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- The work addresses a problem involving environmental and technical challenges due to persistence and poor recyclability of polyurethane. Understanding of these issues is important to mitigate environmental harm and overcome the limitations of existing recycling methods with adoptation of economically viable solutions like DESs for polymer processing and recycling.
- The sustainable advancement lies in the development of a green, energy-efficient, and economically viable process for dissolving and depolymerizing polyurethane using reusable, benign DESs offering a scalable solution for described problem.
- This work advances SDG 12 (Responsible Consumption and Production), SDG 13 (Climate Action), SDG 9 (Industry, Innovation, and Infrastructure), and supports SDG 14 and SDG 15 by reducing environmental plastic pollution through sustainable, green chemistry solutions for polymer waste management.

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ARTICLE

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

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Polyurethane (PU), a synthetic polymer, is of immense commercial use. However, its utility and processing are limited by negligible solubility in available solvents, furthered by its non-biodegradable nature. Herein, a new sustainable approach for the unprecedentedly high dissolution (70 w/w%) and depolymerization of PU to low molecular weight (900 – 3000 g mol^{-1}) depolymerized product is established. PU dissolves in deep eutectic solvents (DESs) comprising lactic acid (LA) and $ZnCl_2$ under white light at 60 ^{o}C, and the dissolved material was regenerated using water. The multi-technique characterization of regenerated material evidenced the cleavage of urethane linkages and the emergence of new functional groups. The impact of change in DES component ratio on its efficiency towards dissolution and depolymerization of PU has highlighted the crucial role played by $ZnCl_2$. The DESs have been reused where the properties of the regenerated material from recycled DES resemble those obtained from native DESs. The ease of PU processing via this environmentally friendly approach will encourage the development of new metal based DESs for processing of various non-biodegradable and hard-to-dissolve polymers. Further, reusability of DESs is expected to elevate the benefit-cost ratio to 15.723, making this process economically viable and attractive for industrial use.

Introduction

Plastics represent a diverse category of polymeric entities encompassing ubiquitous utilization.[1] Among these, Polyurethane (PU), stands out as one of the favourite materials across a broad spectrum of end-user applications[2–4] and the current production of PUs is estimated to be 20 million tons,[5-6] which is expected to increase further. However, ineffective biodegradation, non-sustainable methods of processing with relatively lower yields and inappropriate waste management infrastructure of PU results in substantial volumes of PU waste leaking into the ecosystem.[7] Such a leakage with long-term survival in the environment,[8,9] along with PU's resistance to heat, light, and toxins, is a major obstacle for its sustainable utilization. The inherent structural aspects of PU comprising hard segments (isocyanates such as 2,4 (or 2,6)-toluene diisocyanate (TDI) and 4,4'-diphenylmethane diisocyanate (MDI)), soft segments (polyester polyols or polyether polyols or glycols and other functional groups etc.,),[8] the central to which is the "urethane linkage" render it a hard to process polymer in a sustainable manner. The conjunction of urethane bond with extensive H-bonding in the polymer further hinders the dissolution, depolymerize and processing of PU in conventional solvents under optimal conditions of temperature and pressure. In past, several methods have been explored for the dissolution and processing of PU, including chemical hydrolysis,[10] biological degradation,[11] thermal degradation,[12] photochemical degradation,[13] organo-catalytic degradation and mechanical methods.[14] The chemical hydrolysis of PU materials requires acidic or alkaline conditions and that too at relatively high temperatures (150^{o}C–300^{o}C).[14–16] Similarly, thermal degradation also requires very high temperatures.[17,18] In organo-catalytic degradation method, PU is pre-treated with solvents such as decalin or 1-methylnapthalene and tetralin before pyrolysis. The involvement of toxic solvents, high cost, formation of side products, and instability of organo-catalyst are some of the disadvantages of this process.[19] Mechanical processes are quite tedious and result in low-grade plastic materials.[20,21] Enzymes, microorganisms, or a combination of both have been investigated for their ability to degrade PU, however slow degradation rate limits practical applicability.[9,11] It is clear that these methods have various limitations, which together with the high expense and energy usage, have prompted the scientific community to scrutinize "Green chemistry" goals towards the degradation of plastic materials.

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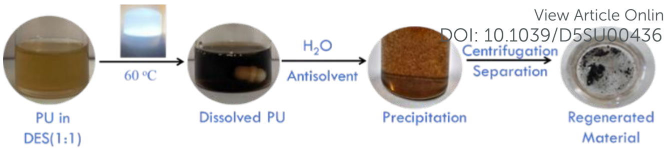
One such method is the dissolution, processing and regeneration of hard to dissolve materials in relatively greener solvents such as ionic liquids (ILs)[22-24] and deep eutectic solvents (DESs).[25,26] DESs represent a new class of sustainable and green solvents, formed by mixing H-bond donor (HBD) and H-bond acceptor (HBA) in an appropriate ratio[27,28] and have many remarkable properties akin to ILs.[29] Along with this, DESs have some additional advantages such as ease of synthesis, low cost, and the use of non-toxic and biodegradable components for their synthesis,[27-30] which proclaims them to be green solvents. In recent past, metal-based DESs have emerged as potential entities for the dissolution of hard to dissolve biopolymers (lignin,[31,32] chitin,[33] cork,[34] keratin[35]) and synthetic polymers such as Polythene (PE),[36] Polyethylene terephthalate (PET),[37,38] Poly (ethylene 2,5-furandicarboxylic acid) (PEF),[39] and Polycarbonate.[40]

