Zinc Chloride Promoted Inimitable Dissolution and Degradation of Polyethylene in a Deep Eutectic Solvent Under White Light

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Electronic Supplementary Information

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Annexure S1

List of merits that our new method/technique holds for the degradation of polyethylene 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** for the dissolution and degradation of polyethylene (PE) can be divided into three steps. Step 1: The synthesis of DES produces no waste as byproduct. Step 2: The dissolution and degradation of PE in DES also does not produce any waste in the form of harmful gases/or solvent vapors during heating or under illumination with the visible light. Further, no waste of other kind (solid or liquid) is generated. Step 3: The regeneration of dissolved material has been performed with water without any waste. The DES was separated and recycled, which further establishes the reported method	Chemical recycling is a most commonly used method for degradation of PE, which involves chemolysis, pyrolysis, fluid catalytic cracking, hydrogen techniques and gasification, where high temperature (500 ^{o}C) and pressure are required while using large and sophisticated equipment's.[1] The degradation of relatively less volume of PE employing the above stated methods produces more waste.[2] On the other hand, mechanical recycling includes collection, sorting, washing and grinding of the PE material, where large number of steps complicate the process and leads to the wastage of resources.[3] Degradation of PE by incineration[4] method releases waste in the form of toxic chemicals and

		as “Zero Waste” method.	pollutants to the environment.
2.	Atom Economy	$ZnCl_2$/LA DES is the central component of this method, where DES acts as solvent for dissolution as well as the catalytic center for the degradation of the PE. DESs formation involves simple mixing of two components at appropriate temperatures, where components are fully retained in the final product without formation of any side product that makes the DESs formation 100% atom economic. Moreover, the dissolution, degradation and regeneration of PE in DES do not produce any side products and the DES is recovered at the end of the process, which make the process greener from atom economic point of view.	In chemical recycling method, besides the formation of monomers, specialized oligomeric products such as α, ω dihydroxy materials (polyols) are also produced, which effects the product distribution and the obtained product loses a substantial part of its value.[1-3] Pyrolysis in chemical recycling degrades the material into three different fractions: solid, liquid and gas with undissolved impurities.[5]
3.	Less Hazardous Chemical Syntheses	The DES itself and the components ($ZnCl_2$ and LA) used for the preparation of DES are chemically safer and biodegradable.[6] $ZnCl_2$ and LA based DESs are non-toxic,	Thermal degradation method in chemical recycling is accelerated by stress and exposure to other reactive compounds, like ozone.[3] Incineration, another method for degradation of

		easily available, non-flammable, easy procurable, recyclable, biocompatible and biodegradable in nature.[7-8] No volatile organic solvents (VOSs) are used throughout the process. Also, the regeneration step is chemically safe and is done by addition of green solvent (water).	PE at high temperature, releases pollutants, heavy metals and organic compounds to environment which are hazardous to human health.[4]
4.	Design for Energy Efficiency (lower energy inputs, temp and pressure)	Firstly, DESs is synthesized at optimum temperature (80 ^{o}C). The degradation of PE is also carried out at ambient temperature (60 ^{o}C) under white light, which minimize the energy consumption as compared to the earlier reported systems. Regeneration step is also carried out using greener solvent (water) at room temperature.	In microbial degradation method, pre-treatments are carried out at high temperature and pressure conditions.[10,11] Large amount of land is required in landfilling process and therefore more resources and energy inputs are required.[12] In mechanical recycling, extruders and equipment are costly and involves multiple number of steps, which requires high energy sources.[13] Degradation of PE in chemical recycling too take place at high temperature (200-500 ^{o}C) and

