Green Chemistry
Cutting-edge research for a greener sustainable future

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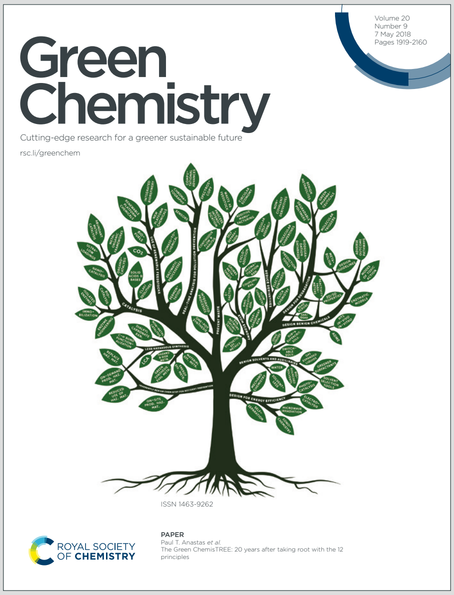

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DOI: 10.1039/D4GC00532E

Deep Eutectic Solvents towards Green Polymeric Materials

Udyani Aloka Weerasinghe,[a,b] Tingting Wu,[c] Pei Lin Chee,[a] Pek Yin Michelle Yew,[a,c] Hiang Kwee Lee,[b] Xian Jun Loh,*[a] Kai Dan*[a,b,d]

a. Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis #08-03, Singapore 138634, Republic of Singapore

b. School of Chemistry, Chemical Engineering and Biotechnology, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Republic of Singapore

c. Department of Biomedical Engineering, Faculty of Engineering, National University of Singapore, Singapore, 117583, Singapore

d. Institute of Sustainability for Chemicals, Energy and Environment (ISCE2), Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis, #08-03 Singapore 138634, Republic of Singapore

Corresponding author: Xian Jun Loh <lohxj@imre.a-star.edu.sg>; Dan Kai <kaid@imre.a-star.edu.sg>

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DOI: 10.1039/D4GC00532E

Abstract

Solvents are essential for chemical synthesis and material preparation, yet traditional options face challenges in meeting safety and sustainability standards. Consequently, there is a growing focus on environmentally friendly solvent systems for polymeric materials, with deep eutectic solvents (DESs) standing out as a promising alternative due to their eco-friendly attributes. In this review, we summarized the studies of this novel solvent system in a broad range of applications, where DES plays multiple roles in polymer synthesis and corresponding material fabrication. In detail, we focus on the utilization of DESs in the synthesis of green polymers and related functional polymeric materials ranging from soft materials such as gels, nanofibers to membranes, films and complex architectures generated from techniques such as 3D printing, electrospinning, self-assembly with their properties. Moreover, we discuss the green credentials with sustainability analysis and life cycle assessment of DES-based polymeric materials. We believe this review will inspire more investigation into the use of DES for functional green polymeric materials toward sustainable future.

Keywords: Deep Eutectic Solvent, Ionic liquids, Green chemistry, Radical polymerization, Biomass, Eutectogels, 3D printing

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1. Introduction

The shift towards green technologies and materials is crucial for mitigating adverse environmental effects, promoting economic growth, ensuring energy security, and safeguarding all life form and the natural environment for the current and future generations. The twelve principles of green chemistry have been articulated since 1998 as a guideline for scientists to unearth environmentally responsible pathways in designing products and processes. Polymer materials achieved a greater attraction from their inception in the virtue of their unique properties towards day-to-day life. However, the excessive production and consumption of synthetic polymer materials has resulted in global issues pertaining severe impacts. In addressing both scenarios while acknowledging the wide demand for polymer materials due to their durability and adaptivity, scientists have focused on ways to cater to this requirement with environmentally friendly approaches.

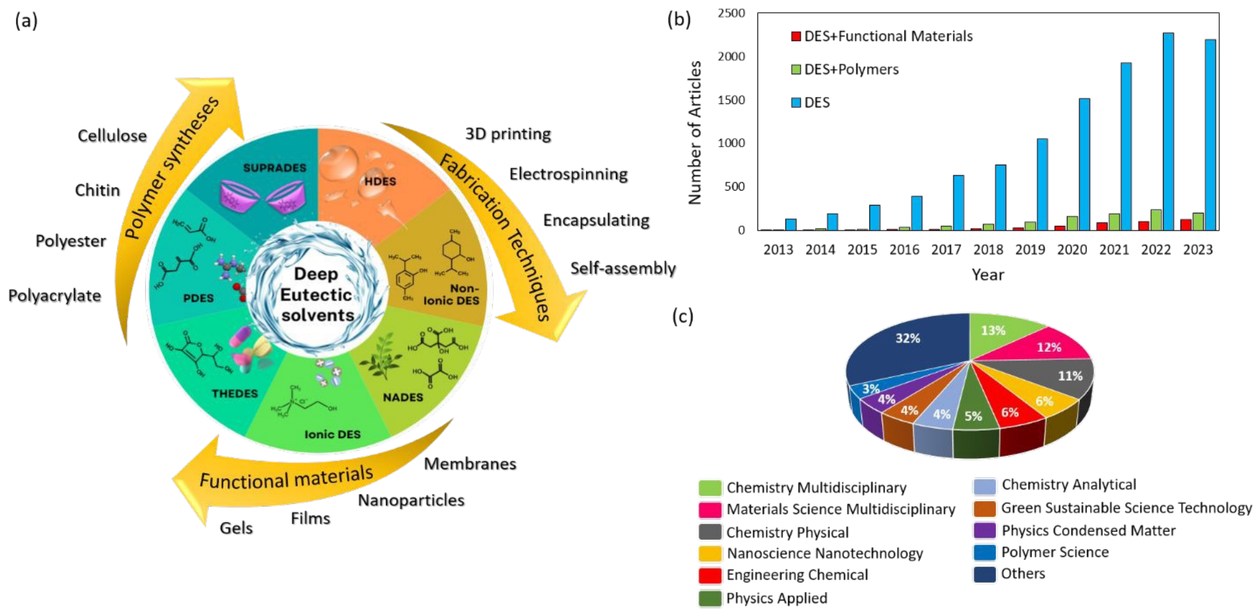

Figure 1. (a) Different DES types (circle): Supramolecular DES (SUPRADES), Hydrophobic DES (HDES), Non-Ionic DES, Natural DES (NADES), Ionic DES, Therapeutic DES (THEDES), Polymerizable DES (PDES), and various polymers, functional materials, fabrication methods which can be engineered within DES. (b) Number of DES related publications over the years. (c) Percentage of DES based functional materials related publications in each field. The data is obtained from Web of Science, 22nd January 2024.

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The conventional synthesis approaches of polymer materials face various difficulties due to harsh conditions (e.g. concentrated solvents), high energy requirements (high heat, pressure), high cost, strict environments (anaerobic), toxic and/or volatile solvents and catalysts, high waste generation coupled with inability to reuse and difficulties to recycle. Deep eutectic solvent (DES) comes into play in this instance for generating a multitude of solvent systems for novel polymeric materials. DES was found by Abbott et al. in 2001[1] which proved its vast areas of applications in subsequent research. DES is categorized as green solvents in the current era, acting as valuable alternatives for conventional solvents due to their extremely low vapor pressure and non-flammability. Even though more than two decades have passed since the finding of this solvent, there exist many possibilities for the exploration of DES in polymer science owing to its low toxicity and natural degradability (Figure 1). Apart from simply using DES as solvent replacement, its ability to act as solvents as well as a monomer simultaneously generates more inroads towards green polymeric materials, surpassing conventional polymer synthesis methods. Moreover, DES presents benefits in allowing for milder conditions for polymer synthesis and leading to enhanced thermal and mechanical properties of resulting polymeric materials. Besides the function in the synthetic polymers and related materials, the use of DES for biopolymer treatment and corresponding material engineering has been widely investigated these years, in which DES overcomes the recalcitrance and structural complexity of biomass, facilitating the subsequent functional biopolymer material engineering.

This review aims to identify the current trends of using DES for green polymer synthesis and related functional polymeric materials with accessing the green credentials and sustainability evaluation of DES-based materials. Even though various applications of DES have been discussed in previous studies, the compilation of it to address functional green polymeric materials has not

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been explored yet. Here, not only the uses and advantages of DES as a solvent or monomer is discussed but also the applications harnessing its unique properties are reported in emerging technologies such as efficient biomass extraction, stimuli-responsive materials, membrane science, nanofibers, and 3D printing, highlighting the future potentials of moving towards a green economy.

2. Background and properties of DES

"*Eutectic*", originating from the Greek language, is a term used to describe substances that are readily melted which can be interpreted in another way using the melting point depression of two components. With the discovery of the preparation of ChCl and urea (1:2) at ambient temperature by Abbott et al[2]., the aforementioned word gained a greater significance over the past two decades. *Deep eutectic solvent* (DES), as the name implies, represent the combination of two or more Lewis or Bronsted acids and bases with at least one solid where the mixture exhibits melting point depression with respect to the ideal constituents of the same chemical substances at relatively low temperature levels. Here, the term *Deep* is mainly attributed to the negative deviations from the thermodynamic ideality where the intermolecular interactions are stronger in the resultant solvent than the liquid phases of pure substances (Figure 2a).[3]

Some researchers considered this solvent category as a sub-class of ionic liquids, which represents the class of ionic fluid generated at temperatures less than 100 °C.[4] However, a clear distinction of this class with DES has been generated eventually, considering the chemical nature of the two starting materials, synthesis methods, bonding nature and greenness. The main constituents of ionic liquids are anions (organic heterocyclic) and cations (organic or inorganic), whereas the emphasis of DES has been given to hydrogen bond donor and acceptor abilities.[5] This gives rise

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to the differences in intermolecular attractions with ionic liquids having Coulomb forces as the main driving force for the ionic interactions with DES having hydrogen bonding. Additionally, the preparation of ionic liquids involves several steps and reagents apart from the main constituents for dilution of compounds and purification to remove by products which gives rise to the generation of waste whilst DES only requires simple steps (mixing of starting materials with heat until it forms a transparent and viscous liquid). As for the components (starting materials), the initial components for DES are often non-toxic, cheap, and environmentally friendly. Compared to DES, the starting materials of ionic liquid cannot be regarded as green and sustainable, where the environmental impact of the ionic liquid system strongly depends on the anions and cations used as the components.[6] However, when considering the low volatility, tunability, low melting temperature and ability to dissolve organic and inorganic compounds both ionic liquids and DESs have their similarities.