Following this, Deng et al., have reported the dissolution (0.4 g of PU in 4 g of DES, solubility ~ 10 w/w%) and degradation of PU via the solvothermal method in an autoclave (140-180 °C in 6-8 h) in choline chloride (ChCl) and urea-based DES.[41] It was observed that the carbamate and urea links in the PU were cleaved while preserving the carbonate bond, which resulted in the formation of Polycarbonate diol (PCDL) and 3,3-Dimethyl-[1,1-biphenyl]- 4,4-Diamine (o-toluidine). Recently, Nataraj et al., also reported the degradation of PU by solvothermal process in an autoclave (180 °C-200 °C in 12 h) employing ChCl and ferric chloride based DESs in the presence of water and observed the formation of carbonaceous material with the yield of ~3 %.[42] These reports have demonstrated the utility of DESs for converting PU into value added materials however are limited by the usage of high temperature and pressure conditions while displaying a low dissolution yield. Therefore, new DESs should be tested for the high solubilization and depolymerization of PU under sustainable conditions at relatively low temperature and at atmospheric pressure. In this methodology, the conjunction of metal based recyclable DES with white light has furthered the sustainability.

Herein, a new and sustainable strategy for the dissolution (solubility ~ 70 w/w%) and depolymerization of PU in $ZnCl_2$ and lactic acid (LA) based DESs under white light at 60 °C is reported. The dissolved PU has been successfully regenerated using water as an antisolvent at room temperature (Scheme 1) and the regenerated material was characterized for possible degradation and transformation in molecular structure employing various state of art techniques. The regenerated low molecular weight material exhibits signatures of different functional groups such as ester, alcohol, amine and amide etc., devoid of urethane linkages. The relative molar ratio of $ZnCl_2$ and LA have been found to affect the extent of dissolution and depolymerization. The recovered DESs have been reused successfully for dissolution and degradation of PU again, which establishes the sustainable nature of the process. It is expected that such a high solubility of PU along with its depolymerization would lay a new platform for the processing and functionalization of variety of hard to dissolve polymers to achieve sustainable development goals.



Scheme 1 Pictorial presentation of dissolution of PU in DES (LA: $ZnCl_2$ = 1:1) and its regeneration using water

Results and discussion

For better understanding, the dissolution process of Polyurethane (PU) in LA: $ZnCl_2$ (1:1) is discussed at first, if not mentioned otherwise. PU does not solubilize in given DES at room temperature under white light. At 60 °C under white light, PU tends to solubilize achieving a highest solubility reported ever i.e., ~70 w/w % in 24 h. The transformation of a clear yellowish DES to a blackish viscous solution upon dissolution of PU confirms the solubilization (Scheme 1). Viscosity measurements have also shown an increase in the value of the coefficient of viscosity (η) with an increase in the amount of PU added to the DES (Fig. S7, ESI). The value of η for pure LA: $ZnCl_2$ (1:1) DES is ~ 24.8 Pa s, which increases to 93.2 Pa s after the addition of 17 % (w/w) of PU. It is further increased to 321.2 Pa s at 34 % and 561.4 Pa s at 52 % loading of PU to the DES, confirming efficient dissolution of PU in LA: $ZnCl_2$ (1:1). The dissolved PU has been regenerated by using water as an anti-solvent followed by its separation from aqueous DES via centrifugation (Scheme 1). The colour of regenerated material is carbon black in contrast to whitish appearance of PU used in this study, which is suggestive of depolymerization and degradation of PU during dissolution. (Fig. 1) shows the comparative Fourier Transform-Infrared (FTIR) and X-ray photoelectron (XPS) spectra of native PU and regenerated material. The band at ~3303 cm^{-1} corresponding to $N\text{-}H_{(\upsilon,\ s)}$ vibrations of urethane bonds in PU gets broadened and shifts towards blue at ~3339 cm^{-1} in the regenerated material (Fig. 1A) suggesting the prevalence of H-bonding interactions between fragmented PU units.[43-44] The formation of 2°-amines exhibiting $N\text{-}H_{(\upsilon,\ s)}$ can't be ruled out at this stage. Relative change in the intensity of the bands ~2915 cm^{-1} $C\text{-}H_{(\upsilon,\ as)}$ and ~2853 cm^{-1} $C\text{-}H_{(\upsilon,\ s)}$ in the native PU[13,45] along with an increase in the intensity of bands at ~ 1445 cm^{-1} and ~782 cm^{-1} related to in ring $C\text{-}H_{(\upsilon)}$ and $C\text{-}H_{(\delta)}$ vibrations of substituted benzene rings respectively signifies the unwinding and fragmentation of PU upon dissolution.[15,42] Two well-defined bands at ~1730 cm^{-1} and ~1640 cm^{-1} corresponding to $C{=}O_{(\upsilon,\ s)}$ of urethane linkage and ester group respectively merges at 1684 cm^{-1} with shoulders ~1714 cm^{-1} and ~1654 cm^{-1}. A broad intense $C\text{-}O_{(\upsilon)}$ band splits into two sharp bands corresponding to $C\text{-}O_{(\upsilon)}$ of urethane linkage (~1230 cm^{-1}) and glycols/esters in polyurethane (~1050 cm^{-1}). The merging of $C{=}O_{(\upsilon)}$ band and the simultaneous splitting of a broad intense $C\text{-}O_{(\upsilon)}$ band is ascribed to structural alterations near the urethane bond related to partial or full deterioration of urethane linkage.[46-48] The appearance of a sharp band ~1520 cm^{-1} in regenerated material is ascribed to $N\text{-}H_{(\delta)}$ of amide-II band resulted as a consequence of destruction of urethane linkage. The breakage or structural alterations near