		Lastly, recycling of DESs is carried out by simply evaporating the water. All the above steps involved in the method are energy efficient as they do not require the use of very high temperatures (200-500 ^{o}C) and pressures (20-40 atm) in comparison to the earlier reported methods.[1-3,9]	pressure, and requires high energy inputs.[1,2] Equipment in both chemical and mechanical recycling need high investment and high operational costs. Thus, all above mentioned methods need high energy, high temperature and pressure which is a major drawback.
5.	Safer Solvents and Auxiliaries	DESs are easy to prepare by simply heating the reactants at relatively low temperature. No solvent was used for the preparation of DES. The degradation of PE is also carried out under white light and ambient temperature (60 ^{o}C) conditions, where no costly auxiliaries are used. Regenerating agent (water) is also greener, safe and economic hence safer solvents and	In chemical recycling, large volume of solvents is used in the process which even can't be recycled at the end and moreover releases toxic pollutants to the environment. Catalyst and solvent regulation in large volume and heavy extruders is difficult, which is another disadvantage.[2] In mechanical recycling, contaminants and impurities are produced and causes phase separation while undergoing degradation by multiple number of steps.[3]

		auxiliaries are used in the whole process. DESs is chosen as a solvent over VOCs as well as ILs due to its non-flammability, low vapor pressure, ease of preparation and cost effectiveness. Thus, both dissolving agent (DESs) and separating agent (water) are safe, biodegradable and environmentally friendly.	In incineration process, volatile organic compounds and toxic chemicals are produced which are unsafe for environment. Degradation of PE by formation of polymer blends also involves the usage of organic solvent (xylene) which is toxic in nature.[14]
6	Inherently Safer Chemistry for Accident Prevention (Ease in preparation)	Synthesized DES are environmentally safe; biodegradable and its preparation does not involve the use of very high temperature and high pressures that usually are the major cause of lab accidents. Dissolution of PE in DES is carried at 60 ^{o}C under white light. Strong hydrogen bonding in DESs make them thermally stable and non-volatile even at high temperature and the use of DES in our method reduces the risk of blast and flammability (very common when using VOCs) to large extent and make handling of	In the incineration method, degradation of PE is carried out at high temperature, which is prone to high accidental risks. This process releases pollutants, heavy metals, inorganic salts and organic compounds in the environment and therefore is difficult to handle under lab conditions. Landfilling process requires large amount of land and microbes for the degradation of PE, and thus the handling these sources is also cumbersome.

		experiment easy and human friendly. Moreover, regeneration step involves only the use of water at room temperature and hence is safer too. Conclusively we have devised an inherently safer method for PE dissolution and decomposition and use of DES and water have prevented the risk accident during handling of whole process. Further no use of acid or base makes this method safer.	Microbes in microbial degradation method need to be incubated (40-60 days) before their usage and these also need a clean and proper environment. Hence, the foremost step in microbial degradation of microbes handling for such a long time is crucial.[15,16] In chemical and mechanical recycling, multiple and complex reactions are involved in degradation of PE, which are not easy to handle. Large number of operating steps in such heavy and costly instruments needs to be regulated and also they need sophisticated set-up to be installed and thus handling such instruments are difficult.
7.	Design for Degradation (Biodegradability)	The components used for the preparation of DESs are biodegradable.[6-8] The prepared DESs are also safer, biodegradable, and soluble in water and can be recycled at the end. The recycling of DESs would limit the wastage and its environmental leakage.	Landfilling and incineration method involves the release of toxic chemicals/ gases in the environment. End products of degradation are also non-biodegradable. Gasification and pyrolysis method in chemical recycling release higher amount of noxious NOx gas in the environment.

8.	Recyclability	The DES used for the dissolution and degradation of PE are recovered at the end of the process and recycled.	Mechanical and chemical recycling involves the formation of impurities and contaminants, which adds to the demerit of these methods. The solvents used in chemical recycling (pyrolysis, methanolysis and glycolysis) can't be recycled and reused again. Microbes are used once and incubated before the degradation in microbial degradation method.
9.	Reuse	We reused DESs for at least 3 catalytic cycles without effecting its catalytic efficiency.	The additives used in microbial degradation can't be reused again. Also, the solvents used in chemical recycling can't be used again.