The evolution of the studies based on DESs has been initially focused on the extensive hydrogen bonding between the constituents which was used to categorize the components as hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD). Afterward, with further investigations on the thermodynamic aspects of eutectic mixtures, it has been found that apart from the hydrogen bonding, the effect of entropy in the system plays a pivotal role.[7] This can be further explained by the high level of disorderness gained by the mixture than the initial components, where the melting point is inversely proportional to the entropy resulting in a melting point depression. Additionally, it has been found that for most eutectic systems the enthalpy change is much less compared to the change in entropy. This can be derived by the Gibbs equation (Figure 2c), where T_e, $\Delta H_{e,}$ and ΔS_e represent the eutectic temperature, enthalpy change, and entropy change, respectively.

Over time, the utilization of molecular simulations further facilitated the visualization of the atomic level interactions within the DES system, whereby new approaches of hydrogen bonds generated have been observed. In one instance, this has been termed as an "alphabet soup", where novel non-covalent type interactions in the ChCl:urea system have been observed representing the deviation of conventional hydrogen bonding definition (Figure 2d).[8] In this study, the HBD ability of C-H bond has been stated as one of the stronger interactions than the traditional N-H or O-H bonding leading to a high number of hydrogen bonds within the system. Even though, DES was introduced a few decades ago, the studies on their interactions are still in a nascent state. Novel ways of interpreting the bonding nature and reaction modes of different DES systems are still emerging, and it is extremely difficult to generalize the behavior of different systems owing to minute changes in the chemical environment.

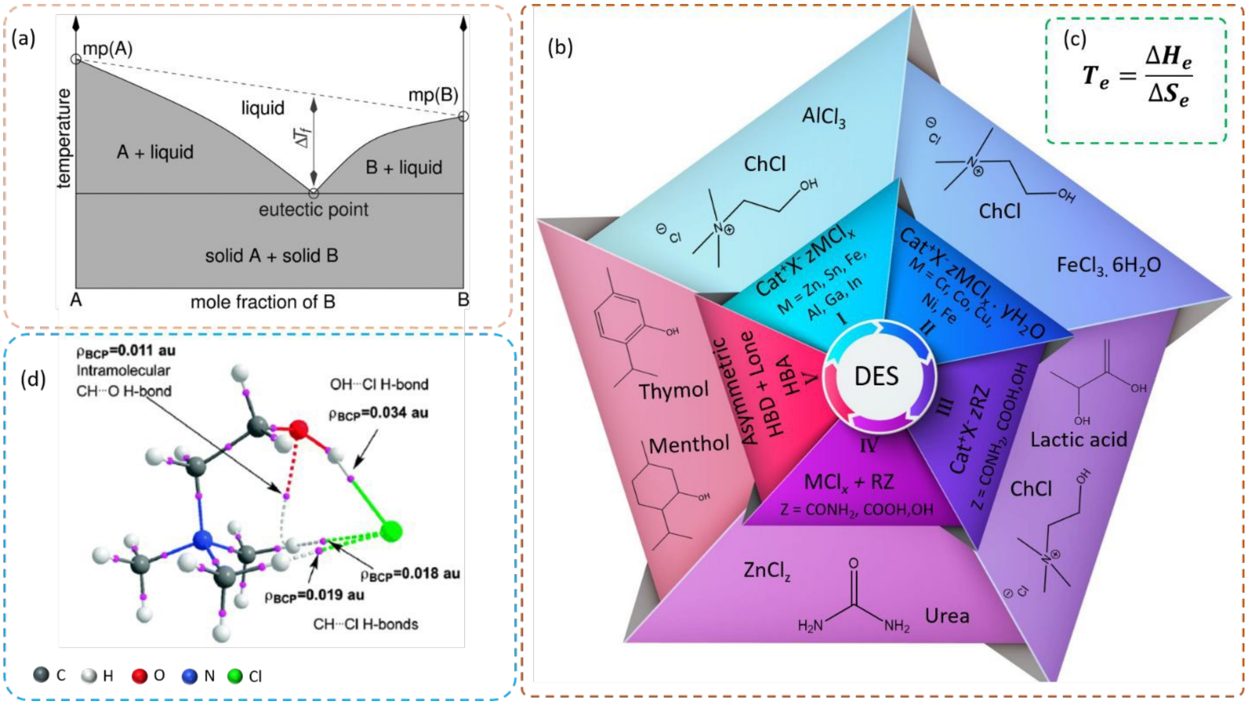

Figure 2. (a) Two component solid-liquid phase diagram with eutectic point.[4] Copyright 2014, American Chemical Society. (b) Schematic illustration of the classification of DES (Cat$^+$ and X$^-$ represents ammonium, phosphonium or sulfonium cation, and Lewis base respectively). (c) Gibbs equation. (d) Non-conventional intramolecular hydrogen bonds generating from H in methyl groups (CH--Cl, CH--OH) with bond critical points (BCP) calculated by Quantum Theory of Atoms in Molecules (QTAIM) molecular graphs.[8] Copyright 2016, Royal Society of Chemistry.

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2.1 Categories of DES

The classification of DES is mainly based on the HBDs and HBAs, where initially four main types of DESs were defined based on ionic components[4] (Figure 2b). Here, the type I DES represents quaternary halide (with ammonium, phosphonium or sulfonium cation) and metal chloride (Lewis base) as the main constituents which was first discovered in 2001.[1] The scope of this has then been further improved with the incorporation of hydrated metal halides in type II by resulting in further reduction of the eutectic point than its anhydrous analogous. The type III DES was introduced after the discovery of ChCl:urea system representing quaternary salts[2] and HBDs where a vast possibility has been suggested afterwards as potential HBDs. The combination of metal halides and HBDs was introduced as type IV DES. With the quest for the requirement for non-ionic applications and the availability of strong negative deviations, type V DES have been defined recently.[9]

A greater attention has been given to the quaternary ammonium salts for the defined types I-III, and among those, the most commonly used HBA for type III DES can be considered as choline chloride (ChCl) with the chemical formula [$HOC_2H_4N^+(CH_3)_3Cl^-$]. However, after the inception of DES systems scientists came up with numerous types of HBAs to tune the desired qualities for different applications. Additionally, owing to the vast adjustability and the absence of metal ions, type III has drawn greater attention among the stated categories.

Apart from the stated classification, various sub-categories have evolved namely, Polymerizable DES (PDES), Natural DES (NADES), Therapeutic DES (THEDES), Hydrophobic DES (HDES) and Supramolecular DES (SUPRADES), indicating the plethora combinations of different chemical species with HBA and HBD properties (Figure 1a). The NADES comprises bio-derived compounds using nature's building blocks to generate eutectic mixtures. This attracts great

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attention of scientists owing to its non-toxic, biodegradable and sustainable aspects. The eutectic mixtures of this kind comprises of bio-derived compounds mainly in sugars, amino acids and organic acids.[10] Further, the fine-tune of the HBD and HBA towards biocompatible molecules enables it to be used for pharmaceutical applications. This is where the THEDES comes into play which highlights the biocompatibility, non-volatility, solubility, retention and controlled release of therapeutic, bio-active compounds of interest with the use of DESs.[11,12] The stability of supramolecular structures, such as cyclodextrins and DNA, has been demonstrated in the context of the formation of hydrogen bonds.[13,14] This characteristic paves the way for extensive applications of these substances as SUPRADESs, which will be explored in greater detail in subsequent sections.

2.2 Physicochemical properties of DESs

The identification of the properties of the DES plays a vital role in determining its functionality for specific applications. Even though the vast tunability of DES systems can be considered as an advantage, the availability of data related to physicochemical properties is still in its infancy when it comes to the novel combinations. However, most of the properties of conventional DES systems have been studied and reported extensively by many researchers. Omar et al. have reported a database of existing DES in 2023 with their physical properties during the period from 2003 to 2021, which can be remarkably beneficial for the researchers to scale up the applications.[15]

A great number of explanations regarding the physicochemical properties of DESs have been explained in past publications with the use of hole theory which explains the inter diffusion and motion,[16] Kamlet-Taft equation representing the strength of noncovalent interactions,[17] and entropy of the system.[7] Herein, we will discuss some of the core observations of the past studies

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conducted which can have an effect on the performance of polymeric materials generated using these systems.

pH- The selection of acidity or basicity is one of the crucial factors to consider when it comes to specific applications of DESs. In certain instances, DESs are identified as Lewis or Bronsted acids and bases, giving rise to different pH values. In most studies, HBD has been considered as the determining factor of the DESs pH value.[18]

