173° scattering angle employing a dip cell (ZEN-212) and quartz cuvette respectively. MALDI-TOF-MS measurements and analyses were carried out using Bruker Autoflex III. Size-exclusion chromatography (SEC) was performed on 1260 Infinity II GPC MDS System configurable to house GPC specific detectors RID, Viscometer, and dual angle LSD system. The system was equipped with a 1260 Infinity II Isocratic Pump, two guard columns (PLgel 5um Guard 50 x 7.5 mm), a 1260 Infinity II Vialsampler, a 1260 Infinity II Multicolumn Thermostat MCT at 50 °C, with two PLgel 5um MIXED-D 300 x 7.5 mm in series. 1260 Infinity II Diode Array Detector (DAD), refractive index detector (RID), and Viscometer Detectors were used to analyze the samples. DMAc containing 5 g/L of LiCl was used as eluent at a flow rate of 0.5 mL/min. The spectra were analyzed using the Agilent GPC/SEC software dedicated to multi-detector GPC calculations. The molar mass and dispersity values were calculated against PMMA standard.

2.4. Toxicity test On *E. coli* strains

E. coli strain (ATCC 25922) was inoculated for 24 hr on nutrient broth at 37°C. It subjected to utilized in toxicity test determining nonhazardous nature of the regenerated materials form both DESs through Kirby Bauer disc diffusion toxicity test. A loop full of bacteria was spread on nutrient agar plate and 50 µl of materials A and B was loaded and kept on incubation at 37 °C for 48 hr.

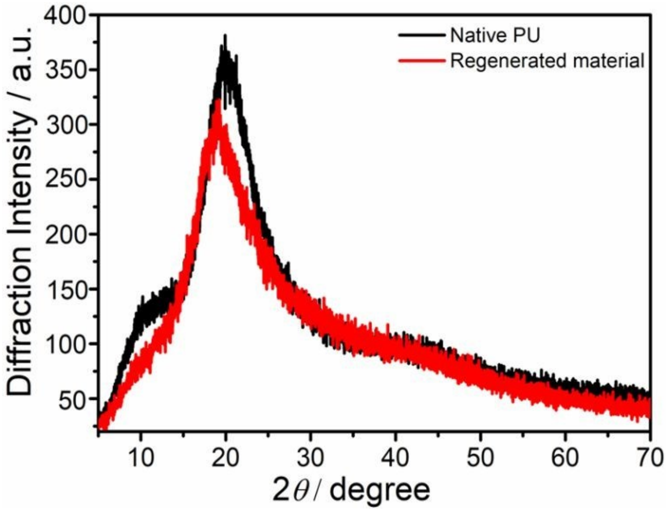

Figure S1: X-ray diffraction pattern of material regenerated from dissolved DES (1:1) in comparison to native PU.

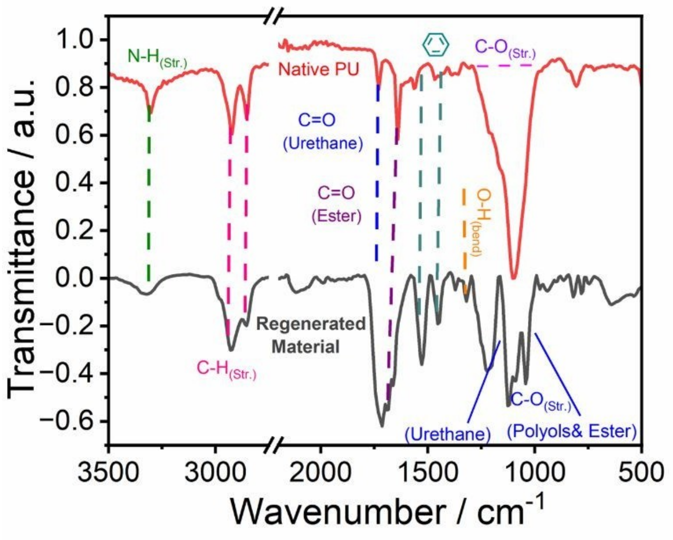

Figure S2: FTIR spectra of native PU in comparison to material regenerated from DES (4:1).