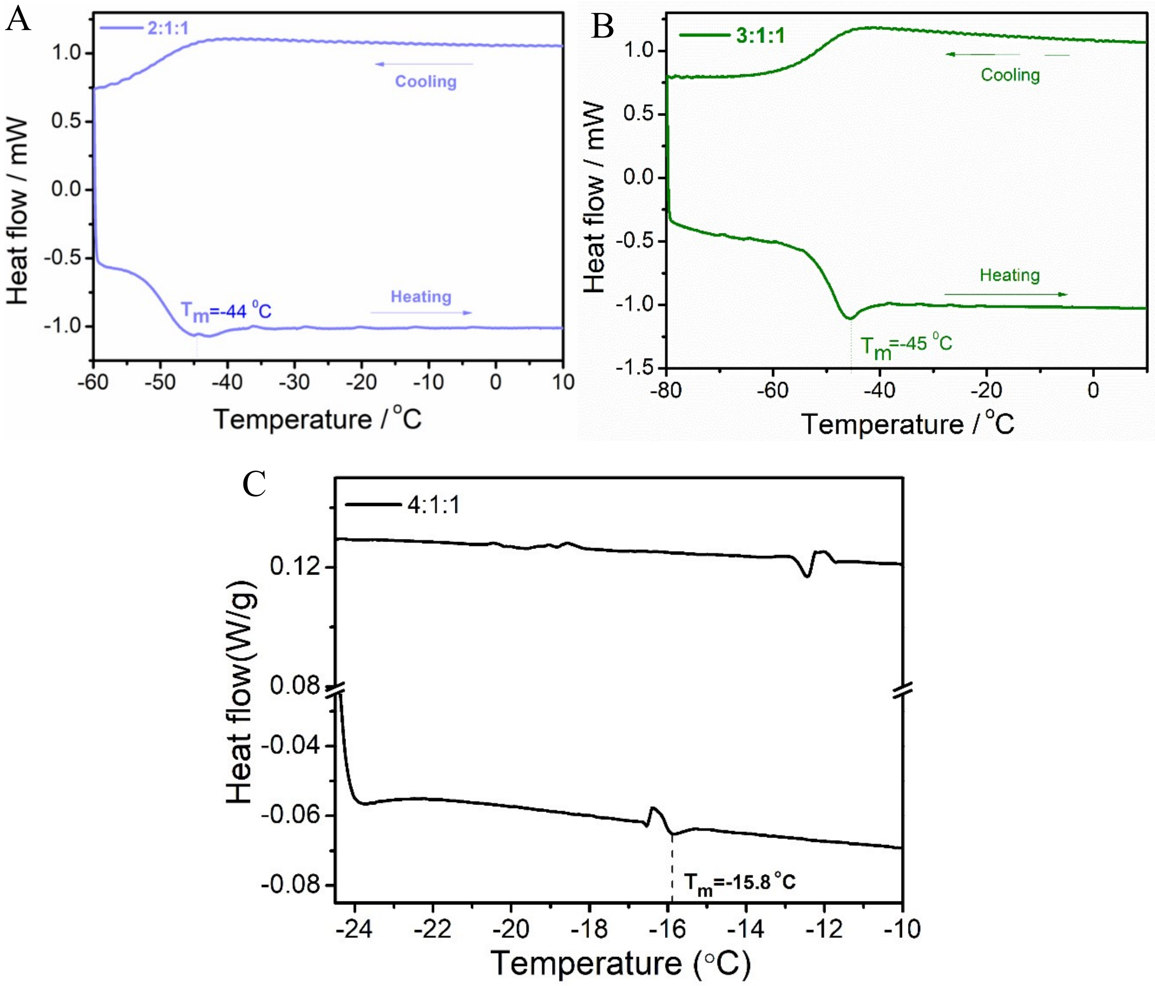

Figure S1: Differential Scanning Calorimeter (DSC) thermograms of LA:$ZnCl_2$:H_2O in the molar ratio of (A) 2:1:1; (B) 3:1:1 and (C) 4:1:1 depicting the melting points (T_m).

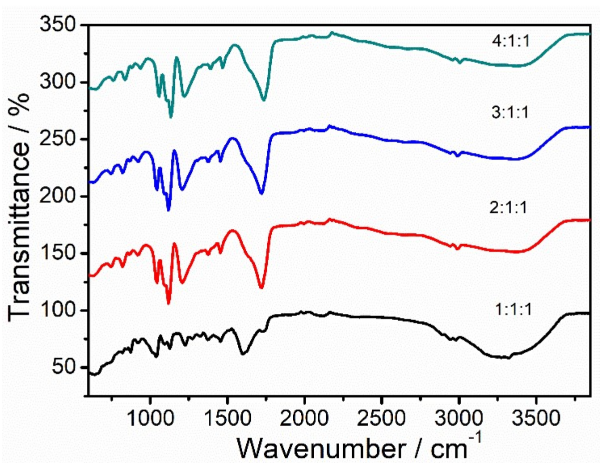

Figure S2: FTIR spectra of DES (LA:$ZnCl_2$:H_2O) in the molar ratio of 1:1:1, 2:1:1, 3:1:1 and 4:1:1.