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urethane linkage could result in the fragmentation of PU to smaller subunits having different functional groups such as -OH and dicyanamide, which is supported by the appearance of -OH$_{(\delta)}$ at ~1320 cm^{-1} and N=C=O$_{(\upsilon)}$ ~ 2320 cm^{-1} in the regenerated material.

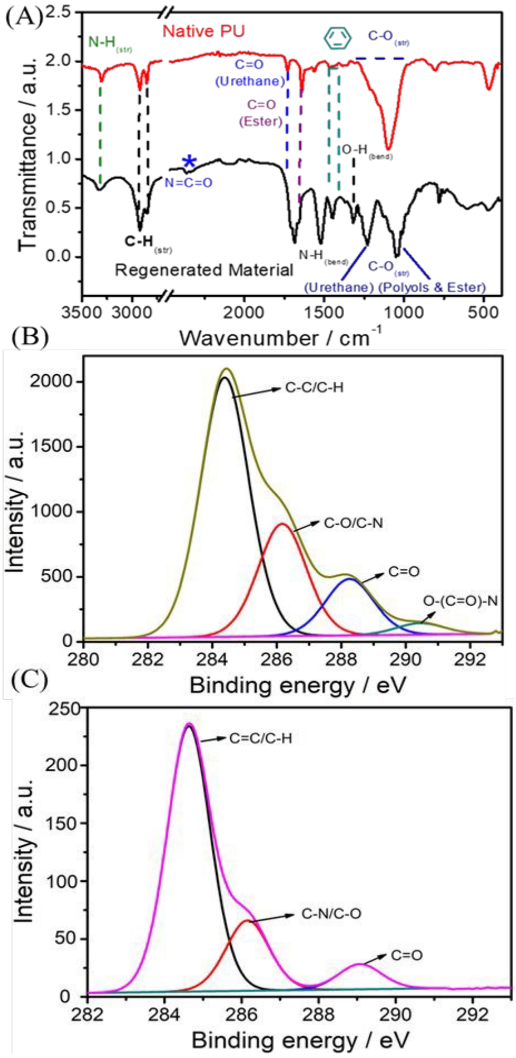

Fig. 1(A-C) (A) FTIR and (B-C) XPS spectrum of the material regenerated from DES (1:1) in comparison to native PU.

The C1s spectra of both the native PU (Fig. 1B) and the regenerated material (Fig. 1C) shows the presence of primary peaks corresponding to C-C and C=C bonds at 284.4 eV and 284.64 eV respectively[47] along with the additional peaks at ~286.16 eV and ~289.1 eV, corresponding to C-O and C=O bonds, respectively.

Notably, a distinct peak at ~290.53 eV attributed to O-(C=O)-N functionality of the urethane bond in PU[48] vanishes in the XPS spectrum of regenerated material, signifying the breakage of urethane bond. Some of the urethane bonds still exists as relatively higher molecular weight fragments of PU, as observed from MALDI-TOF measurements (discussed later), are natural to be stabilized by urethane linkage.

^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) measurements corroborates well with the results obtained from FTIR and XPS measurements (Fig. 2). Resonance peaks were systematically assigned as A onwards, starting from the most shielded proton or carbon. A substantial number of peaks (0.81 ppm – 1.82 ppm) (peak A) in 1H NMR spectra (Fig. 2A) confirms the presence of methyl (-CH$_3$), methylene (-CH$_2$), and methine (-CH) groups supported by peak A (9.54 ppm) in the ^{13}C NMR spectra of regenerated material within the saturated hydrocarbon framework.[15] The appearance of such large number of NMR peaks in both ^{1}H and ^{13}C NMR spectra of regenerated material as compared to native PU[49,50] suggests the depolymerization of PU. The presence of amine groups in the regenerated material is established by the emergence of a resonance peak in the range 3.00-3.50 ppm (peak B) in the ^{1}H NMR spectrum, in line with observations made from FTIR spectroscopy. Different ^{1}H NMR peaks (Figure 2A), *i.e.*, peak E (6.89 ppm); peak F (7.25 ppm); peak G (8.07 ppm)[15,51] and ^{13}C NMR peaks (Fig. 2B), *i.e.*, peak E (143.13, 156.0 and 156.16 ppm) confirms the presence of aromatic ring protons and substituted benzene ring carbon atoms respectively.