Viscosity- The viscosity of a solution, in simple terms, is defined as the resistance of movement of a fluid. This property plays a pivotal role in acting as an efficient solvent which can be substituted for harmful solvents. Compared to the conventional volatile solvents, it has been observed most of the DESs contain high range of viscosities with the lowest viscosity DES (6.6 mPa s) constituting molar ratio 1:1 of trimethylsulfonium bis[trifluoromethylsulfonyl]imide: formamide and the highest (75000 mPa s at 40 °C) being 1:2 molar ratio of ChCl:$ZnCl_2$.[15] These values show the tunability of viscosity in DES systems. This can be dependent upon many factors such as molar ratio, temperature, interactions between HBA/HBD, and molar mass. According to the hole theory, with the rise in temperature, the mobility of molecules increases by the generation of large voids whereas at lower temperatures the smaller voids available, coupled with larger sizes of ionic component hinder the molecular mobility resulting in high viscosity which is represented by Equation 1, where r, k,T, and γ represent the radius of average sized void, Boltzmann constant, absolute temperature, and surface tension of the liquid respectively.[19]

$$4\pi r^2 = \frac{3.5kT}{\gamma} \qquad (1)$$

This is further evident from the Arrhenius equation where an inverse relationship between viscosity and temperature is stated. Further, when considering the interactions between the HBDs

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and HBAs the polar functional groups, anion of HBA present (RCl: HBD < RBr: HBD < RI: HBD),[15] steric hindrance provided by longer chain alkyl groups in the system have a crucial impact. It is worth noting that the effect of the impurities shouldn't be ignored which can have an effect on the interactions. Additionally, for solvent based applications hydrophobic DESs with viscosities less than 20 mPa s has been considered as attractive alternatives for conventional organic solvents (e.g. heptane, octane, nonane, hexyl benzene).[20]

Density- Past studies revealed that a variation of densities are possible ranging from 0.8-1.5 g cm^{-3}, where the vast majority of the DES exhibit densities higher than water, whereas certain hydrophobic DES indicate lower values.[21,15,20] The density of a DES depends on similar aforementioned factors for viscosity such as temperature, water content, composition of DES, type of DES representing the chemical nature, and how tight the constituents are attached to each other. The density play a main role in water miscibility which can provide varying results in different industrial applications especially when it comes to emulsification, processing, and seperation.[20]

Hydrophobicity- The first hydrophobic DESs were reported in 2015 by Osch et al.[22] The hydrophobicity of a DES system can be fine-tuned by two main approaches namely (1) quaternary salts with long alkyl chains (2) mixing of two neutral compounds.[20] In the former case, DES systems with type I-III can be utilized whereas the type V DES comes into play for the latter instance. Abranches et al. in their work published in 2022 compiled various interactions in non-ionic DES where ample possibilities of polar asymmetric solvents with negative deviations in solid-liquid equilibrium diagrams were reported.[3] Here, the team has highlighted the potential threat of the formation of polymorphs within the DES system which then could be avoided by using molecules with unfavorable crystal packing property.

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Ionic Conductivity- DES is widely studied for their conductive properties owing to the ionic species present in the media (type I-IV) which will be further discussed in the sensor-based applications section. Considering the diffusion dynamics, most DES especially choline-based DES provides promising results in the sub nanoscale.[7] The ionic conductivity in the DES media mainly depends on factors such as the availability of free volume, radius of the ions, density, molar mass, molar ratio of HBD/HBA, and viscosity.[23,15] The low viscosity exhibited by most of the DES hinders the ionic conductivity of the system. However, different approaches can be adopted to improve this property to obtain desired output. The addition of water molecules up to a certain extent in DES has been considered as a favorable approach to improve the ionic conductivity.[22]

The preliminary study of the physicochemical characteristics of DES offers a deeper understanding of innovative applications involving polymers. Therefore, comprehending the interconnectedness among DES properties becomes crucial for prioritizing specific attributes at the expense of others. From the aforementioned discussion, it becomes evident that numerous DES properties are intertwined, primarily from the noncovalent bonding tendencies of the constituent species.

3. DES for green polymer synthesis

The use of DESs has been considered as a crucial requirement for polymer synthesis by virtue of the environmental concerns over hazardous solvents and ease of process. DES can be used either as a solvent, which facilitates the polymerization process, as the monomer participating in the final polymer synthesis, or both simultaneously. In whichever case, the basic understanding and careful selection of the constituents of the corresponding DES system is vital to generate a valuable output for the polymer synthesis. The understanding of the properties, such as polarity of both DES and polymer (using Kamlet-Taft parameters) and boiling point of the prepared DES, allows one to

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determine the maximum usable limit of the system.[17] In this part, the function of DES as a reaction medium is summarized based on different polymerization processes.

3.1 DES as a solvent for polymerization

3.1.1 Radical polymerization

The use of DES as solvents for acrylic acid (AA) and acrylic amide derivatives polymerization will be discussed in Section 5 based on different applications and in this section, other polymers are discussed. Ndizeye et al. studied the substitution of traditional solvents such as toluene, acetonitrile, and water with non-ionic DESs (N-methyl acetamide:acetamide/N-methylurea/N, N'-dimethylurea) for the polymerization of methacrylic acid and hydroxyethylmethacrylate (HEMA) with different crosslinking monomers. The study revealed that the resultant polymer products had equivalent elemental compositions (elemental compositions of C, H, N) with tunable surface areas and pore sizes apart from the suppression of surface charge than that of the polymers generated using conventional solvents.[24] Few other enzymatic free radical polymerization studies have been carried out by several groups where the careful selection of DES system is prominent to avoid the deactivation of the enzyme used for the polymerization process.[25,26,27] The catalysis by laccase enzyme has drawn wider attention nowadays owing to its high selectivity, ambient conditions, and non-toxicity. Altundağ et al. studied the inhibition of laccase enzyme by DES system which consisted D, L-menthol:decanoic acid (1:1) in a template based polymerization of aniline. This study revealed that both the selected DES and aniline has a significant inhibition effect on the catalytic activity of laccase. The authors were able to generate a yield of 84% polyaniline product with the addition of 10% DES in the system.[25] Another study carried out by Khlopova et al. were able to generate oligomers with six monomer units of dihydroquercetin (Taxifolin) in betanin:glycerol DES system. Here, the selection of betanin as HBA was specifically considered

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as it didn't inhibit the activity of the laccase enzyme like ChCl. The resultant oligomers had average molecular weight of 1800 g mol^{-1} with a polydispersity index of 1.09 and a yield with 58 ± 7%.[27] The same approach has been utilized by another set of researchers to produce conductive polyanilines by polymerization and copolymerization. In both the cases DES has facilitated favorable environment for the enzyme at the DES:buffer 60:40 ratio.[26]

RAFT (Reversible Addition-Fragmentation Chain Transfer) and ATRP (Atom Transfer Radical Polymerization) can be considered as emerging class of radical-based polymerization approaches for more controlled outputs. The polymerization of HEMA and block copolymerization with methyl methacrylate has been studied by Kumar et al. with the use of ChCl:urea.[28] The study revealed that higher molecular weight polymers (up to 40700 g mol^{-1}) can be synthesized using this DES at a conversion percentage up to 90%. Additionally, the team suggested this DES as a non-aqueous solvent system for polymerization-induced self-assembly (PISA) of block copolymers. Another more convenient RAFT polymerization was revealed by Li and Yu, which proposed a polymerization environment in visible-light and open-air in the presence of DES.[29] Here, the authors used tetrabutylammonium chloride:ethylene glycol DES to generate polymerization of methyl methacrylate, methyl acrylate, dimethyl acrylamide, and styrene. During this study they observed the DES medium provide a photo stability with "protected radical effect" to the chain transfer agents used (trithiocarbonate) than DMSO. This enhanced stability of the chain transfer agents has enabled better control over polymerization kinetics, resulting in uniform chain lengths and end group functionalities in the final polymer product. Both these studies suggested that the high viscosity of DES facilitated polymerization carried out in confined spaces (mainly generated by log-chain RAFT agents), with high concentrations of monomers and radicals, led to improved polymerization rates compared to conventional solvents.[28,29] A study carried out

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by Mendonça et al. revealed the use of ChCl: urea for ATRP for the generation of polymers and block-copolymers using 2-hydroxyethyl acrylate, HEMA, and (3-acrylamidopropyl)trimethylammonium chloride with $Na_2S_2O_4$. The study revealed room temperature polymerization (30 °C) with polymers having polydispersity less than 1.2 throughout the process.[30] Another group compared three ChCl based DES systems (glycerol/urea/ethylene glycol) in the generation of poly(methyl methacrylate) with ATRP.[31] The team studied the homogeneous and heterogeneous Cu(II) catalysis in DES media which resulted in polymer synthesis with polydispersity index valuing approximately 1.2 in both catalytic systems.

Overall, DES as a polymerization solvent has shown to facilitate faster polymerization rates, maintain mild reaction conditions, and enable controlled polymerizations compared to conventional solvents. This is primarily attributed to improved monomer dissolution, interactions with propagating radicals, controlled terminations due to high viscosity, and a radical protection effect on chain transfer agents, optimizing their use. However, the studies on the interactions between DES and the monomers that lead to these properties hold a potential for further exploration in this area to identify the effect of DES in radical polymerization approaches.

3.1.2 Anionic polymerization and Polycondensation

The engagement of highly active organolithium species in anionic polymerization processes has been considered as a ubiquitous approach over the past few years (Figure 3a-b). However, the control of this species became a great challenge for the scientists to gain the expected polymer products with fewer obstacles, mainly due to the high reactivity gained by significant polarity difference in Li-C bond. Several studies have been conducted to probe the utilization of DESs instead of using conventional organic solvents for this purpose. The studies revealed that DESs

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offer a more convenient approach to facilitate polymerization under aerobic conditions, owing to its high thermal stability and low volatility. In contrast, traditional anionic polymerization requires strict oxygen-free conditions.[32,33]

A study carried out by Sanchez-Condado et al. investigated several DES systems for the synthesis of polymerization, copolymerization products (polystyrene, 4-aryl substituted polystyrenes, poly[2-vinylpyridine], poly[4-vinylpyridine], random copolymers, and block copolymers), and revealed that a DES system with ChCl:glycerol enabled the polymerization in greater yields up to 90% and in low polydispersity indexes (1.1-1.3), with a greater stability in the organolithium species than that of conventional solvents (Figure 3b).[32] Recently, another team probed this study for the polymerization of styrene and its derivatives, isoprene, and 2-vinylpyridine using the same DES system in the presence of organolithum species.[33] Here, the team highlighted the importance of factors beyond the selection of the DES system, such as reaction conditions. These conditions include the viscosity of the DES, initiator concentration, and the duration of mechanical treatment (ultrasonication), all of which can significantly affect the resulting polymer properties. (Figure 3d-f).