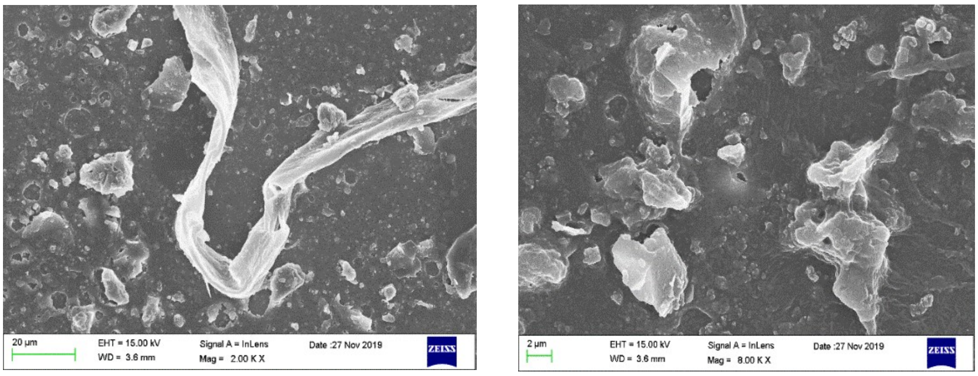

Figure S3: Scanning electron micrographs (SEM) of regenerated material obtained from dissolution of PE in DES (1:1:1) at 60 °C.

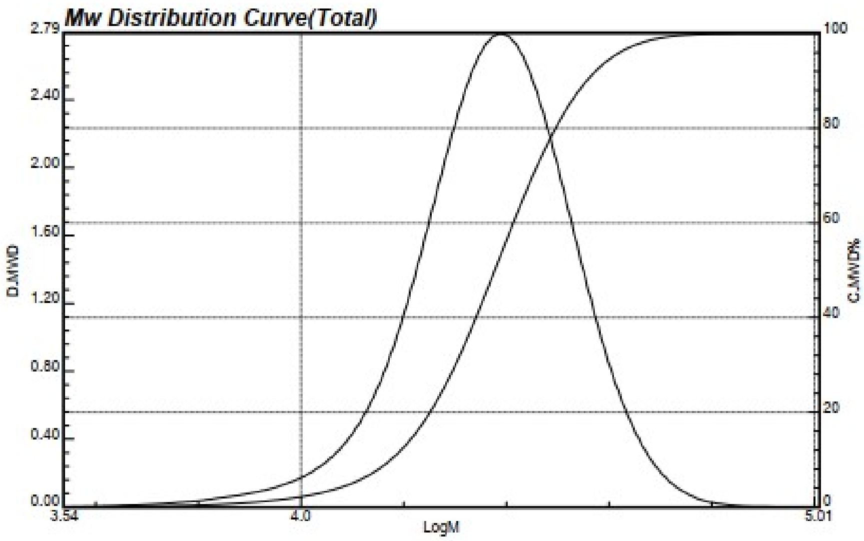

Figure S4: Molecular weight distribution curve of regenerated material using Gel permeation chromatography (GPC).

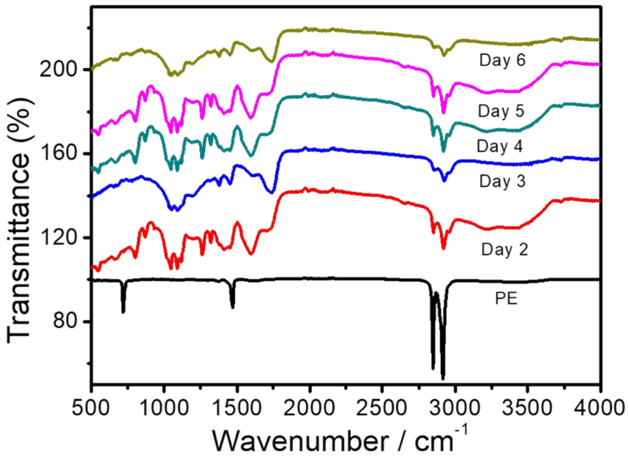

Figure S5: FTIR spectra of regenerated material after washing with water (3 times) for complete removal of DES as a function of time employed for dissolution of PE with days in comparison to native PE.