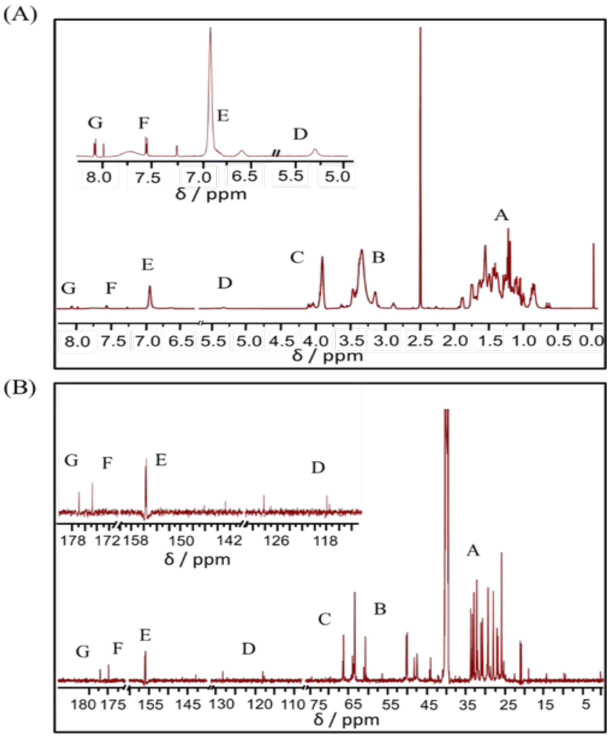

Fig. 2(A-B) (A) ^{1}H NMR; and (B) ^{13}C NMR spectra of the material regenerated from DES (1:1).

Similarly, the peaks at 118.25 ppm (peak D) and 128.49 ppm (peak E) support the presence of C=C of alkenes. A multiplet ~ 3.30 ppm and 3.91 ppm (peak C) (Fig. 2A) indicates the presence of protons associated with the -CH$_2$-O (alkoxy moiety) of an ester group, which is further corroborated by multiple peaks in the range of 60.63 ppm - 66.76 ppm (peak C) in the ^{13}C NMR spectra (Fig. 2B). Two distinct peaks for C=O at 175.12 ppm (peak F) and 177.28 ppm (peak G)[36] in the ^{13}C NMR spectra establish two types of C=O groups related to broken urethane and ester bonds.[49] The absence of peaks at 153.64 ppm and 152.60 ppm (Fig. 2B) corresponding to the C=O of the urethane bond,[50] establishes the cleavage of the urethane bond.

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Additionally, a broad peak at 5.30 ppm (peak D) in the ^{1}H NMR spectrum and peaks at 50.14 - 64.76 ppm (peak B) in the ^{13}C NMR spectra corresponding to a carbon atom attached to -CH_2OH signifies the presence of hydroxyl (-OH) groups, which are otherwise absent in native PU. From the aforementioned investigations, it is inferred that the PU undergoes unwinding and degrades to smaller fragments bearing different functional groups, with some fragments retaining native molecular bonding.

The degradation of PU and the appearance of new functional products is also supported by thermogravimetric analysis (TGA) (Fig. 3A and B). Native PU undergoes a two-step thermal degradation[18,45] with a weight loss of 41.1% in the range of 280-300 °C exhibiting an onset of degradation (T_d) ~ 287.50 °C owing to decomposition of the urethane bond.[45,53] This is followed by a weight loss of ~ 58.6% in the temperature range 300-455 °C ascribed to the decomposition of polymeric fragments of glycols and polyesters.[2] In contrast, the regenerated material exhibits a four-step weight loss with relatively lower T_d ~ 177.8 °C, signifying the decomposition of PU. The weight loss of ~ 27.0 % between 220-340 °C is associated with the decomposition of glycols. The third and fourth decomposition between ~ 415-470 °C (weight loss ~ 33.4 %) and 570-630 °C (weight loss ~ 17.5 %) accounts for the degradation of small chain polyesters[44] and de-crosslinking of the rest of the PU, respectively.[17] Beyond 650 °C, the weight loss in the regenerated material is negligible, indicating the absence of other functional groups in regenerated material.[21]

