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REVIEW

Natural Deep Eutectic Solvents: A New Environment Friendly Solvent

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ABSTRACT

The fabrication of materials and chemical synthesis depend substantially on solvents. They are strategic part of the green chemistry framework. In accordance with green chemistry, solvents need to qualify certain parameters, such as biodegradability, non-toxicity, non-flammability, recyclability & reusability, low cost etc. to be termed as green solvents. Deep eutectic solvents (DESs) are emerging as excellent "designer" alternatives to conventional solvents owing along with the above mentioned eco-friendly properties have exceptional thermal, moisture durability and best tunable features. DESs have a crucial role in several field related to chemical synthesis along with catalysis, material extraction and purification. They serve an array of roles as solvents, monomers, and templating agents. The Deep Eutectic Solvent (DES)-based electrodeposition opens a new era of the development of metal, alloy, and metallic nanocomposite coatings with highly tailored properties. The corrosion resistance of these coatings is multifactorial, dictated by the DES composition, metal ion concentration, and precise electrochemical parameters. The Electrolytes based on DES are also useful and inexpensive replacements for traditional corrosive and environmentally hazardous aqueous acid solutions for metal alloy electropolishing. In this current review, we are providing an overview of recent research on DES in polymer synthesis and material fabrication.

Keywords: Deep Eutectic Solvent; Green Solvent; Polymerization; Electropolishing; Organic Synthesis

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1. Introduction

The shift towards green technologies and materials is critical for alleviating adverse environmental effects, safeguarding energy security, and ensuring a healthy natural environment for the current and future generations. Since 1998, the twelve principles of green chemistry have provided a framework for developing environmentally benign products and processes [1]. These principles prioritize safer chemical auxiliaries, sustainable reaction conditions, and renewable feedstocks [2]. Solvents are a critical focus within this field; while indispensable for pharmaceutical production, coatings, and extractions, they represent a primary challenge in achieving green chemistry goals due to their high volume and environmental impact [3].

To ensure their efficacy and sustainable utilization, researchers have introduced solvent selection guides, which are compilations of comprehensive data that assess and rank solvents based on several criteria such as environmental impact, volatility, air pollution, water pollution, bio-compatibility, human health hazards, toxicity, incineration, and exposure potential etc. [4]. These solvent selection guides provide comprehensive understanding of the eco-friendliness of solvents and their associated risks [5]. Based on these findings, it is evident that most of conventional solvent systems are volatile, flammable and pose serious threats to environment hence unfit for being green solvents. A number of studies have cautioned about the use of volatile solvents as they release hazardous Volatile Organic Compounds (VOCs) hence their exposure and accumulation in land/water/air pose serious risks to environmental health. Due to potent threats of solvents various government agencies have framed stringent regulations for use and disposal of solvents in laboratory and industrial processes. Hence, Green Chemistry principles weighted green solvents to make chemical processes more efficient, safe, cost-effective, eco-friendly, and sustainable [6,7]. In this context, water might be the perfect solvent owing to its abundance, non-toxicity and bio-compatibility. However, despite its potential to be the perfect green solvent, the effect of water vapour and its limited range of solubility for both organic and inorganic molecules restrict its potential applications. In this regard, quest for a suitable alternative to conventional volatile solvents is still ongoing.

Abbott et al. introduced a low-melting mixture of several solid quaternary ammonium ions with solid urea molecules and named them as deep eutectic mixtures [8]. Deep eutectic solvents (DESs) are basically low-melting mixtures of two or more components in which one component is a hydrogen bond donor (HBD) and another is hydrogen bond acceptor (HBA) [9]. The term ‘deep’ may refer to a eutectic temperature much lower than that anticipated by thermodynamically ideal behaviour of the liquid phase [10], which is caused by robust intermolecular hydrogen bonding interactions between the DES precursor components than those present in the pure compounds. These components are associated with each other through hydrogen bonding interactions. Generally, hydrogen bond acceptors are halide salts of ammonium, sulphonium or phosphonium ions, whereas hydrogen bond donors are organic compounds having amides, hydroxyl or carboxylic acid groups [11]. DESs are characterized by sharp decrease in freezing point and are, generally, liquids at lower temperatures. DESs have some unique physico-chemical properties such as extremely low vapor pressure, non-volatility, non-flammability, non-corrosiveness, excellent solubility for organic and inorganic moieties, recyclability & reusability, thermal stability, etc. [12]. Moreover, they are cost-effective, biodegradable and eco-friendly in nature. Furthermore, application of different types of HBAs and HBDs in varying molar ratios makes them an excellent choice for tunable solvents [13]. Owing to these benefits, DESs are termed as green solvents although consideration for green credentials is still being studied but they nevertheless provide an excellent alternative to the hazardous volatile organic solvents hence making the chemical and industrial processes more sustainable and eco-friendly. Deep Eutectic Solvents (DES) have been classified as:

a) Natural Deep Eutectic Solvents (NADES): These are synthesized from bio-renewable metabolites, specifically amino acids, organic acids, and sugars. Beyond water and lipids, NADES are increasingly recognized as the "third liquid" phase within living organisms, playing a vital role in biological solubility and transport. b) DES Derivatives: These include specialized formulations such as Choline Chloride: Glycolic Acid or ternary mixtures like Choline Chloride: Glycolic Acid: Oxalic Acid. While they function similarly to standard eutectic mixtures, their physicochemical properties are specifically tailored for enhanced performance, often deviating from simple binary eutectic points. The basic structure of halide salts and hydrogen bond donors for deep eutectic solvents [9,14] is given in **Figure 1**.

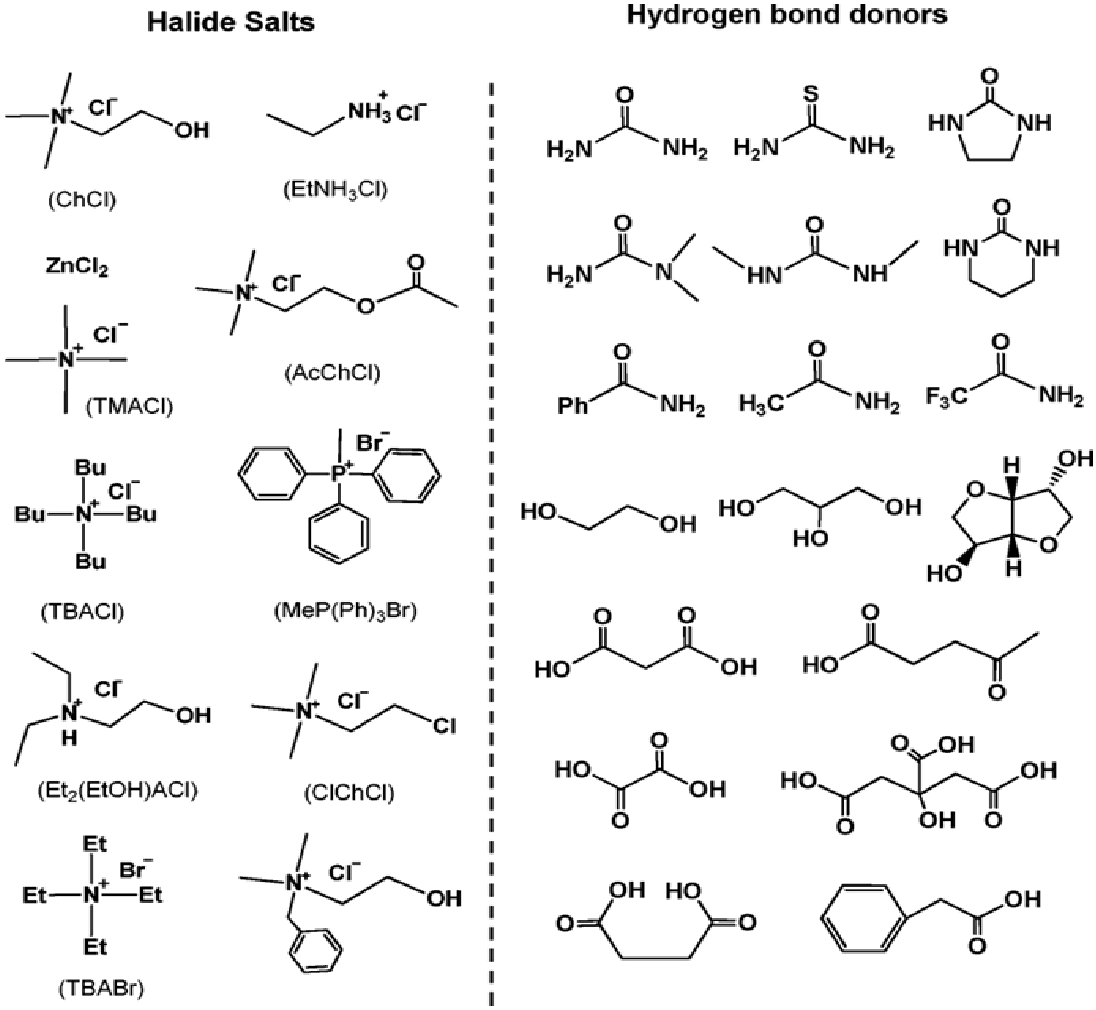

Figure 1. General structure of halide salts and hydrogen bond donors for deep eutectic solvents.