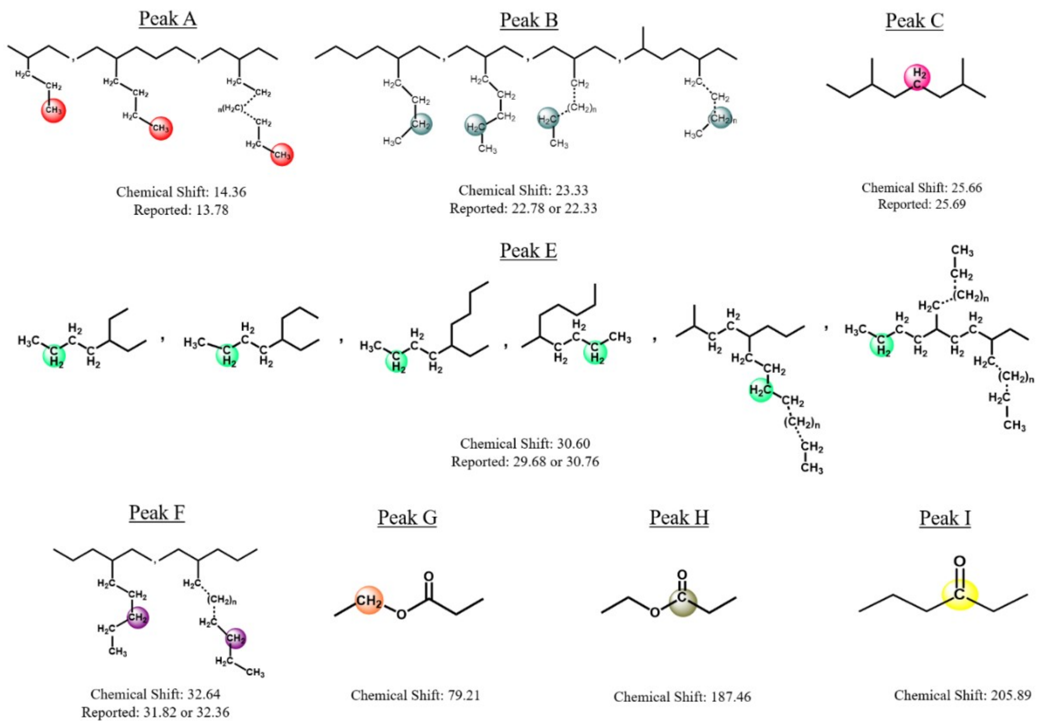

Figure S6: Probable molecular structures of regenerated fragments deduced from ^{13}C and ^{1}H NMR.

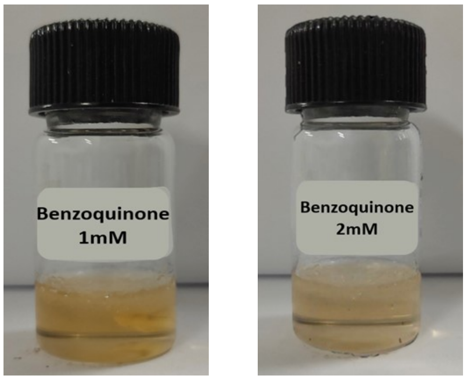

Figure S7: Photographs showing the non-dissolution of PE in DES (1:1:1) at 60 ^{o}C under white light even after 5 days of processing in the presence of quencher (benzoquinone).