Moving towards a sustainable pathway Pedrazzo et al. studied the polycondensation reaction of β-cyclodextrin with the use of NADESs (ChCl:citric acid).[34] The team utilized mechano-chemical approaches using ball mill and twin-screw extruder for the synthesis of water-soluble biopolymer and a crosslinked polymer (Figure 3c). Here, the authors pointed out differences in polymer yield, noting that the inability to remove water from the system when using a ball mill resulted in decreased product yield due to a shift in the equilibrium towards the product side.

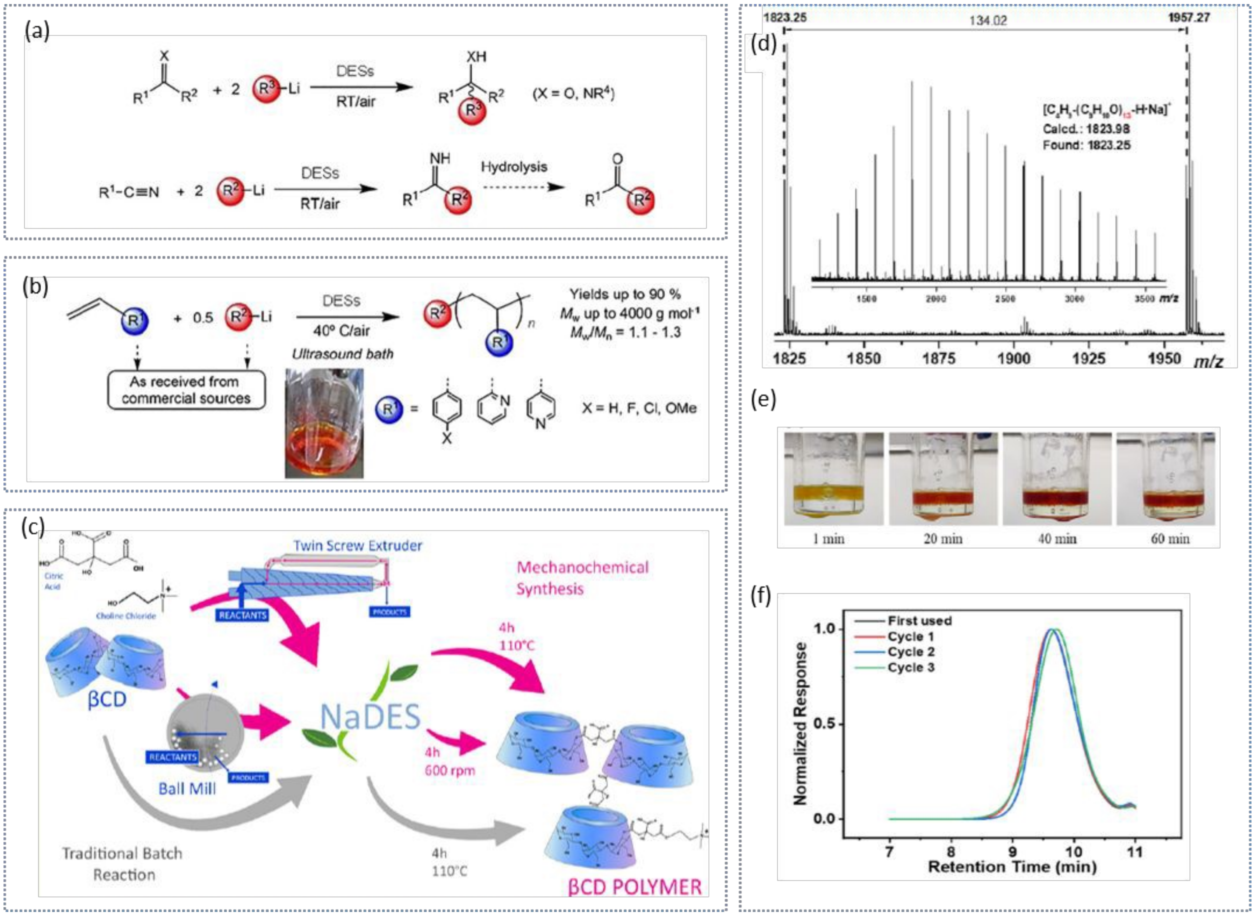

Figure 3. (a) Nucleophilic addition reaction of organolithium compound (R-Li) to carbonyl compounds in DES media; (b) Anionic polymerization of olefins promoted by organolithium compounds and different ChCl-based DESs.[32] Copyright 2019, Wiley. (c) Polycondensation of β-cyclodextrin using NADES using ball mill and twin screw extruder.[34] Copyright 2021, American Chemical Society. (d) Anionic polymerization of MALDI-TOF MS spectra of polyisoprene homopolymer. (e) Colour change during copolymerization between styrene and isoprene in ChCl: glycerol. (f) Weight distribution of synthesized polystyrene with the use of recovered DES up to three cycles.[33] Copyright 2023, Elsevier.

3.2 DES as monomers

Apart from acting as a medium for polymerization reactions to facilitate the environment, the DES components (HBA or HBD) can actively participate in the reaction for the generation of polymer materials (also termed as polymerizable DES or PDES). The main requirements of the monomer component in PDES are considered to be the ability to generate sufficient hydrogen bonding interactions between the selected DES components (HBD and HBA) to generate a eutectic mixture and polymerizability. This limits the number of candidates applicable for PDES compared to vast

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types of conventional monomers. Primarily, research in this area has focused on the incorporation of one or more vinyl groups as the HBD or HBA, which leads to free radical polymerization.

Among these, the majority of the studies have been conducted using AA or methacrylic acid. The traditional way of carrying out AA free radical polymerization requires the addition of inert solvents to dissolve the monomer and eventual removal of the inert solvent. However, the utilization of PDES has demonstrated better solubility of the selected monomers via hydrogen bonding with higher polymer conversion rate and percentage, over the traditional solvents. In a recent study Lin et al. investigated the effect of PDES (consisting quaternary ammonium salts as HBAs and AA as HBD) on the polymerization kinetics of the monomer component (AA) compared to the utilization of inert solvents DMF, DMSO, and methanol.[35] The authors reported a significantly high C=C conversion (~99%) in PDES medium as opposed to the traditional solvents (less than 30% conversion) apart from the high rate of conversion. The main reason for this has been attributed to the increased C=C bond activity of the AA monomer (which acts as the HBD) resulting from the hydrogen bonding with quaternary ammonium salt-based HBAs. Additionally, a vast tunability of the physicomechanical properties of the PDES based ionic gels has been demonstrated by probing the hydrogen bonding levels between different HBAs and AA HBD. Here, one of the main advantage is the utilization of all components of the DES system, even after the complete conversion of the monomers into the final polymer product, unlike the traditional approach where solvents are evaporated. This reduces waste generation by eliminating the solvent evaporation step, while allowing for the tuning of physicomechanical properties through varying hydrogen bond energies within the system.

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With the first report by Mota-Morales et al. on polymerizable eutectics using AA and methacrylic acid a great number of studies based on attractive applications have been published on this topic mainly due to the fast polymerization, and the ability to reduce chemicals in the process.[36] Fazende et al. conducted a kinetic study comparing the roles of DES as solvents, and polymerizable components. The team utilized polymerizable DES (ChCl as the HBA, and AA, methacrylic acid as HBD monomers), comparing it with the polymerization of methyl methacrylate in the presence of nonpolymerizable DES (ChCl:isobutyric acid).[37] In this context, the authors proposed that the increase in rate can be observed in both systems, whether the monomer is a part of the DES or not. Even though, increased viscosity is seen as an unfavorable property in certain applications, for radical polymerization process several studies has indicated that it plays a vital role in increasing the rate of the reaction. However, for the rate of the reaction, other factors such as light intensity, absorption coefficient, efficiency of initiation, diffusion of the reactants, and polarity of the DES should not be neglected.[37,38,36] Jablonský et al. highlighted the enhancement of the monomer reactivity in polar media than the non-polar ones and the ability of the DES (especially ChCl) to influence the rate constant of the initiator decomposition.[17]

Owing to the significant number of studies carried out based on AA monomer based polymerizable DESs Tolmachev et al. recently reported the molecular arrangement and viscosity properties of ChCl:AA with the use of both experimental and simulation studies. The team used different molar ratios from (1:1 to 1:4). The reduction in viscosities of DES with increased AA concentration was attributed primarily to the size disparity between choline ions and AA, as well as the balance of interactions between AA and Cl^- ions. Excess AA, which remains unreacted with Cl^- ions, forms pairs with other AA molecules, resulting in mixtures with higher diffusion coefficients.[39] Further developments of such free radical polymerizations have been probed by modifying the additives

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included in the systems. Wang et al. suggested the use of liquid metal nanodroplets (mixture of indium and gallium) which can act as substitute for initiators and crosslinkers in ChCl:AA PDES.[40] Here, the stabilization of the liquid metal nanodroplets by viscosity of PDES media has been reported. While AA serves as the polymerizable component in the DES system, ChCl contributes to the system's non-covalent interactions, including hydrogen bonding and ionic bonding with Ga3+ ions, as well as its conductive properties. The polymerization has indicated fast curing (6 min), with high transparency (94.1%), and high stretchability (2600%) coupled with other properties such as ionic conductivity, self-healing, resistance to freezing, and drying.[40] Another group generated polymer matrix with antimicrobial properties by incorporating benzalkonium chloride as HBA to AA and methacrylic acid based HBDs.[41]