DESs show similar physico-chemical properties to ionic liquids (ILs) in terms of non-flammability, non-volatility, recyclability, reusability, thermal stability, solubility etc. But there are some basic differences between ILs and DESs;

1. ILs have their physicochemical properties primarily due to coulombic forces along with other forces like hydrogen bonding and Van der Waals forces but DESs have predominant hydrogen bonding interactions.
2. ILs are made up of ionic imidazolium ions and bulky inorganic anions whereas there are so many DESs that are made up of organic molecules only.
3. ILs are made via intricate preparatory techniques that undoubtedly have an influence on the environment, whereas DESs are made by simply mixing their constituents in a specific ratio.
4. ILs have been known to be non-biodegradable, whereas a number of biodegradable DESs are available [9,15,16].

Based on the nature of components and their interactions, DESs are classified into the following major categories and are tabulated further (**Table 1**):

1. Type-I DES: Quaternary ammonium salt and metal chloride;
2. Type II: Quaternary ammonium salt and metal chlo-

ride hydrate;

3. Type III: Quaternary ammonium salt and HBDs as organic substrates containing amides, carboxylic acid and polyhydroxy compounds;
4. Type IV: metal chloride hydrate and HBDs;
5. Type V: molecular HBAs and HBDs.

Table 1. Different Types of DES general formula.

Type	General Formula	Terms
Type I	$Cat^{+}X^{-}zMCl_{x}$	M = Zn, Sn, Fe, Al, Ga, In
Type II	$Cat^{+}X^{-}zMCl_{x}\cdot yH_{2}O$	M = Cr, Co, Cu, Ni, Fe
Type III	$Cat^{+}X^{-}zRZ$	Z = CO, NH_3, COOH, OH
Type IV	$MCl_{x}\cdot yH_{2}ORZ$	Z = CO, NH_3, COOH, OH

Note: where Cat^{+} refers to ammonium, phosphonium or sulfonium cation, X^{-} = a Lewis base, z represents the molar ratio of the hydrogen bond donor and RZ = organic compound.

In addition to this, there are many sub-categories of DESs depending upon their applications.

1. Non-ionic DES (NIDES): In recent years, a new class of type V DES has emerged very rapidly. It is comprised of neutral organic molecules, such as HBA and HBD components hence termed as non-ionic DES [13]. The first discovery of non-ionic DES was reported by Soviet scientists aiming to develop liquid fertilizers. A binary mixture of acetamide (M.P. 80 °C) and urea (M.P. 133 °C) in a 2:1 stoichiometric ratio melts at a eutectic temperature of 56 °C[15]. Computational studies of acetamide/urea (2:1) mixture show a high order intermolecular complexation, which ultimately leads to deviation from ideal behaviour and forming a eutectic mixture [16]. Lazerges et al. studied thymol based binary mixture and found this mixture was liquid at room temperature [17]. Furthermore, van Osch et al. studied 507 mixtures of non-ionic substances, out of which they found 17 mixtures were liquids at room temperature [18]. Later on, studies of thymol/(-) menthol binary mixture show a large deviation from the ideal behavior of mixtures even though both compounds were structurally similar. Recently, it was reported that a 1:2 stoichiometric mixture of thymol/menthol was a deep eutectic mixture. Very recently, Ndizeye et al. successfully used three DES systems, acetamide-N-methylacetamide (AA-NMA), N-methylacetamide-N-methyl urea (NMA-NMU) and N-methylacetamide-N, N'-dimethylurea (NMA-NN'DMU) in the synthesis of cross-linked copolymers- HEMA-DVB, HEMA-EGDMA and MAA-BAP [19]. Ismail et al. have prepared three types of N-methylacetamide based NIDES, with acetamide (DES-1), N-methyl urea (DES-2), and N, N′-dimethyl urea (DES-3) and dissolved them in polyvinylidene fluoride (PVDF) polymer for membrane fabrication [20]. Moreover, numerous other menthol-based non-ionic DESs have been reported with stoichiometric mixtures of menthol with a series of hydrogen bond donors such as methanoic acid, acetic acid, L-(+)-lactic acid, pyruvic acid, acrylic acid, decanoic acid etc. [21,22].
2. Natural DES (NADES): In quest for solving low solubility range of aqueous medium and maintaining non-toxicity, biodegradability and cost-effectiveness of reaction medium, use of nature-derived candidates is imperative. In this regard, natural deep eutectic solvents are pivotal as they are prepared from the components of naturally derived origin [23]. To begin with, Dai et al. prepared DESs composed of primary metabolites like cholinium chloride, natural carboxylic acids, sugars, amino acids, and, in some cases using water as a third component and termed them as NADESs [24]. Depending upon the hydrophilicity and lipophilicity of primary metabolites, NADESs can have a wide range of polarity and have an extensive spectrum of applications. Some components of NADESs are shown in **Figure 2**.

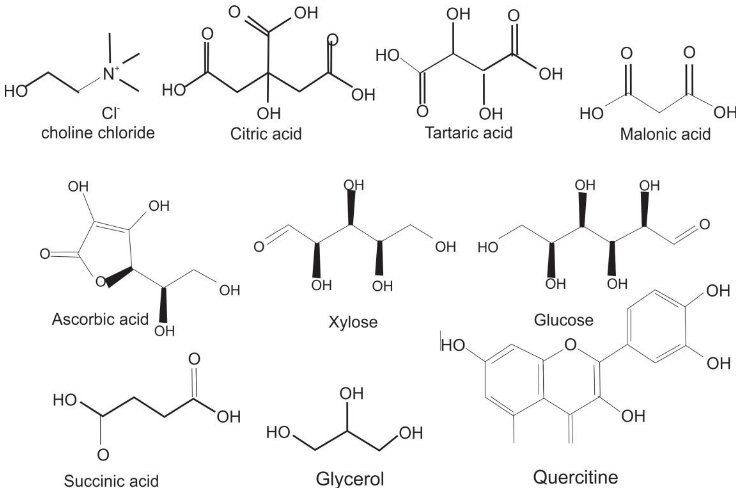

Figure 2. Some natural compounds used in formation of NADES.

3. Hydrophobic DES (HDES): The area of hydrophobic DES system is only a decade old as very recent inception of H-DESs marks the first report in 2015 by van Osch et al. [25]. They reported the first hydrophobic DES prepared by quaternary ammonium salts and decanoic acid. Later, Florindo et al. also developed hydrophobic eutectic mixtures, composed by suitable combinations of two non-ionic compounds, DL-menthol and several carboxylic acids [26]. The hydrophobic nature of DES can be tuned by two approaches: firstly, by introducing large chain of alkyl groups or aryl groups, and secondly by mixing two non-ionic compounds (NIDESs). In a similar manner, Schaeffer et al. also proposed terpenoids, L(-)-menthol and thymol-based novel hydrophobic DES combined with different carboxylic acids [27]. Hydrophobic DESs have gained much attention due to their application in several fields. HDESs are being used for material extraction [28], water purification [29], clean extractions of plant extracts, metal extraction, purification, CO_2 capture [30,31] etc. **Figure 3** enlists common HBAs and HBDs used for obtaining HDESs.