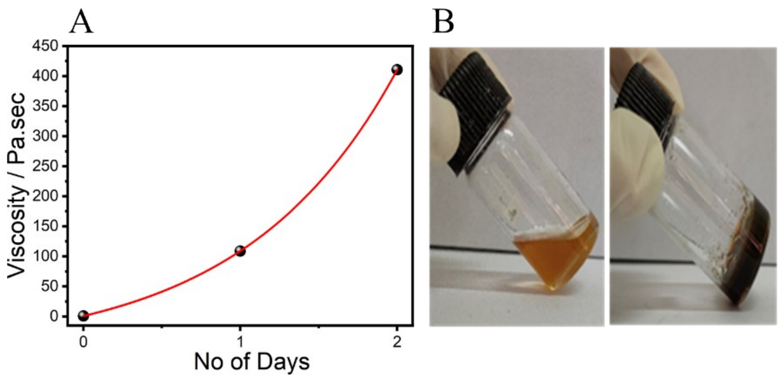

Figure S8: The variation in viscosity of the DES (1:1:1) having PE (A) at 90 ^{o}C as a function of time and (B) the pictures of DES-PE system upon dissolution of PE on 2nd and 4th day of dissolution.

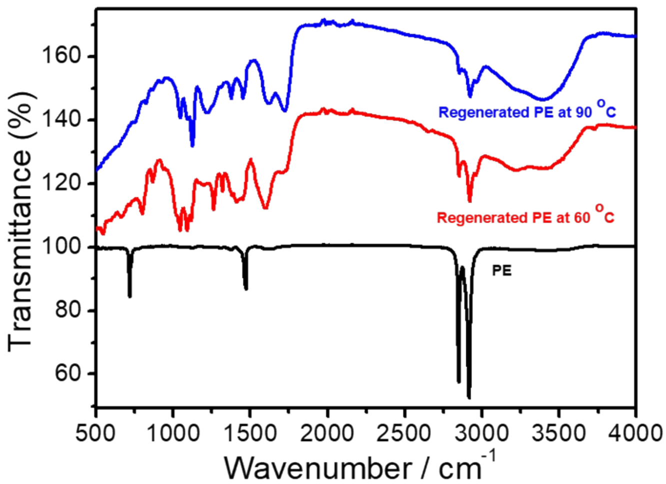

Figure S9: FTIR spectra of regenerated material obtained from dissolution of PE in LA: $ZnCl_2$:H_2O DES (1:1:1) at 60 ^{o}C and 90 ^{o}C in comparison to native PE.

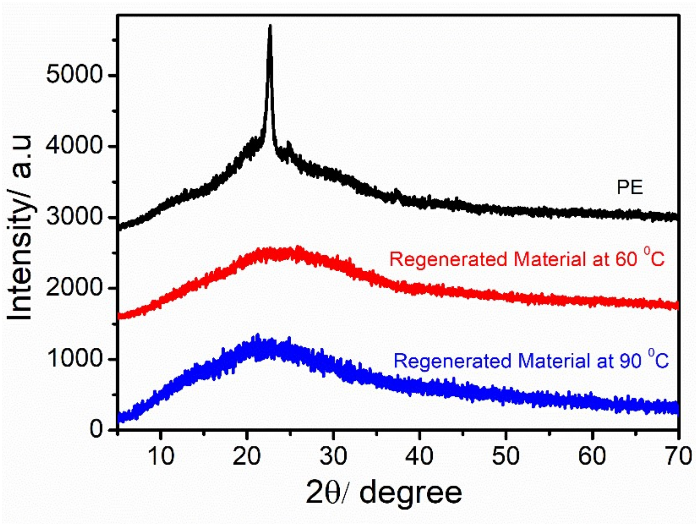

Figure S10: XRD pattern of regenerated material obtained from dissolution of PE in LA: $ZnCl_2$: H_2O DES (1:1:1) at 60 °C and 90 °C in comparison to native PE.

Table 1: Comparison of position of FTIR bands observed in regenerated material as compared to native PE.

Original PE (this work)	Reported in Literature[17]	Regenerated Material	Assignment
2918 cm^{-1}	2915-2919 cm^{-1}	2918 cm^{-1}	CH_2 Asymmetric stretching
2849 cm^{-1}	2845-2851 cm^{-1}	2849 cm^{-1}	CH_2 Symmetric stretching
1468 cm^{-1}	1460-1473 cm^{-1}	1453 cm^{-1} (weak)	CH_2 Bending
1376 cm^{-1} (weak)	1377 cm^{-1}	Absent	CH_3 bending deformation
730 cm^{-1} (shift)	720-731 cm^{-1}	Absent	CH_2 Rocking Deformation

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