In addition to the widely recognized AA, methacrylic acid based HBDs, there is a growing interest in researching renewable monomers such as itaconic acid, caffeic acid, and thermo-responsive monomers such as N-isopropylacrylamide (NIPAM) as PDESs for specific applications. Additionally, in most of the stated polymerizations higher reaction rates and crosslink densities has been achieved than the synthesis in water.[17,38,42,43, 44,45] Further, the use of HBAs with vinyl groups in organic salt unit has been reported as PDESs. HBAs with quaternary ammonium monomers such as 2-cholinium bromide methacrylate, 3-acrylamidopropyl trimethylammonium chloride has also been studied.[17,42] Ajino et al. compared three quaternary ammonium monomers having methacrylate, acrylate, and diallyl units namely, methacroylcholine chloride, [2-(acryloyloxy)ethyl]-trimethyl ammonium chloride, diallyl-dimethyl ammonium chloride respectively with urea to probe the ion conductive ability for lithium-ion battery applications. Here, the authors documented that the diallyl type monomer generated the highest ionic conductivity (5.3 mS cm^{-1} at 25 °C under ambient humidity condition).[46]

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Various attempts to conduct polycondensation reactions using alcoholic HBDs such as resorcinol,[36] 1,8-octanediol,[36] ammonium tetraol,[17] and ammonium triol[17] with the presence of citric acid, formaldehyde has been reported for the generation of polyesters.

Compared to conventional organic solvents, DES offer a new platform for polymer synthesis, with the ability to act as green solvent, which facilitate the polymer syntheses in mild reaction conditions. DES can engage actively in the synthesis process by involving monomers as HBD or HBA components within the system. Further investigations will be required to overcome some limitations based on the hygroscopic nature, and optimizing the yield with narrow polydispersity index.

4 DES in biomass functional materials

Except for its use as a solvent or monomer in synthetic polymers, DES is widely utilized as a solvent for biomass pre-treatment or bioactive compound extraction, due to its ability to disrupt the non-covalent bonds within the biomass substructure. Recently, increasing studies have explored the potential of using these green solvents to convert biomass (such as lignocellulose, chitin, and starch) into functional materials (Table 1).

Table 1. Summary of converting biomass into nanomaterials using DES

Feedstock/ Resource	Materials generated	DES	Major Treatment conditions	Features		Application demonstration	Reference
				Yield	Size/Mw/PDI/CRI		
Bleached cotton fiber	CNC	ChCl:OAd 1:1/2/3	80 °C, 100 °C for 2 h Ultrasonic homogenization	-	Length 122.4-205.9 nm Height 4.7-9.6 nm	-	[47]
Bleached eucalyptus kraft pulp	CNC	OAd:ChCl:FeCl$_3$·6H$_2$O 4:1:0.2	80 °C for 6 h	Over 90%	Diameter range of 5−20 nm and length of 50−300 nm	-	[48]
Grape pomace from red-wine making (Cellulose after fermentation in grape pomace)	CNC	ChCl:LA 1:2	80 °C for 6 h	-	Length 241.5 ± 45.3 nm Diameter 22.0 ± 3.9 nm CRI 95.2%	Self-healing nanocomposite hydrogels	[49]
Microcrystalline cellulose	CNC	ChCl:U (2.71:2.32 by weight)	110 °C for 2-4 days	33-56%	20x100x700 nm	Reinforcing filler/reinforcing fillers for chitosan films plasticized with DES	[50]
Bleached rice straw pulp	CNC	ChCl:OA 1:1	80 °C for 4h	55.1%	Average particle size of 69.3 ± 22.8 nm	-	[51]
Kraft pulp from poplar wood	CNC, CNF	ChCl:OAd 1:1with excess water (10%-30%)	80 °C for 1 h, Microwave, ultrasonic process	80.8-88.8%	CNC: Diameter ~20 nm CNF: Diameter 20 nm, Width 300-2000 nm	-	[52]
Microcrystalline cellulose	CNC, CNF	ChCl:FA ChCl:U 1:2	90 °C for 2 h Ball mill for 8h, 16h	CNF Urea: 85-89% Formic acid: 82-87% CNC Urea: 7-10%	CRI Urea:67-69% Formic acid: 69-72% CNC diameter 8-12 nm	Oil-in water pickering emulsion, plastic/rubber systems or advanced materials.	[53]

				Formic acid: 7-13%			
Microcrystalline cellulose	CNC, CNF	ChCl:OA 1:1 With ultra-pure water	90 °C for 0.5-2.5 h High-rate shear dispersing emulsifier	27.2% (0.5 h) to 65.2% (2.5 h)	Average diameter of 25.1–33.3 nm Length 281.3- 404.2 nm	-	[54]
Wood cellulose pulp	CNF	Sulfamic acid:U 1:4/3/2	150 °C for 30 min	-	Average Width: 4.4 ± 1.6 nm	Rheology modifier, reinforcing additives	[55]
Hardwood bleached kraft pulp	CNF	ChCl:FA/LA/acetic/ MA/ OA/CA 1:2/9/2/1/1/1	50-100 °C for 3h, Mechanical extrusion, Colloid mill treatment	72%–88%	Diameters of mono, di, tri substituted carboxylic acids: 15-30 nm, 20-50 nm and 10-25 nm respectively	CNF-strengthened polylactic acid (PLA) composites	[56]
Bleached softwood kraft pulp	CNF	ChCl:anhydrous CA/CA monohydrate 1:1	80,90,100 °C for 2 h High-pressure homogenizer	Highest: 87.3 ± 1.8% (citric acid monohydrate at 80 °C) Lowest: 74.4 ± 0.9% (anhydrous citric acid at 100 °C)	Diameter Highest: 42 ± 5 nm (citric acid monohydrate at 80 °C) Lowest: 17 ± 2% (anhydrous citric acid at 100 °C)	Flexible cellulose nano paper	[57]
Needle Bleached Kraft Pulp	CNF	ChCl:EG 1:1 with 20-80% water, H_2SO_4 catalysis	120 °C for 2 h Screw extrusion Colloid mill	~80-100%	Mean diameter: 14-38 nm	-	[58]
Ramie fibers	CNF	ChCl:OAd 1:1	100 °C for 4 h Ball mill for 6 h,12 h	-	Mean length 523.4 nm, width 14.3 nm CRI 79.17%	Thin films	[59]
Bleached kraft poplar pulp	CNF	Sulfamic acid:glycerol Mass ratio 1:3	100 °C for 1-1.5 h Grinder (Super mass collider)	80.9% to 95.2%	Diameters from 10 - 25 nm CRI 53-62%	UV-blocking materials	[60]
Thermomechanical pulp	LCNC	ChCl:OA 1:1	80 °C for 3 h	-	Width: ~ 6.0 nm, Thickness: ~3.3 nm	Nano-composites reinforcement,	[61]

		ChCl:OA:p-toluenesulfonic acid 2:1:1				cement additives, and packaging materials	
Energy cane bagasse	LCNF	ChCl:LA 1:10	110 °C for 30 min Microwave assisted, Ultrasonication	45.2%	Average crystal size 3.14 ± 0.01 nm to 3.44 ± 0.02 nm	Reinforcing and UV absorbing agents in polyanionic cellulose (PAC) films, potential packaging material	62
Corncob	LCNF	ChCl:FA/LA/acetic acid 1:2/5/2	90 °C for 9 h Enzymatic hydrolysis High-pressure homogenization	36.3-82.2%	Average diameter 60–90 nm	Fluorescent, hydrophobic, thermally stable, redispersable LCNF	63
Hardwood bleached kraft pulp with varying amounts of lignin from poplar wood chips	LCNF	ChCl:LA 1:9	100 °C for 3h Spiral-squeezing Colloid milling	80-90%	Diameters 20 nm and 100 nm CRI 71-78%	Reinforcing agents for PLA films	64
Pine-wood powder	LCNF	ChCl:LA 1:1/3/5	Conventional heating 110 °C, 130 °C for 2 h, Microwave-assisted heating (80-110 s), High pressure homogenization	Conventional heating: 40-66% Microwave-assisted heating: 42-80%	Diameter 60-90nm Conventional CRI 62-71% Microwave CRI 63-70%	Packaging applications	65
Abaca	LNP	EG:ChCl:$AlCl_3$ 2:1:0.1	100-120 °C 30 min	~5.6-32.4%	30-70 nm With relatively homogeneous morphology	Natural antioxidant	66
Corncob alkali lignin	LNP	ChCl:ethanolamine 1:6	Ambient temp (25 °C) 1 h Dialyze for 72 h	62.7-70.4%	Average diameter 8.9-177.0 nm	Food and medical packaging materials with UV-blocking behavior.	67