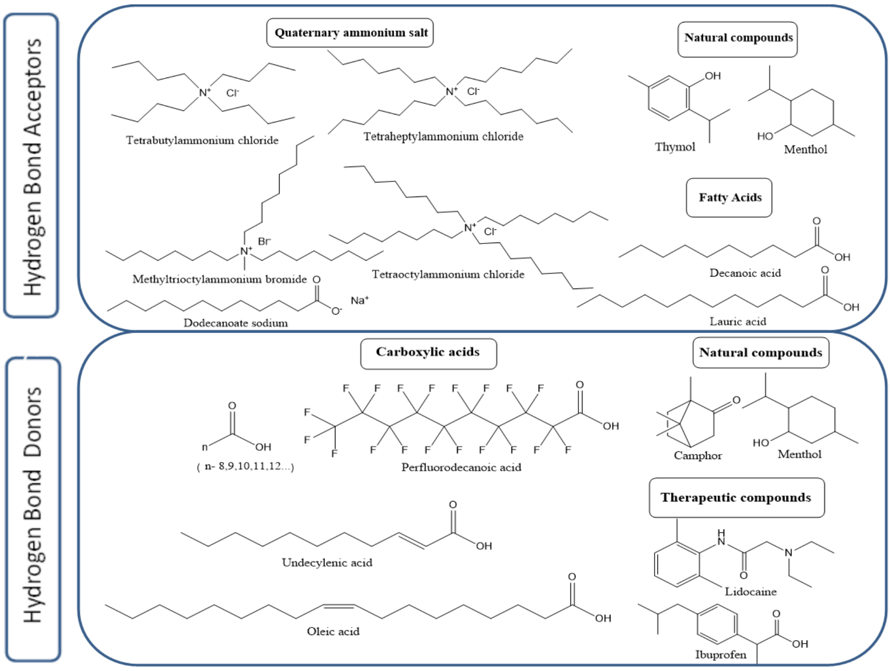

Figure 3. Common HBAs and HBDs used in hydrophobic DESs.

4. Supramolecular DES (SUPRADES): This new type of DESs is integration of unique inclusion properties of supramolecular assembly with DES. In order to get a sustainable alternative medium and tap the tunability of DES, researchers have accentuated the superiorities of supramolecular assemblies by mixing them with DES, and termed this binary mixture as SUPRADES [32]. SUPRADESs are proven to be better than normal DESs because of having synergic properties of hydrogen bonding interactions (due to DES) combined with host-guest interactions (due to supramolecules). Cyclodextrin-based DESs have been thoroughly studied and widely published in recent years [33]. SUPRADES are made either by using supramolecules as HBA component of DES [34] or by mixing supramolecular compounds with DESs [35]. Unique inclusion properties of SUPRADESs have led to various applications such as the extraction of dyes and pollutants [36], enrichment of trace metals in edible oil [37], separation of compounds [38], adsorption and separation of food components and biopolymer modifications etc. [39]. SUPRADESs are regarded as a new milestone in green chemistry because of their wide range of implications.
5. Therapeutic DES (THEDES): This particular category of DESs is incorporated with active pharmaceutical ingredients as a component of DES itself [40]. THEDES are achieving great attention in the field of drug delivery systems as they provide an excellent alternative to conventional drug delivery systems. Low solubility of Active Pharmaceutical Ingredients (APIs) poses a challenge to efficient drug delivery, permeability, bioactivity and bioavailability, hence limiting the efficacy and potency of drug candidates. Therefore, it is important to find out novel technological innovations in medicinal field to overcome these challenges in cost-effective manner and to enhance the therapeutic efficacy of drugs. Conventional drug delivery systems often require organic solvents to enhance solubilization but the usage of organic solvents becomes worse due to their toxicity, environmental risk, and allergic reactions.

THEDESs serve as medium for various APIs by enhancing their solubility and permeability, bioavailability and ultimately efficacy of drug upon delivery [41]. Drug delivery system basically involves:

- Intravenous (IV) infusion that directly injects drug into bloodstream. This allows better, faster, and more precise action in critical care like sedation, chemotherapy or fluid replacement therapy [42,43];
- Implantable drug delivery systems for controlled drug delivery in long-term treatment such as contraception and pain management; subcutaneous (SC) injection for subcutaneous tissue just beneath the skin [44];
- Intramuscular injection of drugs in the muscle tissue for slow and sustained release in the bloodstream [45];
- Ocular drug delivery for treatment of eye-related diseases.

THEDESs are being explored extensively as potential vehicles in these drug delivery systems for improved release, targeted drug delivery, enhanced loading and stability along with prolonged drug release [46]. Wang et al. have demonstrated a transdermal drug delivery system made of lidocaine: ibuprofen eutectic mixture [47]. Shekaari group has demonstrated an acetaminophen based aqueous DES, which was found to enhance solubility up to 40-fold with increasing molar weight of DES. It was observed that higher amount of ibuprofen was absorbed in it than absorbed in water [48]. Mokhtarpour et al. have recently reported ascorbic acid-based ion gel for targeted delivery of sunitinib malate [49]. Silva group has reported ibuprofen-based THEDES with perillyl alcohol [40]. THEDESs have shown great potential in designing novel drug delivery vehicles for technological innovation and refinement in therapeutic advancements.

6. Polymerizable DES (PDES): These are a particular type of DESs in which at least one component is polymerizable. Emergence of DES in polymerization process is based on two themes: i) polymerization in DES; ii) polymerization of DES. Polymerizable DESs are those systems in which monomer is used as HBD component in DES [50]. The primary necessities of the monomer component in PDESs are to have capacity to create adequate hydrogen bonding interactions with particular DES components (HBD and HBA) to generate a eutectic mixture and the

polymerizability. Monomer component of PDES must have at least one double bond to facilitate the polymerization. Extensive hydrogen bonding present in DES system decreases the activation energy for polymerization hence facilitating polymerization of vinylic monomers efficiently [51]. Acrylic acid is a much celebrated monomer unit for DES system and Numerous studies on the diverse uses of PDES based on acrylic acid have been published [52,53]. Along with the broadly documented AA and methacrylic acid-based HBDs, there is a rising curiosity in exploring renewable monomer candidates, like itaconic acid and caffeic acid, and thermos-responsive monomer units, such as N-isopropylacrylamide (NIPAM), as PDESs for specific applications in generating valuable materials. PDES have been used in several applications, from electrospinning of nanofibers to drug delivery systems, electro-conducting iono-gels to bio-relevant polymers, 3D printing techniques to other important fields, which are discussed in further sections in this review.

2. Application of DES in Material Science

2.1. Use of DESs in Polymerization Reactions

DES has witnessed a significant emergence in the field of polymer chemistry in two ways: first, as PDES where DES is a part of polymerization; and secondly as a reaction medium for polymerization reactions. Over the years, both applications of DESs have been well studied and documented in reputable Q1 publications.

2.1.1. Free Radical Polymerization

Very recently, Ndizeye et al. successfully used three DES systems, acetamide-N-methylacetamide (AA-NMA), N-methylacetamide-N-methyl urea (NMA-NMU) and N-methylacetamide-N, N'-dimethylurea (NMA-NN'DMU) in the synthesis of cross-linked copolymers- HEMA-DVB, HEMA-EGDMA and MAA-BAP. Polymerization was performed using 2,2'-azobis(2-methylpropionitrile) (AIBN) or 2,2'-azobis(2-amidinopropane) dihydrochloride (ABAH) as an initiator and cross-linking monomers like ethylene glycol dimethyl acrylate (EGDMA) or divinylbenzene (DVB) or 1,4-bis(acryloyl)piperazine (BAP) [19]. Resulting polymers were compared with polymers synthesized by conventional organic solvents like acetonitrile, toluene and aqueous medium as well. The effect of respective DES on corresponding polymers was analysed by various techniques such as Brunauer–Emmett–Teller (BET) N_2-adsorption, Fourier transform infrared spectroscopy (FT-IR), elemental analysis, scanning electron microscopy (SEM) and zeta potential measurements and it was found that polymers formed with comparable physical properties such as surface volume, surface area, pore diameters etc. to those polymers formed by conventional medium.

2.1.2. Photopolymerization

DES systems are also being employed in photo-initiated free radical polymerization reactions of monomers under mostly mild reaction conditions. Fazende et al. underlined the impact of PDESs with respect to accelerated reaction kinetics via photo-polymerization of acrylic acid (AA) and methacrylic acid (MAA) by using diphenyl(2,4,6-trimethylbenzoyl) phosphine oxide (TPO) as photo-initiator [54]. In this study, it was observed that no polymerization of AA and MAA occurs on visible light irradiation. In contrast, using AA:ChCl (cholinium chloride) and MAA:ChCl eutectics with a loading of 0.1 mol% of TPO displayed fast polymerization reaction. The authors asserted that increased rate kinetics might be due to hydrogen bond interactions and polarity of DES as well. Mecerreyes group has displayed a further example of photo-initiated DES systems. They used 2-cholinium bromide methacrylate (ChBrMA) which was prepared via the quarterisation of (2-dimethylamino) ethyl methacrylate with 2-bromoethanol and mixed with citric acid or amidoxime to prepare a polymerizable DES. These PDESs were clear viscous liquids at room temperature, and efficiently enabled photo-initiated polymerization with the UV initiator 2-hydroxy-2-methylpropiophenone to produce poly(ionic liquids) for application in CO_2 capture [55]. Ren'ai et al. reported an AA-based PDES for preparation of conductive paper and strain sensors. They use AA:ChCl (2:1) mixture and photo-polymerized by using 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (Irgacure 2959) as photo-initiator (2% w/w) in the presence of ethylene glycol diacrylate as cross-linker. The polymerized liquids were used in pre-designed paper origami circuits and carefully integrated into designing input/output 3D circuits [56].