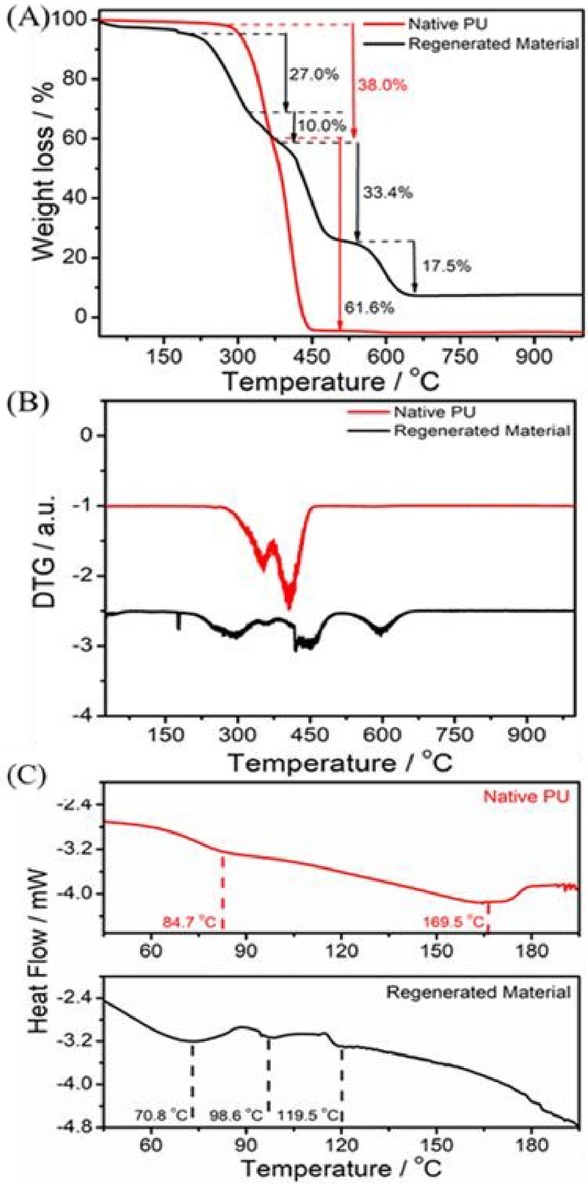

Fig. 3(A-C) (A) TGA profile; (B) DTG profile (it is scaled to show the difference) and (C) DSC thermograms of material regenerated from DES (1:1) in comparison to native PU.

A decrease in intensity of the prominent X-ray diffraction (XRD) scattering peak around 2θ ~ 18° (Fig. S1, ESI) along with a shift towards lower 2θ values in regenerated material suggests it to be relatively disordered.[51-54] Further, the native PU exhibits a peak at 2θ ~ 11°, the absence of which in regenerated material supports the breakdown of bonds of hard segments during dissolution.[45,55]

Two but rather weak endotherms in differential scanning calorimetry (DSC) thermograms (Fig. 3C) of PU at ~84.7 °C and ~169.5 °C[55,56] are assigned to the breakdown of soft segments and the dissociation of the crystalline hard segment having inter-urethane *H*-bonds respectively.[49,56-57] On the other hand, three endotherms at relatively lower temperatures, i.e., 70.8 °C, 98.6 °C, and 119.5 °C are observed in the regenerated material (Fig. 3C). The endotherms at ~70.8 °C and ~98.6 °C correspond to the melting of polyester/glycols of fragmented PU, while the endotherm ~119.5 °C corresponds to phase transitions in the fragments formed from breakdown of hard segments of PU.[58-60] The appearance of endotherms at relatively lower temperatures supports the unwinding of PU accompanied by the formation of relatively small fragmented units with different functionalities which interact varyingly among themselves after degradation.[47,61]

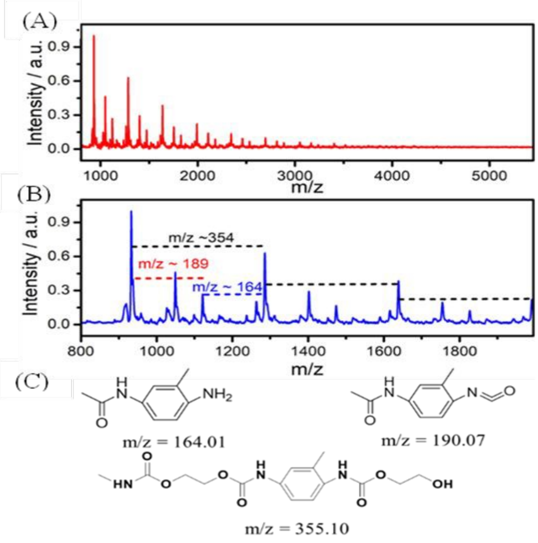

Fig. 4 (A-C): (A) Mass spectrum of material regenerated from LA: $ZnCl_2$ DESs 1:1; (B) enlarged counterpart of (A) and (C) molecular structures of probable fragments.

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MALDI-TOF measurements have provided further insights in this regard (Fig.4). The regenerated material exhibits a high intensity peak at m/z ~ 934 followed by several correlated peaks at different m/z values separated by m/z ~ 354, where the intensity of peaks decreases while going towards higher m/z values (Fig. 4). Along with those other fragments at m/z ~ 1049 and m/z ~ 1121 show different associated peaks separated by m/z ~ 354. It is natural to assume that these fragments originate from a common precursor via non-specific breakage of polymeric chain and thus, are structurally correlated to each other. The analysis of the data revealed that the major fragments that correlate three main peaks (Fig. 4) have m/z ~ 354, 189 and 164. It would be problematic to discuss further in this regard, however, considering the structure of PU employed, and based on inferences gained from various techniques, some of the probable fragments (Fig. 4C) are proposed. Further, the non-breakage of phenyl groups and their repetitive arrangements in the regenerated material hinders it from being water soluble, which, however, solubilizes in ethanol, DMSO, and DMA. Such solubilization indicates the induction of polar functional groups in the fragmented lower molecular weight PU.