Rice straw	LNP	ChCl:OA:LA 1:0.5:1	Microwave irradiation (680 W) 4 min	63.4% high lignin purity (86.8%)	Average particle size 48–95 nm	-	68
Dealkaline lignin	LNP	Betaine:LA 1:2 30 wt% ultrapure water.	Ambient temp (25 °C) for 12 h dialyze, 72 h	74.8 ± 1.6%	Average size 57.7 ± 1.4 nm	Stabilizer in pickering emulsions	69
Kraft lignin	LNP	ChCl:ethanolamine 1:6	Ambient temp (25 °C) for 2 h Dialyze for 72 h	-	Average diameter 123.6 to 140.7 nm	Nanocomposite gel beads using a sodium alginate (SA) matrix to remove methylene blue (MB) from the aqueous solution	70
Corn cob	LNP	ChCl:LA 1:1/5/10	100-150 °C for 6-18 h	Up to 85.6% (treatment with 1:10, 150 °C for 18h) highest purity of 97.8%	Hydrodynamic diameter 48.7 nm	-	71
Eucommia ulmoides wood	LNP	ChCl:malic acid 2:1	Hydrothermal pretreated fiber treatment with DES at 120 °C, 130 °C for 3h	-	60-110 nm Mw 1130-8500	Drug delivery, biomedical and tissue engineering applications	72
Poplar wood chips Pine wood shavings Moso bamboo powder Wheat straw Rice straw	Activated nano carbon, LCNF, LNP	ChCl:LA 1:2	Hydrothermal pretreated fiber treatment with DES at 130 °C for 3h	ANC: ~1.0-2.7% LCNF ~40.5-65.7% LNP ~5.7-13.7%	ANC: specific surface area ~ 2680 m^2 g^{-1} LNP 200-600 nm LCNF: aspect ratio ~ 150, CRI 72.3-83.3%	-	73
Wheat straw	LNP	K_2CO_3:glycerol 1:5	100 °C for 16h pH 6,4,2	1.2-7.8%	200-700 nm	-	74
Bamboo powder	LNP, LCNF, carbon	ChCl:LA 1:9	Microwave-assisted (maximum 300 W) 100-130 °C, 20 min	-	LNP: 30-75 nm LCNF: Average diameter 8.8-12.8 nm	Drug delivery, water treatment, and nano-fillers	75

	quantum dots				Carbon quantum dots: 9.8 nm		
Rice straw	Activated nanocarbon (ANC), lignin nanosphere (LNS), LCNF	ChCl:LA 1:2	130 °C for 3 h Hydrothermal pretreatment	LNS: 31.8% LCNF: 99.7%	LNS: 262 nm LCNF CRI: 76.9%, Mw: ~ 6500 g mol^{-1}	ANC: energy storage application LNS, LCNF: green agriculture, green nano-carrier for enhancing pesticide deposition and retention	76
Chitin	Chitin nanocrystals	ChCl:p-toluene sulfonic acid 1:1	95 °C 30 min	-	Width: ~12-44 nm Length: ~ 206-399 nm	Enzyme Carrier	77
Chitin from crab shell	Chitin nanocrystals	ChCl:OAd/LA/MA/CA monohydrate/DL-malic acid 1:2	100 °C 1-3 h Ultrasonication	Highest 87.5% ChCl:LA 1 h Lowest 77.9% ChCl:CA monohydrate 3h	Average diameter: 42-49 nm Average length:257-670 nm Mass yield ranging from 78 % to 87.5 %	Emulsifiers for pickering emulsions	78
Alpha (α)-chitin from shrimp shells	Chitin nanocrystals	Betaine chloride: ferric chloride hexahydrate 1:1	70-100 °C 1-4h Ultrasonication	83.2-88.5%	Average diameter of 10 nm and length of 201-259 nm CRI 89.2%	Emulsion stabilizers	79
Alpha (α)-chitin from shrimp shells	Chitin nanocrystals	ChCl:$ZnCl_2$ 1:2	90 °C 3-6 h Ultrasonication	53.8-97.4%	Diameter 20-80 nm Length 100-700 nm CRI 84.5-89.8%	-	80
Waxy maize starch	Starch nanoparticles	ChCl:OA 1:1	60 °C for 0.5,1,1.5,2 h	Highest (0.5 h): 84.3 ± 2.7% Lowest (2 h): 14.1 ± 2.1%	Thickness of crystalline lamellae decreased from 6.4 to 5.6 nm (from 0 to 0.5 h treatment) Mw Highest (0.5 h): 1.8 ± 0.4 Da Lowest (2 h): 0.3 ± 0.1 Da	Food and pharmaceutical industry; film enhancer, rheological modifier, pickering emulsion stabilizer	81

					CRI Highest (0.5 h): 28.1 ± 0.4% Lowest (2 h): 25.2 ± 0.4%		

Abbreviations: ChCl-Choline chloride; LA-Lactic acid; OA-Oxalic acid; OAd-Oxalic acid dihydrate; MA-Malonic acid; FA-Formic acid; CA-Citric acid; EG-Ethylene Glycol; U-Urea; CNC-Cellulose nanocrystals; CNF-Cellulose nanofibers; LCNC-Lignin containing cellulose nanocrystals; LCNF-Lignin containing cellulose nanofibers; LNP-Lignin nanoparticles; Mw-Molecular weight; CRI-Crystallinity Index; PDI-Polydispersity Index

DOI: 10.1039/D4GC00532E

4.1 Lignocellulose

Lignocellulose biomass is the most abundant natural biopolymer primarily comprising of three sub units viz cellulose (35-83% of dry mass), lignin (0-43%), and hemicellulose (0-30%) combined with complex structural arrangement.[82] The composition of each may vary with the plant category, age, and position of the plant material depending on its designated purpose. Cellulose is a homo-polymer containing D-glucose monomers linked by β-1,4-glycosidic bonds with strong hydrogen bond attachments among polymer chains, leading to crystalline and amorphous regions within the structure (Figure 4a). Hemicellulose, on the other hand, is a heterogeneous polymer mainly consisting of xylose, pentose, and hexose. Lignin, being the most abundant natural aromatic feedstock, is composed of a complex arrangement of coniferyl, sinapyl, p-hydroxyphenyl alcohol units. The availability of the aromatic groups (mainly linked with β-O-4 aryl-ether bonds) generates hydrophobic characteristics to lignin. Owing to the recalcitrant nature of these lignocellulose biomass, pretreatment is essential to generate value-added functional polymers. Utilization of DESs for this purpose has been stirred up during the last two decades mainly due to factors such as recyclability/low waste generation, ease of preparation, and non-toxicity. Vast amount of studies are conducted for the isolation of lignin, cellulose biopolymers whereas the isolation of hemicellulose is still in its infancy.[83]

The fractionation efficiency of the biomass using DES may depend on various factors of DES itself (molar ratio, temperature, viscosity, acidity/basicity) and the bonding nature within the lignocellulose biomass (number of cleavable bonds available). DESs are widely popular for its specific ability in dissolution of hemicellulose and lignin without disturbing cellulose which was first found by Fransisco et al. in 2012.[84,85] The main reason for this has been attributed to the strong cohesive energy existing within the cellulose structure preventing the dissociation of it in the

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presence of DES. Further, the formation of robust hydrogen bonds between DES and cellulose stabilizes the DES-cellulose system, simultaneously selectively disrupting other non-covalent interactions with lignin and hemicellulose.[84] This is commonly referred to as the 'delignification' process, and a significant amount of studies have been published on it up to the present time (Figure 4b).

Apart from the fractionation of lignocellulose biomass, DESs can reduce the size of these natural polymeric materials towards the nanoscale including cellulose nanocrystals (CNC),[85,52,51,54,48] cellulose nanofibers (CNF),[58,57,63] lignin nanoparticles (LNP),[69,66,70] lignin containing CNCs/CNFs[61,62,61,86,64] (Figure 4c). Even though it was stated that DES can selectively dissociate the bonds of lignin to detach from the lignocellulose biomass structure primarily, the studies of DESs on the cellulose as a starting material in microscale has revealed the effect on the hydrogen bond cleavage of cellulose structures to generate nanoscale materials (Table 1). In most cases this has been achieved by the synergistic effects of DES treatment with physicomechanical treatments (e.g. milling, high pressure homogenization, screw extrusion, microwave, ultrasound) or chemical treatments (addition of catalytic amounts of strong acid/bases, lewis acids).[76,87,88,89] Luo et al. explored the use of different DES systems to develop stable and uniform LNPs, and incorporate into a polyvinyl alcohol matrix as a nanocomposite material for medical and food packaging applications.[90] The addition of LNP increased its tensile strength and thermal stability, as well as introducing UV-blocking properties. A recent study carried out by Shen et al. revealed the utilization of hydrothermal pretreatment (with 0.5% H_2SO_4) coupled with ChCl:lactic acid on straw waste to generate three value added nanomaterials hemicellulose derived activated nanocarbon, lignin nanosphere, and lignin containing CNF (Figure 4c).[76]

DOI: 10.1039/D4GC00532E

Wang et al. reported the generation of nanocellulose materials in the range of 3-90 nm width with CRI ranging from 44-96% with the use of ChCl and carboxylic acid-based DESs.[89] However, even though oxalic acid based treatment provide promising results in many instances, the dimer formation owing to the dicarboxylic groups in oxalic acid cannot be overlooked since it may have an effect on the mobility of choline cations.[91] Additionally, when considering the scale-up operations, the pulp charring, and release for CO_2 at high temperatures has also been observed in this system.[84] Other types of acids such as lactic acid, citric acid, acetic acid has also been utilized over past years. However, the main challenge with these carboxylic acid based DES treatments is known to be the high viscosity level, which affects the yield. Even though the addition of water result in promising outputs by reducing viscosity, ionizing H^+, and delocalizing Cl^-, the optimization of this approach is still in the nascent state.[92,76,93,52]

The effect of DES treatment on lignin and cellulose structure has been studied in several occasions. The DES treated lignin often exhibit high thermal stability (selective cleavage of abundant β-O-4 aryl ether linkages of lignin structure) and high reactivity (increased phenolic hydroxyl groups of the lignin structure due to β-O-4 bond cleavage and demethylation of methoxy groups) compared to conventional technical lignin.[74,94,95,92] Additionally, several studies indicated the carboxylic acid based DES treatments leading to the esterification on the γ-hydroxyl group of lignin substructure and cellulose hydroxyl groups.[88,96,89] The generation of cellulose carbamates with different nitrogen contents by urea based DESs has also been reported as an alternative to viscose process which consist of adverse environmental effects and reduced recylability.[97] These modifications with tunable conditions pave pathways to disturb the recalcitrant nature of the lignocellulose biomass compared to the conventional chemical approaches which creates high waste, oxidation of the biomass, and introduction of sulfur groups to the structure.