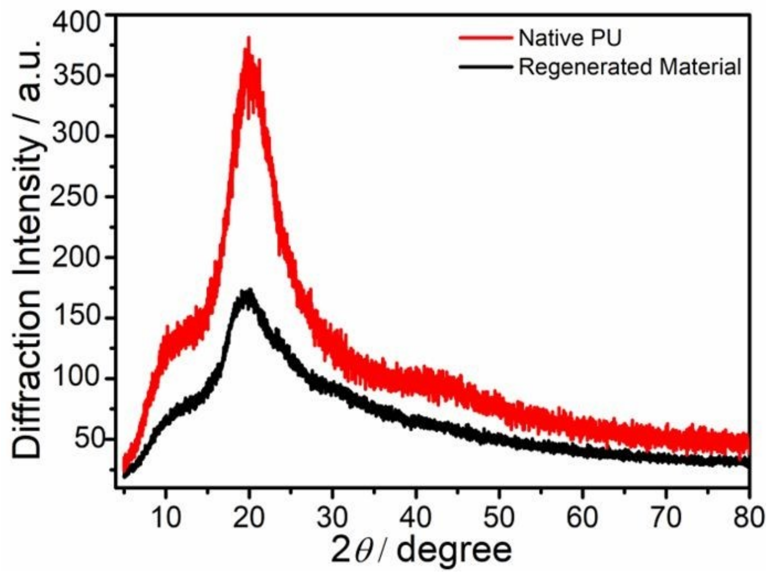

Figure S3: X-ray diffraction pattern of material regenerated from dissolved DES (4:1) in comparison to native PU.

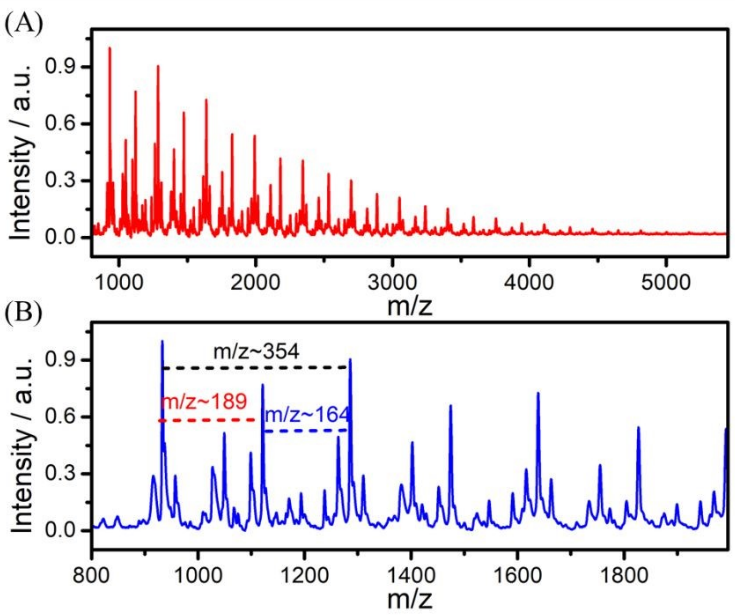

Figure S4: (A-C): (A) Mass spectrum of material regenerated from LA:$ZnCl_2$ DESs 1:1; (B) enlarged counterpart of (A) and (C) molecular structures of probable fragments.