2.1.3. Reversible Deactivation Radical Polymerization (RDRP)

RDRP techniques of polymerization involve mainly nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) polymerization [57–59]. These polymerization techniques have advanced the polymer synthesis by enabling one to control polymerisation and generate polymers of targeted length and low dispersity. The first report of RDRP in a DES was presented by Maximiano et al., who demonstrated the supplemental activator and reducing agent (SARA)-ATRP of several acrylates and methacrylate monomers [60]. They have reported a detailed the SARA-ATRP of MA using reline (a 2:1 urea: ChCl DES) as a co-solvent with ethanol (90% v/v) as primary solvent and Cu catalyst for successful polymerization. Polymers with low Polydispersity Index, (or Dispersity (D), measures the breadth of molecular weight distribution in a polymer sample).

The Polydispersity Index (PDI), or dispersity (D) PDI (D < 1.2) was generated and Cu catalyst was recovered and reused for two additional SARA-ATRP experiments. In subsequent efforts, demonstration of ATRP performed in neat DES systems was reported by them. Mendonça et al. used ChCl:urea (1:2) DES as the solvent for the SARA-ATRP of 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), (3-acrylamidopropyl) trimethyl ammonium chloride (AMPTMA) and sodium sulphite as the SARA agent and Cu-based metal catalyst [61]. In situ CuI/CuII regeneration was controlled by SARA agent and slow feeding of SARA agent resulted in PHEA-Br with high chain-end functionality. PHEA-Br was further used to produce various well-defined block copolymers (PHEA-b-PAMPTMA and PHEA-b-PMA). Likewise, Quirós-Montes et al. demonstrated a successful heterogeneous ARGET-ATRP of MMA in glycerol:ChCl (2:1) DES, using tin (II) 2-ethylhexanoate as reducing ARGET agent and copper-based MOF catalyst in an open-air atmosphere [62]. Poly(methyl methacrylate) (PMMA) was synthesized with low PDI (D ≈ 1.2) for investigation. Santha Kumar and Singha performed the RAFT polymerization of HEMA in reline facilitated by the RAFT agent 4-cyano-4-[(dodecylsulfanylthio carbonyl) sulfanyl] pentanoic acid (CDTSPA) with a high conversion ratio (~90%) of polymerization. Reaction kinetics were carefully monitored by Differential Scanning Calorimetry (DSC) and comparative studies between reline and other solvents highlighted greater ability of DES than DMF and ILs [63]. In additional reports, Chou et al. have done a study on visible light-induced RAFT polymerization in tetra butyl ammonium chloride (TBACl) and ethylene glycol (EG) DES (1:2). The group employed PET-RAFT method for generation of PMMA using MMA as monomer and dithiobenzene-type chain transfer agent. They synthesized ultrahigh molecular weight PMMA with high conversion rate (96.8%) and found that gel effect of DES boosted the rate of polymerization [64].

2.1.4. Anionic Polymerization

It is a powerful technique for controlled generation of well-defined targeted polymer with low PDI. However, use of highly reactive organolithium compounds poses serious limitations to their action condition since a highly pure and inert environment is required for these reactants. A comprehensive study demonstrated by group of Sanchez-Condado explored different DES systems for the synthesis of polymer and copolymer entities (polystyrene, 4-aryl polystyrenes, poly[2-vinylpyridine], poly[4-vinylpyridine], random copolymers, and block copolymers), and this study discovered that a ChCl:glycerol DES system was best suited for polymerization with enhanced yields and low dispersity indexes (1.1–1.3), with substantially better stability for the organolithium species compared to those obtained with conventional solvents. Furthermore, the anionic polymerization of p-chlorostyrene was conveyed for the first time in this work [65].

2.1.5. Enzymatic Polymerization

DESs have also been tested for enzyme-promoted polymerization reactions in recent years. A well-demonstrated study of the effect of DES on laccase enzyme led to the polymerization of aniline to afford polyaniline moiety, which was reported using several DES combinations**.** According to a study's findings, aniline and all other DES systems have an inhibiting effect on the activity of the laccase enzyme, whereas only the DL menthol-decanoic acid DES system has the ability to catalyse the polymerisation of aniline. Decreasing the concentration of DESs was associated with the enhanced yield of polyamine [66]. Additionally, Khlupova group has investigated enzymatic polymerization of taxifolin in betaine-based DES. In the study, they have investigated the scope of catalytic ability of laccase enzyme actions for polymerization of flavonoid dihydroquercetin (taxifolin) Betaine-glycerol (1:2) mixture afforded oligo-DHQ in high yield with number average molecular weight of 1,800 g mol^{-1} and low PDI (1.09). Oligo-DHQ had shown linear structure with average chain length of 6 DHQ molecules [67].

2.2. DESs in Biomass Functionalization

DESs are commonly used as solvents for pre-treatment of biomass and extraction of bioactive compounds because they have unique potential to disrupt noncovalent interactions within the chemical structure of biomass materials. Due to this, investigations into the possibilities of employing these green solvents to transform readily available biomass (such as lignocellulose, chitin, and starch) into various valuable ready-to-use materials are increasing steadily.

2.2.1. Lignocellulose

Lignocellulose biomass is the most abundant natural biopolymer, which is made up principally of three subunits: cellulose (35–80% of dry mass), lignin (10–40%), and hemicellulose (20–40%) [68]. These subunits are joined in a complicated structural arrangement and each of these subunits can have different compositions depending on the plant category, age, and geographical location. Cellulose is a homopolymer that is composed of D-glucose monomer units linked by β-1,4-glycosidic linkages, with strong hydrogen bridges between the polymer chains. In contrast, hemicellulose is a heterogeneous polymer that is composed primarily of xylose, pentose, and hexose sugars [69]. Lignin, the most prevalent natural aromatic feedstock, is made up of a complicated structure comprising coniferyl, sinapyl, and p-hydroxyphenyl alcohol units. Lignin has several aromatic groups joined with β-O-4 aryl-ether linkages, and these groups provide hydrophobic nature to lignins. The use of DESs for pretreatment of these biomasses has grown over the last two decades, because DES provide certain benefits in this process such as recycling/low waste creation, ease of preparation, and non-toxicity, eco-friendly and greener routes. A large number of experiments have been done to isolate lignin and cellulose biopolymers. Lignocellulosic biomass has gained extensive attention in industry and research owing to its renewability, availability, and low cost.

The ability of deep eutectic solvents (DESs) to selectively promote the degradation of hemicellulose and lignin components, while preserving the integrity of cellulose, is well established by Mankar et al. [70]. This selective action of DES is referred to as the 'delignification' process, and numerous studies have been conducted on it so far. In addition to separating lignocellulose biomass, DESs have the ability to reduce the size of these naturally occurring polymeric compounds, such as cellulose to nanoscaled cellulose nanocrystals (CNC) [71]. Although it is claimed that DESs can selectively dissociate lignin bonds to promote isolation from the lignocellulose biomass, and do not disrupt cellulose structure, microscale studies of DESs' actions on cellulose have revealed that nano-materials from cellulose could be made through cleavage of hydrogen bonds between two chains of cellulose. In most cases, this has been done through the synergistic effects of DES treatment in conjunction with physico-mechanical actions (e.g., milling, high-pressure homogenization, screw extrusion, microwave exposure, ultrasound exposure) or chemical treatments (addition of catalytic quantities of strong acids and bases) [72]. Luo et al. explored the utilization of various DES methods to create stable and homogenous LNPs, which were then mixed into a polyvinyl alcohol matrix to make a nanocomposite material for medical and food packaging applications [73]. The addition of LNPs significantly boosts tensile strength and thermal stability of the matrix, along with providing UV protection properties. Shen et al. recently discovered that hydrothermal pre-treatment with 0.5% H_2SO_4 combined with ChCl:lactic acid DES system on straw waste produced three value-added nanomaterials: hemicellulose-derived activated nanocarbon, lignin nanospheres, and lignin-containing CNFs [74]. Wang et al. used ChCl-carboxylic acid-based DESs to create nanocellulose materials ranging in width from 3–90 nm and crystallinity index (CRI) from 44–96% [75]. DES-treated lignin has been found to have higher thermal stability due to selective cleavage of abundant β-O-4 aryl-ether linkages and enhanced reactivity due to increased phenolic hydroxyl groups of lignin structure (shown in **Figure 4**) exposed by β-O-4 bond cleavage and demethylation of the methoxy groups in comparison to traditional technical lignins.