These inferences are further supported by the GPC analysis of the regenerated material. A significant reduction is observed in the number average molecular weights (M_n) and weight average molecular weights (M_w) of the materials, regenerated from degraded PU in both the DESs, as compared to the molecular weight of PU (~10,000 g mol^{-1}). It is observed that the regenerated material obtained from DES (LA:$ZnCl_2$=1:1) shows the presence of at least 4 degraded fragments of PU correlated with peaks (M_w) at 1964, 2447, 3454, and 4631 g mol^{-1}, respectively, with relative peak areas of 12%, 35%, 22% and 31%, respectively (Fig. S8, ESI). Average M_n is ~ 2477 and M_w is ~ 3070 g mol^{-1}. Similarly, 4 peaks are observed in case of LA:$ZnCl_2$ (4:1) DES, with M_w ~ 1866, 2539, 3505, 4464 g mol^{-1}, having relative peak areas of 12%, 8%, 22% and 58%, respectively (Fig. S8, ESI). Average M_n in this case is ~ 2870 and M_w is ~ 3795 g mol^{-1}. These inferences support the successful degradation of PU to fragments of low molecular weights, which are ~ 20-30% of the molecular weight of the native form of PU.

The TEM images (Fig. 5A) indicate the regenerated material to be consisted of small spherical (~ 3-10 nm in size) as well as agglomerated particles (~ 80-120 nm). Small particles (Fig. 5A and B) of varying size and shape suggest the polymer's degradation into fragments in a non-selective way.[62] AFM height profile shows that the particles have a thickness of ~ 5-10 nm and a breadth of ~ 50-200 nm (Figure 5C). The hydrodynamic diameter (D_h) of the particles comprising regenerated material is further confirmed to be in the range of 30-70 nm by dynamic light scattering (DLS) measurements (Fig. 5D), which corresponds to agglomerated particles. A small positive ζ-pot. value ~15.4 mV (Fig. 5E) indicates the presence of functional groups that undergo dissociation or protonation in water, resulting in positively charged groups in regenerated material.

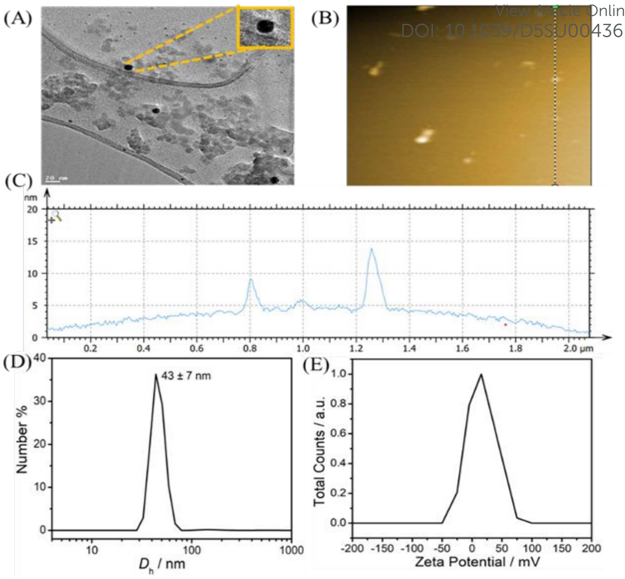

Fig. 5 (A-E) (A) TEM image; (B) AFM image; (C) corresponding height profiles of AFM images; (D) distribution of D_h and (E) ζ-potential of regenerated material.

Effect of Composition of DESs

DES having different molar ratios of LA and $ZnCl_2$ as 4:1 also dissolves PU under given conditions however, the extent of solubilization decreases (30 w/w%). The appearance of a less viscous solution with a brownish hue (Fig. 6A) as compared to the highly viscous black solution observed in the case of LA: $ZnCl_2$ (1:1) supports the decreased solubility of PU. Further, the chemical as well as elemental composition of material regenerated from DES (4:1) has been found to be similar to that of the material regenerated from DES (1:1) (Fig. S2, ESI and Fig. 6B).

However, the material regenerated from DES with higher LA content exhibits a relatively lesser decrease in crystalline order (Fig. S3, ESI) while displaying a marginally higher thermal stability (Fig. 6C). The surface morphology of regenerated material is also observed to be similar to that of material regenerated from DES (1:1) in addition to the formation of sheet-like structures (Fig. 6D). The regenerated material obtained from both the DESs shows similar structural features, however DES with LA: $ZnCl_2$ (4:1) is relatively less efficient in breaking the polymeric structure, as also evident from the large number of peaks with high intensity at higher m/z values than that observed in the case of LA: $ZnCl_2$ (1:1) (Fig. S4, ESI). This is also confirmed by the relatively lower solubility of material regenerated from DES with LA: $ZnCl_2$ (4:1) in ethanol.