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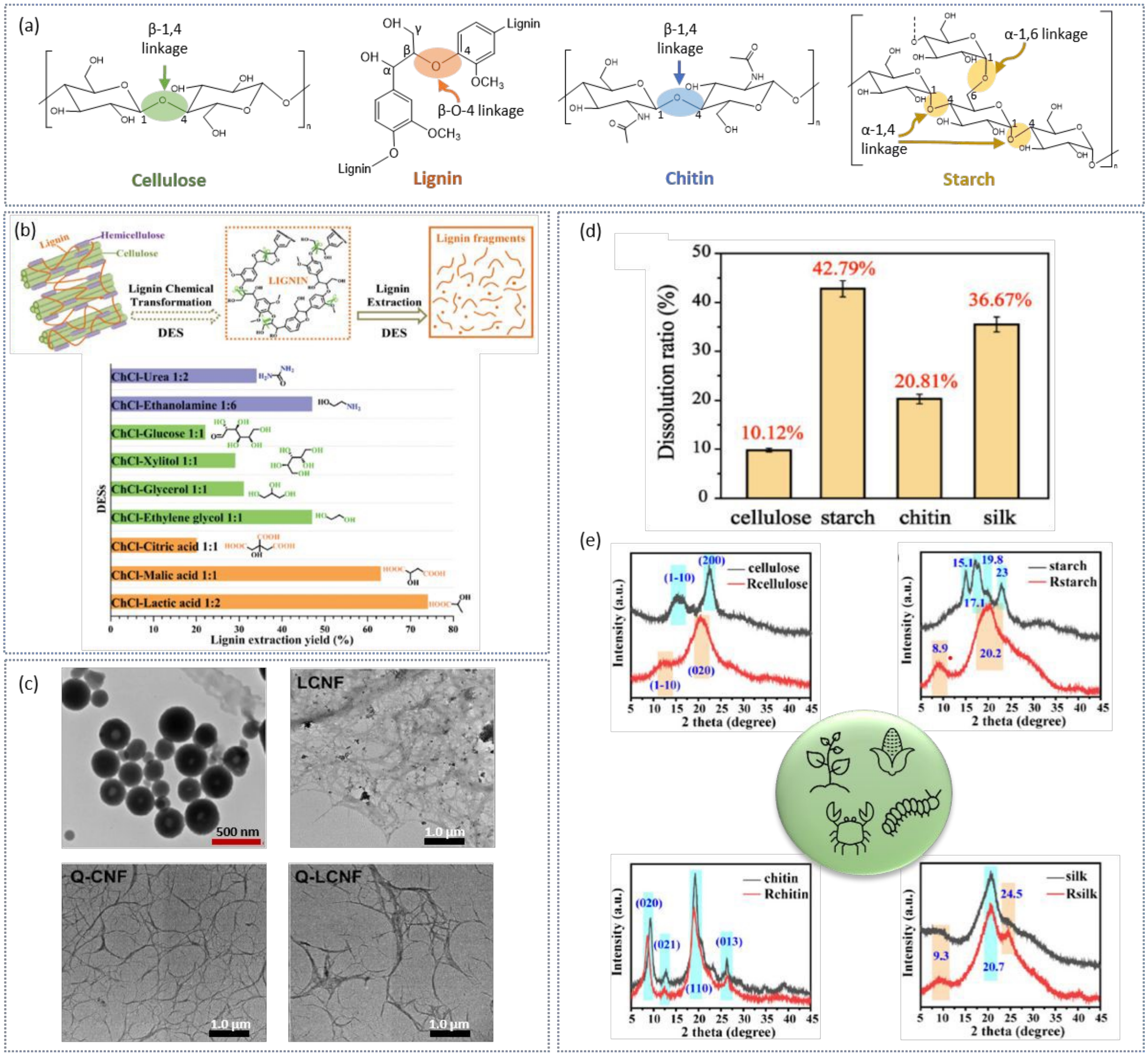

Figure 4. (a) Main chemical linkages of cellulose, lignin, chitin, and starch. (b) Lignin fractionation using DES and extraction yield.[88] Copyright 2020, Royal Society of Chemistry. (c) TEM image of Lignin nanospheres, LCNF, quaternized CNF(Q-CNF), and LCNF (Q-LCNF).[76] Copyright 2023, Elsevier. (d) Dissolution of biopolymers at room temperature using DES, and (e) XRD of biopolymers and regenerated materials at room temperature with $ZnCl_2$:water:formic acid 1:1:4.[98] Copyright 2023, Royal Society of Chemistry.

4.2 Chitin

Chitin is the second most abundant polysaccharide biopolymer consisting of N-acetyl-glucosamine and N-glucosamine units. This is mainly found in sources such as crustacean shells, insect exoskeletons, and some fungi and algae.[99] The β-1-4 bonds make it comparable with the structure

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of cellulose and there exist mainly three configurations viz α-, β-, and γ-chitin owing to the molecular arrangement. The N-deacetylation process (at least 50%) leads to the generation of chitosan which is considered as an alternative biopolymer derived from chitin.[100]

The extraction of chitin consists of two main steps namely demineralization and deproteinization where the former explains the removal of $CaCO_3$ with the use of acidic media and the latter by alkali treatment. This procedure facilitates the efficient utilization of chitin, allowing it to be applied effectively in specialized uses within the biomedical industry and other consumer sectors. With the introduction of DESs researchers has applied the knowledge to process this biomaterial where the first attempt has been conducted in 2017 by Zhu et al.[100] Since then, numerous studies have been published in this area over the past years owing to ease of processing (one step) and attractive properties of DESs. The highly organized nature of chitin demands strong DES systems mainly consisting of acidic HBDs.[101,99,100] Here, the utilization of type III DESs with carboxylic acids as HBDs has indicated the acylation of the hydroxyl groups of the chitin which enhances the dispersibility (in water) of the regenerated polymer structures.[101,102] Further, these acidic DESs display specific ability to reduce the particle size into nanoscale where Yuan et al. highlighted the dual role of aforementioned DES as hydrolysation and acylation reagent.[78] Among the different acidic systems used, ChCl:malonic acid has indicated remarkable outcomes in the light of both purity and yield with the effective removal of protein and minerals.[101,99,100,103,102]

Li et al. reported the detailed mechanism of chitin extraction with the demineralization by the hydrogen ions of acidic DESs generating soluble calcium salts, water, and CO_2. This leads to a loosely bound chitin-protein structure whereby the DES molecules can penetrate in to the microstructure of the chitin to swell and disrupt the hydrogen bonding network.[104] The yield of chitin may depend on various factors such as temperature, acidic nature, and reaction time within

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the system.[102] Additionally, numerous nanomaterials viz nanocrystals and nanofibers has been isolated by chitin with the use of DESs coupled with mechanical treatments, by removing the amorphous zones in raw chitin.[103] The synthesis of Chitin nanomaterials has been reported with diameters ranging from 20-80 nm, 12-44 nm, 42-49 nm with the use of $ChCl:ZnCl_2$,[80] ChCl:p-toluenesulfonic acid,[77] ChCl:carboxylic acids (oxalic acid dihydrate, lactic acid, malonic acid, citric acid monohydrate, DL-malic acid)[78] based DESs respectively. In the latter study, where the comparison of acidic DESs is concerned, Yuan et al. observed O-acetylation in all the nanocrystals, while the ChCl:lactic acid-based system generated the optimum option, yielding the highest mass of 87.5 wt% along with a stable aqueous suspension.[78]

Owing to the compositional changes of chitosan the main application of DES in those systems has been identified as the enhancement of mechanical properties and plasticity of chitosan based films.[101] Additionally the chemical property variance between chitin and chitosan leads to different solubilities in same DES system.[103]

4.3 Starch

Starch is another class of natural polymeric material with a complex assembly made out of amylose and amylopectin based polysaccharides with varying arrangements of α-1,4-linkages and α-1,6-branches.[105] Various attempts have been carried out in the past to dissolve and isolate this complex polysaccharide with numerous solvents such as water, DMSO, and pyridine.[106] Owing to the attractive abilities of polysaccharide treatment as well as green credentials, several researchers tried to utilize DESs to unveil the structural transition of starch. The use of DES based starch treatment has been categorized into two main parts namely the dissolution and plasticizisation.[107]

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The solubility of starch with the use of different DESs has been studied, where in many studies the maximum solubility up to 10% has been observed.[108] A study carried out by Zdanowicz and Spychaj indicated that the treatment of carboxylic acid-based DES on potato starch led starch degradation. As a result, most of the researchers probed ways to utilize this polysaccharide with the use of non-destructive constituents of DES, mostly containing substituents as imidazole, urea, and glycerol, where no chemical structure alterations have been realized in most instances.[106,109] The dissolution process is mainly observed via microscopic observations and DSC analysis. Zdanowicz studied the effect of urea based DESs (with polyols and monosugars) on potato starch and reported DES with glycerol has better performance over sorbitol and the urea content of the system affected the dissolution temperature of starch.[107] In a state where synthesis of starch nanoparticles using DES is still in its infancy. Xiao et al. successfully utilized ChCl:oxalic acid dihydrate treatment for the generation of waxy maize starch nanoparticles.[81] The team observed a dissolution of crystalline and amorphous regions of the starch with DES treatment of 2 hours generated aggregated nanoplatelets in 38-117 nm (Figure 5b). An esterification on the nanoparticles due to the effect of oxalic acid in the DES has been observed with increased treatment time.