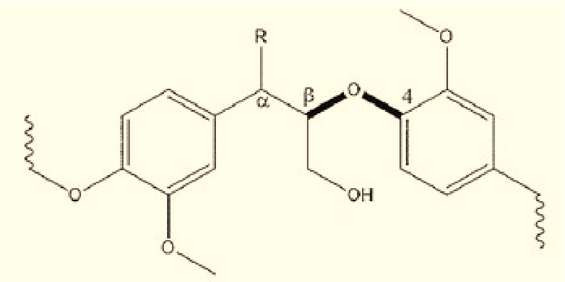

Figure 4. The main linkages in the lignin structure: β-O-4.

Furthermore, it is found in studies that carboxylic acid-based DES systems can esterify both the γ-hydroxyl group of the lignin substructure and cellulose hydroxyl groups [76]. Willberg-Keyriläinen et al. have reported using urea-based DESs to synthesize cellulose carbamates having various nitrogen levels as an alternative to petroleum-based solvents, which may negatively affect the environment and make recycling more difficult [77]. In contrast to conventional chemical techniques, which have a number of drawbacks, such as producing a large amount of waste, oxidizing the biomass, and adding sulphur groups to the structure, these changes under controllable conditions provide alternate opportunities to change the resistant nature of lignocellulose biomass.

2.2.2. Chitin

Chitin is the second-most prevalent polysaccharide biopolymer that is primarily composed of N-acetyl-glucosamine and N-glucosamine units, and is mostly found in crustacean shells, insect exoskeletons, and some fungi and algae [78]. It mainly exists in three configurations, namely α-, β-, and γ-chitin, depending on the molecular arrangements. Chitosan, an alternative biopolymer generated from chitin, is produced through N-deacetylation process (at least 50%) of chitin. The extraction of chitin has two main steps, namely demineralization and deproteinization. The demineralization process involves removal of $CaCO_3$ with use of acidic media and is followed by alkali treatment. Yuan et al. have used five acidic DES systems for the fabrication of chitin nanocrystals (ChNC) and emphasized that acidic DES shows dual activity as a hydrolysis and acylation reagent. Certain deep eutectic solvents (DESs), considered analogues of ionic liquids (ILs) and commonly based on choline chloride, have also demonstrated the ability to dissolve chitin. DESs are formed through appropriate combinations of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). These components interact via extensive hydrogen bonding, leading to self-association and the formation of eutectic mixtures. As a result, the melting points of DESs are significantly lower than those of their individual constituents [79].

Among the different acidic systems used, ChCl:malonic acid has produced remarkable results in terms of purity and yield, effectively removing proteins and minerals. Li et al. have also described similar methodology for chitin extraction, which involved demineralization by acidic DES hydrogen ions, resulting in soluble calcium salts, water, and CO_2 [80]. This demineralization results in a loosely coupled chitin-protein complex and DES molecules can penetrate the complex and expand overall structure, disrupting the hydrogen bonding network. Furthermore, chitin has been used to isolate a variety of nanomaterials, including nanocrystals and nanofibers, by the use of DESs [81]. Because of the alterations in chitosan's composition, the primary use of DES in those systems was found to be the improvement of chitosan-based films' mechanical characteristics and plasticity. Chitin was extracted from crab shells using the DES consisting of choline chloride and lactic acid, achieving a purity of up to 95% by optimizing the reaction conditions and minimizing energy consumption [82].

2.2.3. Starch

Starch is another prominent class of natural polymeric material, which has complex association composed of amylose- and amylopectin-based polysaccharides with different molecular arrangements of α-1,4-linkages and α-1,6-branches [83]. Several thoughtful attempts have been carried out in the past just to dissolve and isolate this complex polysaccharide using different solvents, such as water, DMSO, and pyridine. Due to the many attractive attributes of polysaccharide treatment, along with its environmental credentials, a number of research groups have endeavored to use DESs to reveal the structural alteration of starch. The use of DES-based starch treatment can be divided into two main parts: dissolution and plasticization. Many studies have investigated the solubility of starch in various DESs, and they have discovered that the maximum solubility is up to 10% [84]. Mechanistically, starch solubility is governed by the disruption and reorganization of hydrogen bonds at both the granular and molecular levels. Deep eutectic solvents (DESs) are rich in hydrogen bond donors and acceptors, which facilitate strong intermolecular interactions. When starch is combined with a DES, the hydroxyl (–OH) groups of starch form new hydrogen bonds with the solvent components. Simultaneously, thermal treatment breaks the existing inter- and intramolecular hydrogen bonds within the starch granules. These hydrogen-bonding interactions between starch and DES constituents reduce the crystalline regions of starch. Consequently, the increased amorphous character enhances the solubility of starch in DESs [85–87]. An important study conducted by Zdanowicz and Sałasińska demonstrated that the administration of a carboxylic acid-based DES on potato starch culminated in the decomposition of starch [88]. The dissolution process is usually scrutinized via microscopic inspections and DSC analysis. According to Zdanowicz's research, urea-based DESs (including polyols and monosugars) had a greater effect on potato starch than sorbitol [89]. Moreover, the urea concentration of the system had a notable impact on the dissolution temperature of starch. Moreover, prolonged treatment of DES has been related to esterification of the nanoparticles as an outcome of acid action in the DES. When it comes to starch-based applications, DESs are generally trendy because of their superior plasticising capabilities. When the DES systems break down the granular structure of starch moiety by its robust hydrogen bonding, the starch gets plasticized and ultimately swells. This plasticizing phenomenon is governed by several factors such as temperature, water content, force, and chemical components. Zdanowicz compared different DESs and ionic liquids with the conventional plasticizer such as glycerol to treat potato starch, and discovered that urea-based DESs and ionic liquids have shown a better dissolving capacity along with lower viscosity values as compared to glycerol, which is a key advantage for thermoplastic starch processing. In the study, Zdanowicz has investigated the impacts of sugar-alcohol-based DESs and established that a sorbitol-based DES had appropriate mechanical abilities such as elongation at break of 33% and tensile strength of 8.6 MPa). In a different investigation, the group has evaluated several DES mixtures based on urea, polyol, and sugar with starch treatments and reported that urea:glycerol system created flexible films with the maximum elongation at break greater than 200%. Xiao et al., at a very early stage of DES application in nano-material synthesis, effectively used the ChCl:oxalic acid dihydrate treatment to generate waxy maize starch nanoparticles [90]. The scientists noted that the crystalline and amorphous parts of the starch dissolved after two hours of DES treatment, producing aggregated nanoplatelets ranging from 38 to 117 nm in size.

It is clear that DESs can be used to create value-added functional materials from renewable feedstocks, which is consistent with the seventh principle of green chemistry. This can open up the possibility of more environmentally friendly and sustainable methods of material synthesis.

2.3. Functional Materials Engineered in DES

DESs are actively employed in engineering functional materials with specific qualities such as self-healing properties, stimuli responsiveness, biodegradability, electrical conductivity and many more. The versatility and tenability of DES make them an ideal medium for creating such valuable materials in emerging area of science and technology. In the present section, some of the significant contributions towards the synthesis of functional materials by using DES will be discussed.

2.3.1. Gels

As an alternative to the development of ionic liquid-based gels, research on DES-based gels has been developing extensively in recent decades. Due to its eutectic nature, this class of gel is commonly termed as eutectogels. Preparations of eutectogels can be categorized into three main based on their chemical characteristics, i) with polymerizable-DES where one component of DES is involved in gel formation; ii) where DES is used as solvent; iii) where self-assembly leads to supramolecular gels [91,92].

The utilization of DES in gel materials has attributed major advantages over the conventional hydrogels and ionic liquid-based gels, as DESs are far cheaper, biodegradable, easily prepared and eco-friendly in nature. In addition to covalent bonds, PDES give polymeric chains a strong hydrogen bonding backbone, which increases the mechanical strength of gel materials when used for branching in polymeric chains.

Excellent solubilizing potential for organic and inorganic compounds enables diverse applications for eutectic gels. Low or no water content in eutectogels leads to overcome the inherent limitations of conventional hydrogels. In addition, profuse hydrogen bonding in DES-based gel systems contributed to self-healing properties of DES-gel systems [93]. Incorporation of ionic components also results in enhanced conductivity for DES-gel materials. These explicit advantages have significantly increased the investigation of DES-based gel materials in scientific and research community over the last few years. Bednarz et al. introduced an approach for the utilization of polymerizable itaconic acid for synthesis of poly(itaconic acid-co-bisacrylamide) hydrogels with ChCl: itaconic acid DES [94]. In this investigation, it was discovered that copolymerisation in DES occurred far quicker than in water.