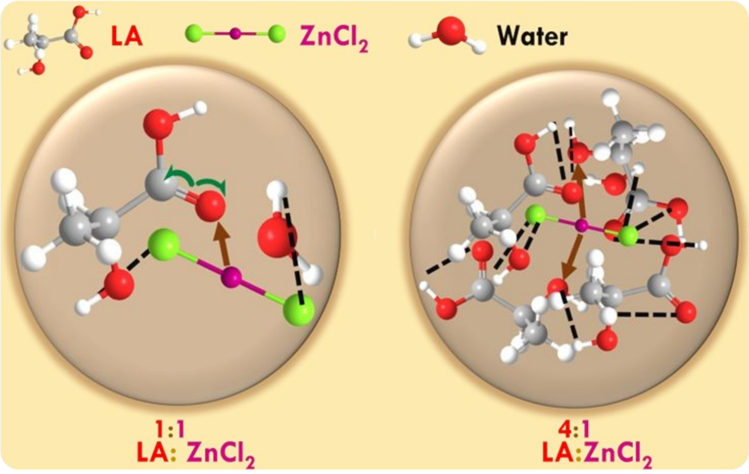

Figure S5: Plausible interactions between the different components of DESs.

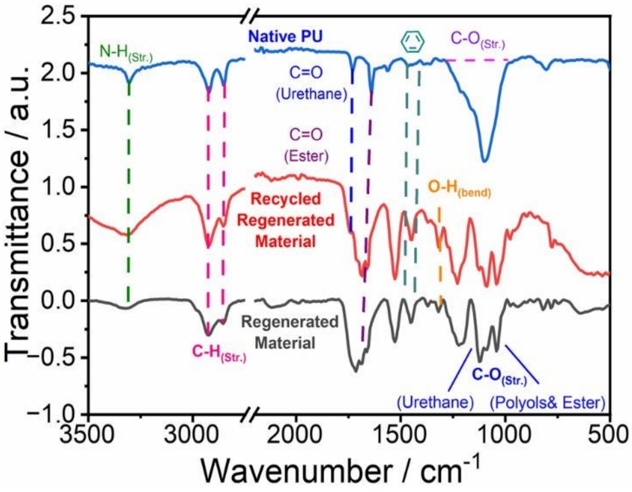

Figure S6: FTIR spectra of native PU, regenerated material and material regenerated from reused DES (4:1).

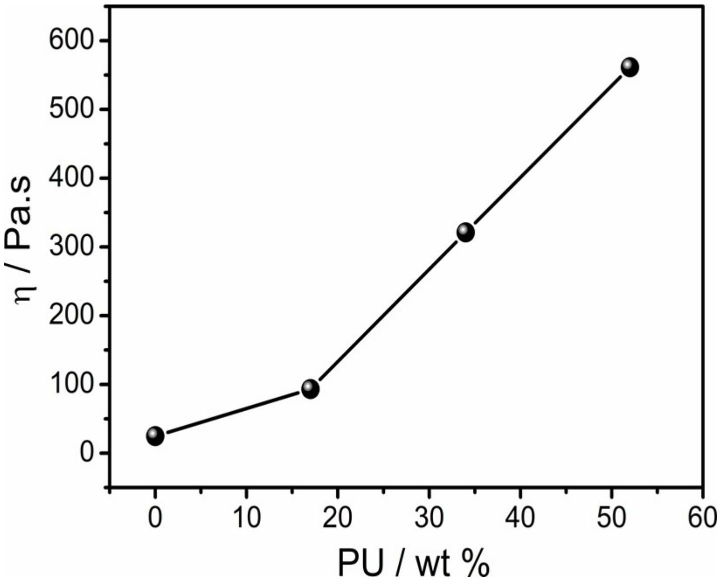

Figure S7: Variation in coefficient of viscosity with loading of PU (w/w%) to LA:$ZnCl_2$ (1:1) DES.