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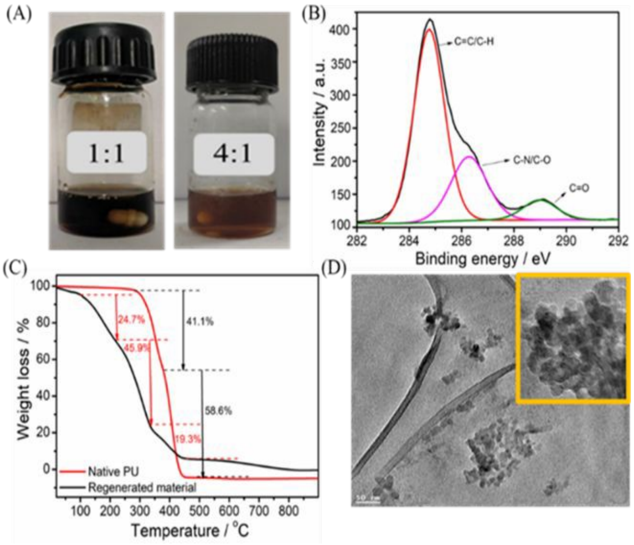
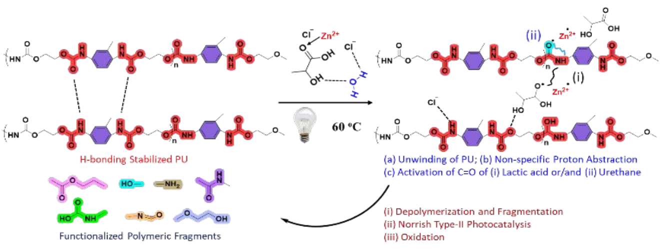


Fig. 6 (A-D) (A) Images of solution of PU in DESs; (B) XPS spectra; (C) TGA profile and (D) TEM image of material regenerated from DES (4:1).

Mechanism of Dissolution and Depolymerization

The capability of Cl^- to undergo *H*-bonding with the polymeric network, as observed during the dissolution of cellulose[32] is expected to aid in unwinding of polymeric chains during dissolution. This is followed by $ZnCl_2$ mediated fragmentation of PU. $ZnCl_2$ is a Lewis acid, which interacts and activates the C=O group of LA, and in the presence of white light, the energy of activated π-bond decreases.[23,62] As a result, a free radical is formed on the C=O group of LA, which initiates the reaction by abstraction of a proton (Scheme 2).

The free radical is regenerated on the PU chain without any selectivity, and consequently, it extracts the proton from its immediate vicinity. The formation of free radicals during the dissolution process is confirmed by the addition of benzoquinone, a free radical quencher, which inhibits the reaction when added to DES. This results in the breakage of the PU chain and, following the Norrish type II mechanism, leads to the formation of an alkene chain or shorter hydrocarbon chain with different functional groups in the presence of O_2. O_2 may also combine with the free radicals formed upon abstraction of protons, resulting in oxidation of the material. It is quite likely that C=O group of urethane bond may also be activated by $ZnCl_2$, which in cooperation with activation of C=O group of LA results in depolymerization of PU and enhances the solubilization.



Scheme 2: Schematic presentation of degradation of PU in DES under white light.

The dissolved PU and fragmented products are anticipated to be stabilized by DES via *H*-bonding interactions at the cost of decreased *H*-bonding interactions between the entities comprising DES at the temperature of investigation (60 °C), which would enhance the extent of dissolution. The free radical generated on the oxygen of LA or urethane bond regains its structure, and DESs could be reused for the dissolution of PU. It is natural to assume that the Cl^- and OH^- could potentially cleave the bonds of PU *via* nucleophilic attack.

The different extent of solubilization of PU in DESs with varying compositions can be explained based on the proposed free-radical induced solubilization. The interaction of Zn^{2+} with C=O is expected to be more probable through a coordination bond in DES with a 1:1 molar ratio of LA:$ZnCl_2$. This hypothesis is supported by negligible dissolution of PU in 1:1 DES in dark conditions, further pointing to the role of light in PU depolymerization.

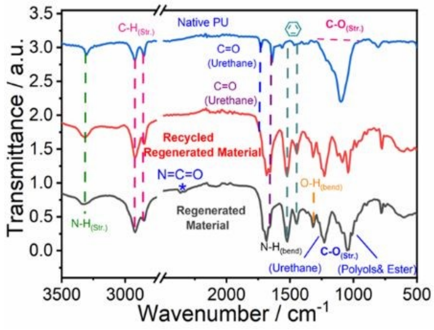


Fig. 7: FTIR spectra of native PU, regenerated material, and material regenerated from reused DES.

Conversely, LA: $ZnCl_2$ (4:1), having a relatively higher content of LA, fosters an increased extent of intra-molecular H-bonding interactions (LA-LA) (Fig. S5, ESI).[23] This, in turn, leads to a reduction in the intermolecular interactions between LA and $ZnCl_2$, thus partially hindering the activation of C=O by $ZnCl_2$. The possible coordination of the Zn^{2+} with any of the -OH group of LA instead of the C=O group could hinder the activation of the C=O group. Therefore, in the presence of more LA acid, the formation of free radical from the C=O group by Zn^{2+} through the coordination bond, required to initiate the dissolution and breakdown of PU initially, is less probable.