In 2021, Wang et al. demonstrated a DES-based strain sensor silicone tube weavable on fabrics to identify human motions [95]. They used ChCl: AAPDES for incorporation into silicone tube. This system efficiently worked within the temperature range of −2 °C to 100 °C and was unaffected by CCl_4, which is used in dry-cleaning process. Wu et al. carried out a study exploring the effect of the self-assembly of biopolymer agar in the ChCl:urea:water-based ternary DES using Al^{3+} cross-linked polyAA [96]. This particular gel has good ionic conductivity with a conductivity of 2.1 mS cm^{-1} at room temperature. It was also found that Al^{3+} was adversely affecting the conductivity but also enhancing the mechanical strength of the gel system. The Prasad group, demonstrated some polysaccharide-based ionic gels that were found to be responsive to pH, heat, solvent, and shear changes [97]. In their effort, the team examined the efficacy of self-polymerizable HEMA for pH-responsive drug release of indomethacin in DES made up of ChCl:fructose (2:1). In the same publication, ChCl:orcinol (1:1.5) DES was used to achieve HEMA-based gel with a highly stretchable and good capacitance behaviour. Fan et al. developed a eutectogel using ChCl:glycerol DES by polymerization of 1-vinylimidazole. This eutectogel has properties like high stretchability (2,300% elongation at break), self-healability, and ionic conductivity in a wide temperature range (−30 °C to 60 °C). The produced eutectogel has similarly shown excellent adhesion properties to diverse substrates, with the maximum adhesive strength of almost 70 KPa with a glass substrate [98]. Recently, Mercadal et al. established a non-cytotoxic bio-based eutectogel having strain-sensing abilities and 3D printable properties by application of ChCl: ethylene glycol-based DES systems. In this study, tannic acid-coated CNC (1–2 wt%) was employed in the form of a reinforcing agent and the consequential gel exhibited a strength of 30 KPa and elongation at break of 180% [99]. Biswas et al. demonstrated a ChCl: urea system for CO_2 capture using solubilizing capacity of DES system for CO_2 [100].

2.3.2. Fibres

Material fabrication has been a lucrative field in exploratory research for a long time. Considering about environmental concerns, green solvents for an eco-friendly and economical generation of fibres have been proven to be the heart of industrial endeavours and DES, seems as a viable option for achieving the objectives of cost-effective and sustainable value-added material production.

Hence, a large number of reports are being presented for the demonstration of potential utilization of DES in synthesis of nanofibers. Nanofibers in conjunction with electrospinning are being applied in various fields of biomedical research, agricultural innovations, energy storage devices, pollutant removal techniques etc. [101]. The first instance of using DES in electrospinning technique for the formation of agar nanofiber was demonstrated by Sousa et al. [102]. ChCl: urea DES and several polyvinyl alcohol combinations were used to create agar nanofibers with varying surface characteristics, including roughness and fiber diameter.

A similar approach by the Mano group was reported fabrication of electrospun polyvinyl alcohol fibers with NADES. Wet electrospinning using the ChCl:lactic acid DES system produced lignin fiber aerogels, which were carbonised and utilized as supercapacitor electrodes due to their exceptional electrochemical stability [103]. Non-volatility, non-flammability and recyclability of DES have shed light on these systems as suitable alternatives to volatile organic solvents in fabrication techniques. These qualities have led to application of DES in generation of protein-based electrospun nanofiber, which are rather hard to electrospin with conventional solvents. Mouro and co-workers have pioneered a method for electrospinning polyvinyl alcohol and keratin protein regenerated from waste wool in various DES systems such as ChCl:Urea and L-cysteine:lactic acid. These nanofibers were found to exhibit anti-microbial and anti-oxidative properties [104]. DES-led nano-fibres have been known to be promising candidates in advancements of drug delivery systems as well. Polyvinyl alcohol combined with honey or acetyl salicylic acid (ASA) was dissolved and electrospun in DES to fabricate nanofibers that were demonstrated in fast release drug delivery. PVA-DES-honey system was found to have wound healing properties, whereas PVA-DES-ASA nanofibers exhibited rapid oral drug release in oral mucosal systems [105]. Polycaprolactone fibers electrospun with ChCl:Urea DES and ChCl:glycerol DES systems for release of analgesic drug ibuprofen and they were found to be hydrophilic in nature, which in turn could potentially alter the drug release profile [106].

2.4. DES in 3-D Printing Materials

In this era of expedient scientific innovations, scientists are endlessly catering for newer ways to develop novel printable materials for different industrial applications. Several studies have inclined with DES in this avenue, due to its non-volatile, non-flammable, environmentally benign nature. DESs have been utilized in a number of printing techniques such as Direct Ink Writing (DIW), Stereo Lithography (SLA), Digital Light Processing (DLP) and Liquid Crystal Display (LCD). Lai and Yu used a ChCl: ethylene glycol-based system with polyAA crosslinked by Al^{3+} for 3D printing applications. Here, the authors used CNC to generate the shear-thinning behaviour of the ink for direct ink writing (DIW) [107]. Sheikhi et al. proposed an approach in 3D printing technique by using L-arginine:glycerol based DES with polymeric network of vinyl functionalized gelatin, AA and glycidyl methacrylate to coat 3D printed jammed microgels and resulted in enhanced mechanical strength with self-standing gel materials [108]. Wang et al. suggested a unique one-pot method for production of 3D printing ink using lactic acid and maleic acid-based DES systems along with glycidyl methacrylate polymer system and CNCs. In this study, the group concluded a higher strength in the maleic acid-based DES system due to the unsaturation present in maleic acid causing additional chemical crosslinks within the structure [109]. Furthermore, ChCl:lactic acid was employed for a DIW application for annealing process at 50 °C for 16 h for the fabrication of conductive patterns. Su et al. investigated the scope of DES systems for SLA printing in fabrication of antistatic transparent material. In this effort, group used ChCl:AA (1:2) based PDES system and observed that PDES was contributing to enhanced antistatic property. Photopolymerization of this system has shown rapid curing within 10 s and maximum mechanical strength was detected with 20% DES loading along with up to 90% of polymer conversion [110]. Cai et al. investigated similar DES system with the SLA technique to calibrate the printing structure in the form of interlocked pyramids for application in pressure-sensing techniques. The group used ternary PDES with acrylamide:ChCl:maleic acid (1:1:2) for the purpose of which led to highly transparent structures (95.6%) combined with a quicker curing period of 6 s (24 W UV light 410 nm) [51]. The same group probed the utilization of this PDES in a DLP-based printing method and emphasized that the printed material was thermally stable over a wide temperature range (−70 °C to 120 °C) without disturbing its physical properties (conductivity, compressibility, and transparency) on the production of capacitive ionic skins [111]. An LCD-based printing approach was employed in another study by Zhu et al. to create printable materials containing a ChCl:HEMAPDES. They stressed that the antibacterial qualities of the printed materials were greatly enhanced by adding tannic acid (10–40 weight percent), and that the inks produced were homogeneous [112]. A stimulating demonstration on the 3D printing of a sacrificial mould was led by Li and co-workers using the application of a ternary PDES (ChCl:acrylamide:4-acryloylmorpholine) with an LCD [113].

2.5. DES in Membranes and Films

The evolution in exploration of advanced materials in membrane science is pivotal. Transient shift from conventional size separation to selective filtration and plastic-based thin films to functional polymeric materials from materials of natural origin has drawn notable attention to the application of DESs due to their distinctive ability of hydrogen bonding interactions, and aiding both as modifiers for structural improvement and as vital functional materials. The past decade has seen the beginning of a major investigation into the plasticizing capabilities of DESs. In 2013, the Ramesh group stated that DES might be used as a plasticizer for systems based on cellulose acetate [114]. Pulyalina et al. reported $ZnCl_2$:acetamide DES with Torlon polymer and showcased that at 50% DES loading, the hydrophilicity of polyimide Torlon membrane was enhanced by nearly 25% due to generation of pores within the membrane [115]. Some other investigations into membrane fabrication with polyvinylidene fluoride (PVDF) were carried out by different groups and membranes of different morphology, pore sizes and thickness values were generated for various applications [20,116]. DESs have also been utilized in the membrane formation based on several biopolymers (chitin [117], pectin [118], starch [119], agar [120], cellulose [121], lignin [122], and chitosan [123] based films [124,125]. Yu et al. studied different properties such as antibacterial activity, antioxidant properties, and UV-barrier properties of chitosan-based films for using them as food packaging materials [123]. ChCl:oxalic acid and ChCl: glycerol-based DES systems were probed for generation of cellulose-lignin-based films with enhanced UV protection properties for production of transparent packaging materials. Utilizing wood powder treated with ChCl:oxalic acid DES, Xia et al. created a recyclable lignocellulosic bioplastic film with a toughness of 2.8 MJ m^{-3} and a tensile strength of around 128 MPa. In further efforts, ChCl and citric acid monohydrate-based DES systems were applied in different ratios for fabrication of pectin-based edible films, which exhibited various structural transitions and film properties [122].