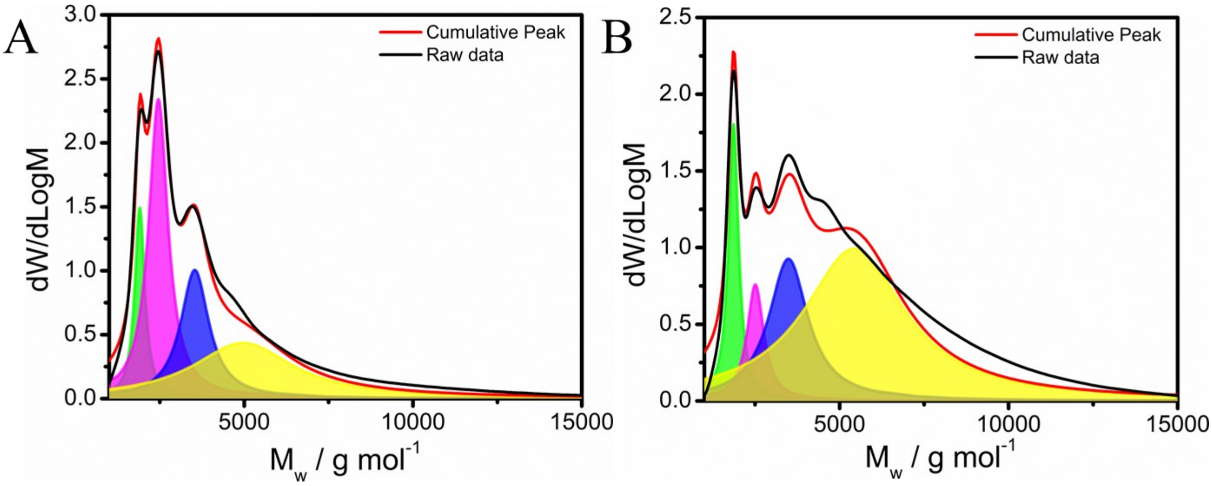

Figure S8: GPC analysis of the material regenerated from DES comprising $ZnCl_2$ and LA in different molar ratios as (A) LA:$ZnCl_2$ = 1:1 and (B) LA:$ZnCl_2$ = 4:1 .

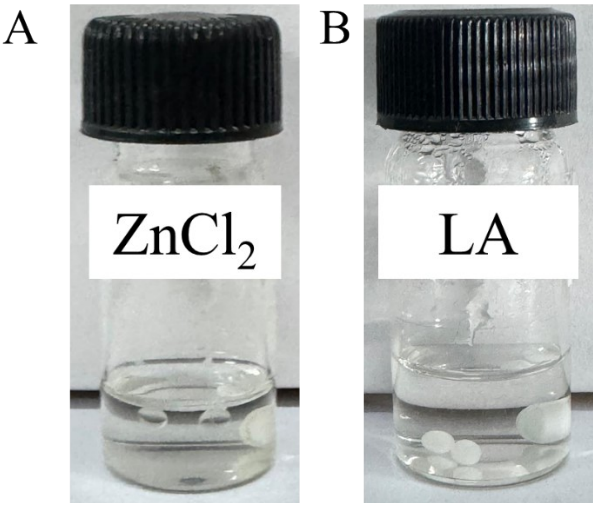

Figure S9: Photographs showing undissolved PU in concentrated aqueous solutions of (A) $ZnCl_2$ and (B) Lactic acid (LA) in 1:1 molar ratio with water under visible light at 60 °C.

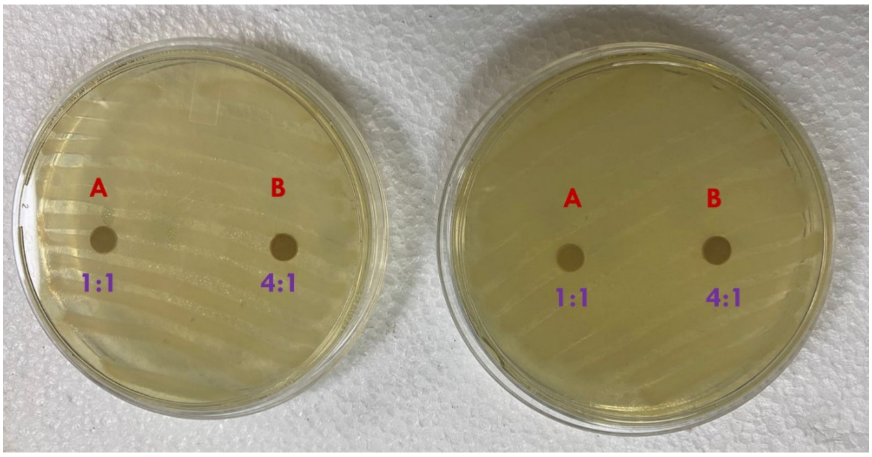

Figure S10: Photograph (results in duplicate) showing no zone of inhibition in *E. coli* cultures in the presence of degraded material obtained by PU dissolution in DESs as LA: $ZnCl_2$ (A) 1:1 and (B) 4:1, respectively.