The role of individual components in the dissolution of PU under similar reaction conditions has been investigated. It is observed that individual concentrated aqueous solutions of $ZnCl_2$ [1.8 M] and LA [2.7 M] are not able to solubilize and degrade PU even in the time period of 72 h of visible light exposure (Fig. S9, ESI). This observation points towards the combined role of intermolecular *H*-bonding network and varied electronic structure of $ZnCl_2$ and LA in the vicinity of each other that depolymerizes PU, which is in continuation of the discussion made above that $ZnCl_2$ helps in activating the C=O bond of LA and proton abstraction, which aids the depolymerization, not probable in the absence of any one of the components.

Further, the recyclability of DESs has also been investigated. The DES was successfully recovered after the dissolution of PU by the separation of dissolved material followed by the evaporation of water. The DESs were recycled for at least three cycles of PU dissolution and regeneration without observing any compositional alterations in DESs. The regenerated materials from recycled DESs have shown similar structural features as shown by those regenerated from pristine DESs (Fig. 7 and Fig. S6, ESI). It is inferred that PU undergoes unwinding and depolymerization via the breakage of urethane bond in specific along with other bonds where the regenerated material has different functional groups. The present work, along with the previous reports on the processing of PU, is expected to offer a new perspective not only for solubilizing a variety of hard-to-dissolve materials in industrially relevant quantity in a sustainable way but also for processing as well as specific functionalization such polymers for diverse applications while adhering to sustainable development goals.

Toxicity test on *Escherichia coli* strains

Toxicity of the regenerated material obtained by depolymerization of PU in DES has been investigated. Growth inhibition of bacterial strains of *Escherichia coli (E. coli)* have been taken as model experiment to check the toxic nature of the obtained material. The results show the non-hazardous nature of the material as no inhibition zone has been observed in *E. coli* cultures in the presence of both materials obtained by dissolution of PU in DES (Fig. S10, ESI).

Cost-benefit Analysis

The total cost incurred for the dissolution and regeneration of depolymerized PU (70 w/v%) in 1 ml of DES amounts to ₹22,899.49, which includes both capital expenditure (CapEx) and operational expenditure (OpEx) (Fig. S11, ESI). A significant portion of this cost, approximately 96.24%, is attributed to CapEx, while OpEx constitutes only 3.76% of the total expenditure, which suggests that the initial investment in equipment and infrastructure is the primary financial burden, whereas the recurring operational costs are relatively lower. This makes the first cycle of dissolution, depolymerization and regeneration of PU in DES economically non-feasible (Annexure S3, ESI) considering the processing fee of INR 50 per gram of PU. However, by considering the recyclability of DES and 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 (Annexure S3, ESI). Thus, 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.

Experimental

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Materials

Metal based DESs comprising ZnCl2 as H-bond acceptor (HBA) and lactic acid (LA) as H-bond donor (HBD) (LA: ZnCl2) 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 ZnCl2: H2O = 1:1 in both DESs. Polyurethane (PU) Selectophore and dimethyl sulphoxide-d6 (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.

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 yellowish colour 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.

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^{o}.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 ^{o}C at a heating rate of 10 ^{o}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 ^{o}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.

Toxicity test On *E. coli* strains

E. coli strain (ATCC 25922) was inoculated for 24 hr on nutrient broth at 37^{o}C. It subjected to utilized in toxicity test determining nonhazardous nature of the regenerated material from 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 ^{o}C for 48 hr.

Conclusion

Polyurethane (PU) has extensive commercial use, but its non-biodegradability and lower solubility in conventional solvents under sustainable conditions, hamper its recyclability and pose a serious environmental problem like bioaccumulation. Working in this direction, we have developed an efficient and sustainable method for the dissolution of PU and its depolymerization in neat LA: $ZnCl_2$ DESs (1:1) under white light at an ambient temperature of 60 ℃. The impact of varying molar ratios of DESs on the dissolution of PU is investigated. DES composing LA: $ZnCl_2$ in molar ratio 1:1 shows the maximum efficiency for PU dissolution of 70 w/w% whereas the dissolution power of DES decreases to 30 w/w% with the increase in the LA content in DES from molar ratio 1:1 to 4:1. Herein, we have shown for the first time that neat DESs, without the addition of any solvent can degrade PU into small fragments bearing different functional groups in the presence of air at low temperature and normal pressure conditions in a short time. The reusability of DESs contributes to the process's sustainability, where it is used again for dissolving PU. It is also important to mention the fact that the components of DESs are benign, biodegradable, and cost-effective, which could open up new commercial opportunities and eventually aid in the dissolution and degradation of other synthetic polymers.

Author contributions

Harmandeep Kaur (major experimentation, data analysis and drafting of manuscript); **Rajwinder Kaur** (experimentation and data analysis); **Muskan** (data analysis and discussions); **Manpreet Singh** (data analysis and discussions); **Ravi Dutt** (data analysis and discussions); **Kanica Sharma** (data analysis and discussions); **Harjinder Singh** (data analysis); **Kuldeep Singh** (experimentation and discussions); **Arvind Kumar** (conceptualization and data analysis); **Gurbir Singh** (data analysis, discussions, review and writing manuscript) **Tejwant Singh Kang** (funding, conceptualization, supervision, data analysis and manuscript writing). All authors have given approval to the final version of the manuscript.

Conflicts of interest

"There are no conflicts to declare".

Data availability

The data will be made available on request.

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Data availability

The data will be made available on request.