2.6. DESs in Metal Processing

2.6.1. Metal-Electro Deposition

Electrodeposition is a well-researched field for obtaining thin films of metal oxides and chalcogenides. It is also termed as electroplating and used traditionally for decorative purposes only. However, research on electrodeposition techniques and their effects on metal surfaces opened up a number of new material science research avenues. Electroplating has attracted much attention in recent years since it is used in so many cutting-edge technological developments. Currently, electroplated metal oxides are being utilized in solar cells, electrochromic devices, electrochemical supercapacitors, gas sensors, batteries, photocatalysts etc. [126]. Traditionally, metal electroplating has been done in aqueous medium but hydrogen liberation due to electrolysis of water molecules, low electrochemical window, low conductivity, evaporation, low thermal stability and passivity of metal electrodes were some associated drawbacks with aqueous electrolytes. Hence, non-aqueous electrolytes are proving to be crucial candidates for metal electrodeposition technique [127]. DES, in this regard, provides a powerful alternative to aqueous electrolytes due to its aforementioned advantages over the aqueous medium. Broad solubility range of DESs offers better solubility of metal salts including metal oxides and hydroxides. DES also solves the problem of passivity, which is caused by the formation of insoluble metal oxide layer over the electrodes in aqueous solvent as metal oxides get dissolved in DES. DESs may also provide potential remedies to evade legal restrictions in technologically important plating of Ni, Co and Cr in which aqueous electrolytes were found to be carcinogenic in nature.

Chromium electroplating by using Cr(III) metal salt with DES has been reported by Ferreira et al. Choline chloride and $CrCl_3 \cdot 6H_2O$-based DES was used for the task [128]. Electrodeposition was operated at very high current efficiency (>90%) and coating may be obtained in various morphologies such as dull black, dull gray and mirror bright. Further, by adding LiCl salt to the $ChCl:CrCl_3 \cdot 6H_2O$ mixture, crack-free, nanocrystalline black chromium films with good corrosion resistance were obtained. Al electrodeposition has been tested with type I DES using ChCl and $AlCl_3 \cdot 6H_2O$ mixture but low anodic reaction was limiting the scope. Recently, type IV DES with simple amide and $AlCl_3$ as an electrolyte was explored for Al deposition and it was found that anodic reaction was still slow. Characterization of electrolyte revealed that it had both anionic and cationic aluminum species as $[AlCl_2 \cdot urea]^+$ and $[AlCl_4]^-$ [129]. Similarly, Popescu et al. have demonstrated a method for copper plating with the help of $CuCl_2$ combined with ChCl mixed with hydrogen bond donors like urea, malonic acid, oxalic acid, and ethylene glycol [130]. Among all DES ChCl:oxalic acid and ChCl:ethylene glycol DES was found to display the best plating properties. UV-Visible spectroscopy indicated that Cu^+ in the form of $[CuCl_3]^{2-}$ and Cu^{2+} in the form of $[CuCl_4]^{2-}$ were present in electrolyte system. The Pollet group has displayed ultrasonication effect on electrodeposition of copper in aqueous KCl and ChCl: glycerol and it was demonstrated that in DES system 5 times more currents were generated in ultrasound than in non-ultrasound condition [131]. In similar fashion, nickel electrodeposition, zinc electrodeposition, silver coatings and alloy coatings were achieved in DES systems.

2.6.2. Metal-Electro Polishing

Metal electropolishing involves controlled dissolution of metal surface in suitable medium. It enhances the resistance against the corrosion, lubrication and optical reflectivity of surface. DESs are very interesting mediums for achieving the polished metal surface through non-conventional approach since they provide major advantages in the form of:

1. Negligible gas evolution at electrodes and solution interfaces;
2. High current efficiency;
3. Green and non-corrosiveness in comparison to aqueous medium. Electropolishing of steel has been done by ChCl: ethylene glycol DES and it was observed that no passivation was occurring in DES in contrast to the aqueous medium where passivation was observed at 1.3 V. However, DESs have mainly been utilized in stainless steel electropolishing but electropolishing of Al, Ti, Ni-Co alloy and some super alloys has also been explored [132].

2.6.3. Metal Recovery and Extraction

Scientists have long pursued a renowned procedure for metal extraction. Researchers have been searching for a suitable substitute for the traditional extraction procedure in recent years. Since DES offers several advantages over traditional media, it has become very popular in the extraction process. Tunable property of DES is one major advantage among other benefits discussed in earlier sections as metal ligands such as urea, thiourea, oxalates etc. can be incorporated into DES systems depending upon the nature of metal and extraction process. Extraction of metal in form of metal oxides is also a challenging area for researchers as most metal oxides are insoluble in molecular solvents. DESs have shown excellent solubility for metal oxides hence are actively utilized in metal oxide extractions. Moreover, metal recovery, separation and extraction have been put under strict environmental regulations as discharge of solvents at final step requires complete separation of solute particles [133]. Abbott et al. have reported a study comparing 17 metal oxides belonging to 3d-series of transition metals. They used three different DES systems-maline, reline and ethaline. For most of these oxides solubility follows the order maline > reline > ethaline. Further, more ionic metal oxides (e.g., ZnO) were more soluble in DES than more covalent metal oxides (e.g., TiO_2). This observation was analogous to aqueous solution where similar trend was also observed. During the study, it was inferred that dissolution of metal oxides depends heavily on proton affinity of metals and complexing ability of DES systems [134]. In a recent study, Tran group reported Co recovery from used lithium ion batteries (LIB) with the help of ChCl: EG (1:2) DES [135]. Almost 74% Co was extracted from $LiCoO_2$ in the form of Co_3O_4 after precipitation and calcination at 500 °C for 6 h. Recovered Co was further reused in preparation for new LIBs . In a similar study, Roldan-Ruiz et al. demonstrated a process for Co recovery with a PTSA-based DES system [136]. They observed that $LiCoO_2$ could be easily dissolved in just 15 min at 90 °C in DES. Approximately 94% Co was recovered from LIBs in the form of Co_3O_4 after subsequent precipitation with Na_2CO_3 or $(NH_4)_2CO_3$ and calcination. In a likewise effort, Wang et al. reported 95% of Co extraction from spent LIBs in reline DES through consecutive dilution-precipitation-calcination sequence [133].