Annexure S3:

Cost-Benefit Analysis

First Cycle

The cost-benefit analysis for the dissolution of PU using a DES under white light in the first cycle highlights key financial considerations. The total cost incurred for this process amounts to □22,899.49, which includes both capital expenditure (CapEx) and operational expenditure (OpEx). A significant portion of this cost, approximately 96.24%, is attributed to CapEx, while OpEx constitutes only 3.76% of the total expenditure. This indicates that the initial investment in equipment and infrastructure is the primary financial burden, whereas the recurring operational costs are relatively lower.

In terms of dissolution efficiency, the process achieves a dissolution rate of 70 g of PU per 100 g of solvent. Given this efficiency, 70 g of polyurethane dissolution requires 100 g of the DES. The density of the solvent is reported as 1.801 g/cm^3, which provides insight into the physical properties influencing the dissolution process. The revenue generated from this operation is calculated based on a processing fee of □50 per gram of polyurethane dissolved, resulting in total benefits of □3,500 for the first cycle.

The cost of the solvent required for this operation is □3,352.25, which constitutes a notable portion of the total expenditure. Since this analysis is limited to the first cycle, the cost incurred for solvent procurement directly impacts the overall financial assessment. Given that the solvent is used for a single round, this adds to the financial strain. Here, the cost relief from recyclability of the solvent is not taken into account.

From a financial evaluation perspective, the Net Present Value (NPV) for the first cycle is calculated at □-19,717.68, considering a discount rate of 10%. A negative NPV of this magnitude suggests that the process is not financially viable under the given conditions, as the total costs significantly outweigh the benefits generated. Additionally, the benefit-cost ratio is determined to be 0.153, indicating that for every rupee invested in the process, only 15.3 paise is recovered as revenue. This low ratio further reinforces the lack of economic feasibility in its current form.

The analysis suggests that, under the existing parameters, the dissolution of polyurethane using a deep eutectic solvent under white light results in substantial financial losses in the first cycle.

Solvent Recyclability

The updated cost-benefit analysis considers solvent recyclability and presents a more comprehensive financial evaluation of the PU dissolution process using a DES under white light. The total expenditure is categorized into capital expenditure (CapEx) and operational expenditure (OpEx), with CapEx contributing □22,899.49 (96.24%) and OpEx accounting for

□3.76%. This distribution indicates that the major financial commitment is associated with the initial investment in infrastructure and equipment, while ongoing operational costs remain comparatively lower.

The dissolution efficiency remains at 70 g per 100 g of solvent, meaning that 70 g of polyurethane requires 100 g of solvent for processing. The density of the solvent is 1.801 g/cm^3, which provides an indication of the material's handling and storage requirements. The cost of operation for the first cycle, considering OpEx, is □3,352.25. However, in this scenario, the solvent is reusable for five rounds, thereby reducing the per-cycle solvent cost.

The financial assessment now reflects the revised processing fee of □50 per gram of polyurethane, which results in a total benefit of □3,500 per cycle. Since the solvent is used across five cycles, the total benefits for these five cycles amount to □17,500, whereas the corresponding total cost for these cycles is □23,040.85. While this still indicates a cost burden over multiple cycles, the financial viability improves significantly when scaled to a yearly operational capacity.

Assuming 1,000 cycles per year, the total benefits for the first year are estimated at □35,00,000, while the total cost for the first year stands at □2,22,608.93. This results in a positive Net Present Value (NPV) of □29,59,209.25 for the first year, indicating a strong financial gain over time. Additionally, the benefit-cost ratio for the first operation is 15.723, meaning that for every rupee invested, approximately □15.72 is recovered, which represents a substantial economic advantage.