2.7. DESs in Energy Storage Devices

Very recently, lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) and zinc bis(trifluoro methane sulfonyl) imide (ZnTFSI) based DES have been used as electrolytes in Li-betteries and it was observed that LiTFSI-DES shows decreased corrosion, stable cycling performances, and side reactions were avoided significantly [137]. Azmi group developed a ChCl-Urea DES based electrolyte for supercapacitors and observed high stable electrochemical window, corrosion resistance with even 1% water addition, and high cell voltage up to 2.2 V [138]. Addition of water increased conductivity and DES + 1% water showed high capacitance retention of 88% after more than 25,000 cycles. Zhang et al. have reported DES-trimethylolpropanetriacrylate (ETPTA) based solid polymer electrolytes for Li-batteries with high voltage range high conductivity, high Li^+ transference number (68%) and high safety standards of batteries [139]. Ruiz-Olles et al. reported an excellent work on polymeric conductive gel formation using urea/ChCl DES. 1,3:2,4-Dibenzylidene-d-sorbitol (DBS) mixed with urea/ChCl DES for formation of supramolecular eutectogels and observed high ionic conductivity [140]. Gel formation was also tolerant to Li^+, Mg^{2+} and Ca^{2+} ionic additives. Additionally, application of DESs in Al-batteries has also been investigated. Li et al. proposed a novel ternary $AlCl_3$-Urea-[EMIm]Cl electrolyte system to observe improved ionic conductivity and coulombic efficiency in Al/graphite batteries [141]. They obtained discharge voltage plateau in the range of 1.9–1.5 V along with specific discharge capacity of 60 mAh g^{-1} upon 150 cycles. Ng et al. have also developed an economic Al-battery system using $AlCl_3$:Urea DES system and observed an average specific capacity of 50 mA h g^{-1} and 96% coulombic efficiency upon 1,000 cycles [142]. Recently, efficacy of DES as durable deep eutectic electrolyte (DEE) for lithium oxygen batteries (LOB) has been investigated by Li group. They have used *N*-methylacetamide (NMA) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI) as DES counterparts. This NMA-based DEE has shown exhibiting notable properties like high ionic conductivity, excellent rate performance, good thermal, and electrochemical stability, superb compatibility with the Li-anode, high discharge capacity (8,647 mAh g^{-1}), and satisfactory lifetime cycling (280 cycles) [143]. In addition to this, a new class of deep eutectic gel electrolytes (DEGEs) has been found to exhibit unique applications in lithium-ion batteries owing to their enhanced ionic conductivity and tunable nature to control molecular interactions. Utilization of fluorinated amides as uniquely modulated low energy LUMO precisely enables binding affinity with Li^+ which is crucial for its high performance such as stable cycling for over 9,000 h and extraordinary lifecycle of 2,500 cycles with remarkable 81.7% retention in capacity [144]. In order to illuminating newer insights into the role of DEEs, Zhang group have studied ChCl: DMF-based DEE in Zn ion batteries. This particular DEE was able to generate anion-dominated solvation structure. An organic-inorganic hybrid solid interphase electrolyte film over Zn was crucial in achieving an exceptionally long lifetime of 18,175 h and ultra-high cumulative capacity of 42 Ah cm^{-2} at 20 mA cm^{-2} [145]. Apart from electrolytes, a recent report in 2026, a study by Stettler et al. demonstrates piezoelectric effect of different DESs such as ChCl:EG, ChCl-Gly, ChCl:PD (1,3-propanediol) and ChCl:urea. In their study, they found that DES was exhibiting direct piezoelectric response after exerting the pressure. ChCl:polyol DES along with ChCl:EG corresponded to the highest response (8.5 pC/N) followed by ChCl:PD (5.6 pC/N) and ChCl:gly (2.4 pC/N) [146].

2.8. Organic Synthesis in Deep Eutectic Solvents

Sustainable organic synthesis of heterocyclic compounds using green reaction medium has been a crucial convergence towards environmentally benign synthetic approaches in recent times [147,148]. DESs have also been used as green alternatives to conventional volatile organic solvents. Recently, Shuheil group has published a sustainable synthesis of imidazopyridine derivatives using DES as reaction media [149]. The group has proposed a three-component one-pot reaction of 2-aminopyridines, benzaldehydes and terminal alkynes in ChCl:urea DES media with magnetically recoverable Cu(II) functionalized Fe_3O_4-SiO_2-TCCP catalyst to afford imidazopyridines as shown in **Figure 5**. A range of aminopyridine derivatives and several aromatic and heterocyclic aldehydes were tested for substrate scope and reacted very well, generating high yields of falseproducts (up to 98%).

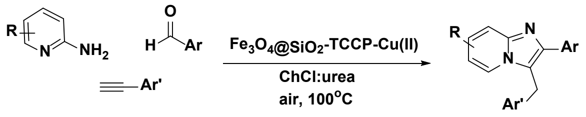

Figure 5. Synthesis of imidazo[1,2-a]pyridines in ChCl:urea DES media.

Chegeni group has recently demonstrated an impressive study of catalytic ability of DES in multicomponent synthesis of pyrano[2,3-*d*]pyrimidines from 4-hydroxycoumarines, morpholine, barbituric acids and aromatic aldehydes using arginine:gallic acid (1:2) NADES system (**Figure 6**). Mixtures of reactants were simply stirred in solvent free condition along with arginine:gallic acid DES.

Catalyst was recyclable and easily recoverable due to water miscibility of DES [150]. This method has broad substrate scope and excellent functional group tolerance over range of electron-withdrawing groups as well as electron-donating groups.

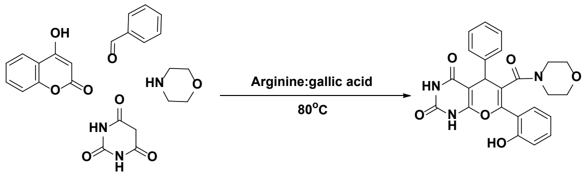

Figure 6. DES catalysed a one-pot four-component synthesis of pyrano[2,3-*d*]pyrimidines.

A Brønsted acid-based DES system made up of betaine and p-toluenesulfonyl acid (PTSA) was recently employed to serve as catalyst for a one-pot four-component synthesis of tetrasubstituted imidazole derivative (**Figure 7**). This DES was successful in promoting reaction of benzyl, aniline, ammonium acetate and benzaldehyde derivatives affording 45%–82% product yields in short reaction time of 3 h under mild reaction conditions. DES was recoverable and reusable. Further, in-vitro cytotoxicity studies suggested that some synthesized products were exhibiting cytotoxicity against HepG2 cell lines [151].

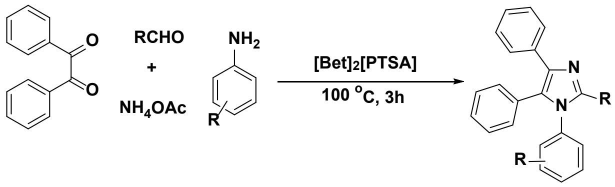

Figure 7. DES catalysed synthesis of imidazole derivatives.

Xiong et al. have investigated the efficacy of different DES systems for selective production of 5-methylfurfural from rhamnose derived from *Enteromorpha prolifera* (**Figure 8**). In their study, they used many DES systems and found that ChCl:oxalic acid (1:1) DES was best suited for the purpose. DFT studies have confirmed that synergistic effect within ChCl:OA DES network promoted substrate activation and dehydration for speedy generation of furfural derivative while choline chloride was able to stabilise intermediates thus controlling the reaction and avoiding side product formation. Further, enhanced weak interactions and narrowed HOMO-LUMO gap were crucial to facilitate reaction initiation [152].

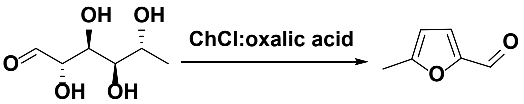

Figure 8. DES catalysed Synthesis of 5-methylfurfural with Rhamanose derived from *Enteromorpha prolifera.*

Apart from heterocycles, DES has also been very useful for synthesis of organic compounds through C–C bond formation. L-isoleucine catalysed asymmetric cross-aldol reaction was reported in ChCl:EG (1:2) DES system (**Figure 9**). Cyclohexanone and several aldehyde derivatives were reacted in ChCl:EG DES media with 20 mol% of L-isoleucine organocatalyst at room temperature. The reaction afforded high enantiomeric excess (up to 99%) and anti-diastereoselectivity as high as 95:5 (anti/syn) [12].

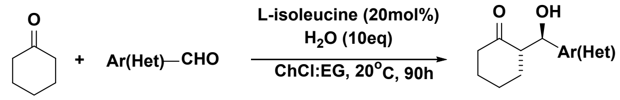

Figure 9. falseL-isoleucine catalysed asymmetric cross-aldol reaction in DES media.

3. Conclusions

This review highlights an inquisitive summary of current trends in application of DESs in polymer synthesis and functional material formation with cost-effective, non-hazardous and green methods. DESs have widely exploited in the field of synthetic chemistry having played multiple roles as solvents, polymerizable monomers, catalysts etc. They can be used in biomass functionalization, material extraction, formation of variable polymeric electrochemical materials-gels, membranes, films and nano-fibres. DESs can utilize renewable feedstocks, such as natural-DES (NADES). They can be fine-tuned along with their tunable properties just by altering the hydrogen bonding interactions among constituent moieties. Their viscosity, water-holding capacity, and solubility can be tuned according to the requirements. Non-toxicity, biodegradability, non-flammability, cost effectiveness, recyclability and reusability align with 12 principles of green chemistry. DESs can be applied in large-scale synthesis of value-added polymers and materials on industrial scale in sustainable manner. They have prominent applications in the medicinal and therapeutic fields, as they show promising results in drug delivery and biocatalysis. They have wide utilization in drug delivery systems as therapeutic agents. They are also being used as plasticizers in the formation of polymeric membranes, which can be used further in several fields of electrochemistry, food packaging, wound-healing etc. Generation of functional nano-materials such as metal nanoparticles, nano-sheets, nanofibers etc. has also been successfully achieved with DESs. Additionally, DES-based materials have gained a unique prominence in the field of electrochemistry.

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The authors declare no conflict of interest.

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