The inclusion of solvent recyclability significantly improves the financial feasibility of the process. Compared to scenarios where the solvent is not reused, the cost per cycle is greatly reduced, leading to a highly favorable NPV and benefit-cost ratio. This analysis suggests that the dissolution of PU using DES under white light can be an economically viable process when solvent reuse is implemented, making it more attractive for industrial applications.

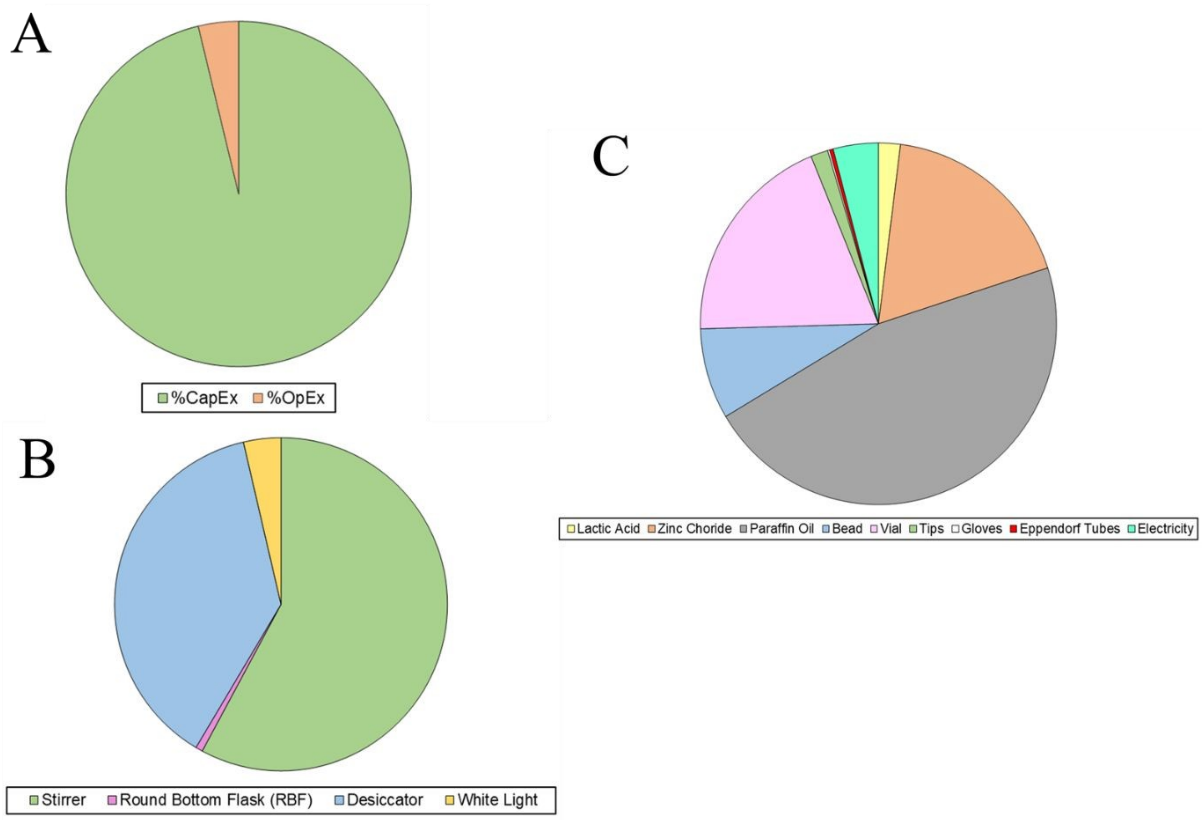

Figure S11: (A-C): (A) Relative share of CapEx and OpEx for the first cycle; (B) Cost components for CapEx and (C) Cost components of OpEx (one cycle).

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