DES is usually popular for its plasticizing ability when it comes to starch-based applications. The plasticization of the starch takes place when the DES constituents disrupt the granular structure of starch via hydrogen bonding, resulting in swelling.[108] The main factors of plasticizing scenario can be listed as the temperature, force, water content, and chemical constituents.[108,109] Zdanowicz compared different DESs and ionic liquids with conventional plasticizer glycerol to treat potato starch, and revealed that urea based DESs and ionic liquids generated better dissolving capacity

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while having lower viscosity values than that of glycerol, which is a beneficial property for thermoplastic starch processing (Figure 5a).[110]

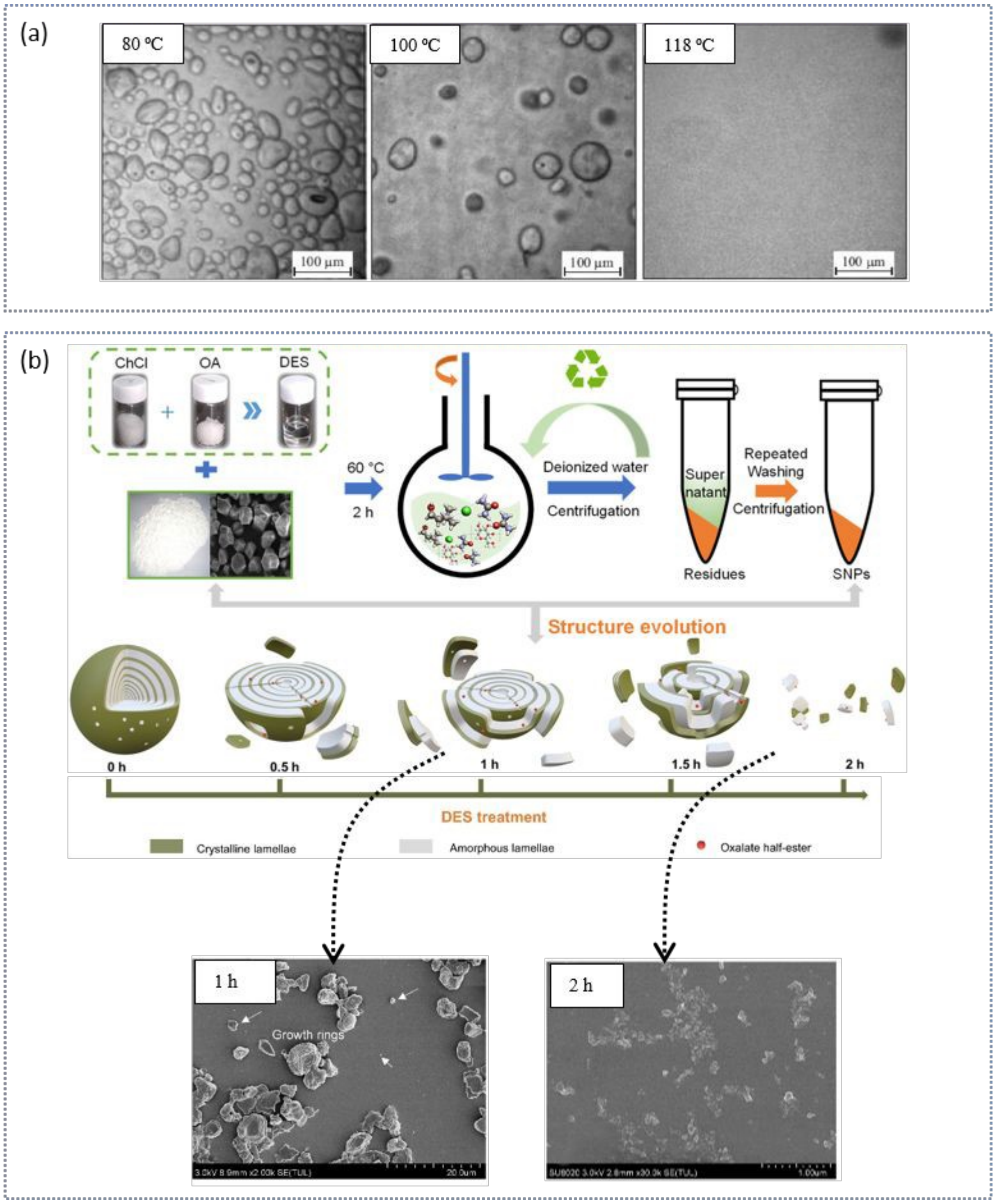

Figure 5. (a) Plasticization effect of ChCl:urea DES on dried potato starch at 80 °C, 100 °C and 118 °C.[109] Copyright 2018, Elsevier. (b) Illustration of the formation of starch nanoparticles: DES treatment (ChCl:oxalic acid dihydrate) on waxy maize starch for 1 h and 2 h.[81] Copyright 2022, Elsevier.

The addition of a plasticizer for starch processing plays a vital role owing to the glass transition temperature lying close to its degradation temperature. It has been found that the use of DESs

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enhances the surface properties of starch when compared to conventional plasticizers such as glycerol and urea.[107] The effect of sugar alcohol based DESs studied by Zdanowicz et al. revealed that sorbitol based DES provided attractive mechanical properties (tensile strength 8.6 MPa, 33% elongation at break).[111] Another study carried out by Zdanowicz compared different DES combinations with urea, polyol, and sugar-based starch treatments, resulting the production of flexible films with highest elongation at break greater than 200% with urea:glycerol system.[107] The plasticizing ability of DES can depend on several factors such as temperature, force applied as well as the technique used (e.g. extrusion, thermo-compression).[108] A study carried out by Deng et al. discussed about the importance of the use of ChCl:ethylene glycol DES on corn starch for the utilization of non-destructive starch processing with structural analysis.[106]

Utilizing renewable feedstock (in accordance with the seventh principle of green chemistry) to produce value-added functional materials with the help of DES can pave the way for environmentally friendly alternatives to synthetic materials. Here, the effect of hydrogen bonding in the dissociation of biomasses plays a prominent role, whilst the plasticizing effect of DESs on starch provides attractive physicomechanical properties in the subsequent composite materials. The treatment of DES on biomass materials discussed has the ability to generate nanomaterials with high purity levels compared to the harsh conditions generated by the conventional approaches. The most common chemical modification arises with the acylation of the abundant hydroxyl groups of the biomasses especially esterification with the carboxylic acid-based DES treatments. This functionalization is deemed to be favorable owing to the improved dispersibility of the regenerated biopolymers with high storage stability which ensures the effective utilization for most applications.

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5. Functional materials engineered in DES

In the above two chapters, we summarized that DES facilitates the polymerization of synthetic polymers as monomers or solvents and biomass pretreatment. All these DES adoptions aim to assist the engineering of DES-synthetic polymers and biomass into functional materials. Some of the specific properties of these functional materials include stimuli responsiveness, self-healing properties, electrical conductivity, and biodegradability apart from improved mechanical strength. The versatility of DESs enables it to play an important role in this context as a green alternative, which appears as an emerging area of concern (Figure 1b). In this section, we will unfold the strategies and properties of the functional materials generated by the application of DES in the following categories.

5.1 Gels

5.1.1 Eutectogels

The study on DES based gels received considerable attention of the scientific community over the past decade with the evolution of developments related to ionic liquids and then reaching for more stable, eco-friendly approaches. This class of gel materials was also termed as "Eutectogels" with the development of various applications to distinguish its chemical behavior. The preparation of eutectogels has been classified into three main sectors according to the chemical constituents, namely (1) the polymerization of one constituent of the DES especially HBDs with unsaturation (PDESs); (2) the DES act as solvents/medium for polymerization reactions of the constituents present in the medium; (3) the self-assembly of the components within DES to generate supramolecular solids which lead to gel-like structures.[112] The ability to fine tune the DES by changing the HBA and HBDs enabled researchers to move further towards the sensor-based

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applications in recent years, where ionic DESs can participate in conductive pathway. ChCl being the most widely used nontoxic and economical ionic HBA, the use of it to generate polymeric eutectogels was of high interest for most researchers.

5.1.1.1 Eutectogels using PDESs

The application of DES in gel materials has indicated beneficial results over conventional hydrogels and ionic liquid gels mainly owing to its non-volatility, non-toxicity, and ease of preparation. The utilization of PDES further enhances the properties by the noncovalent ionic and hydrogen bonding within the DES components and polymer chain apart from covalent bonds arising with the polymer backbone of the HBD or HBA. This leads to the enhanced mechanical properties of the system with high fatigue resistance.[113] The vast tunability of DESs enables effective dissolution of organic and inorganic additives enabling versatile applications.[114] The low or no water within the eutectogel system further impede the drawbacks associated with conventional hydrogels due to evaporation of water at high temperatures and freezing at lower temperatures.[114,115,116] The self-healing effect arising from the abundant hydrogen bonding is also another added advantage of the DES in gel based systems which enhances its robust nature. Collectively, these properties of DES pave attractive pathways in DES-based gel materials compared to traditional gel materials.

The utilization of polymerizable, renewable itaconic acid for hydrogel has been proposed by Bednarz et al. Here, the team generated a poly(itaconic acid-co-bisacrylamide) hydrogels using ChCl:itaconic acid PDES and highlighted a faster copolymerization in DES medium than in water.[44] Another dual network eutectogel with more properties such as visual strain sensing ability has been developed recently by Liu et al.[114] with the use of ternary DES ChCl:glycerol:N-acryloyl glycinamide (NAGA) with a conductivity of 0.7405 mS cm^{-1} and temperature tolerance of -20 °C

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to 60 °C. Here, the incorporation of photonic crystals into the gel enabled colour changes at different strains while the polymerized NAGA provided mechanical stability. Most of the gel based applications have been reported using AA, acrylamide, and acrylic acid derivatives in DES medium.[117]

In 2021 Wang et al. suggested a different approach to incorporate PDES (ChCl:AA) into a silicone tube.[115] This silicone tube was weavable on fabrics and could be used as a strain sensor to identify human motions. Additionally, this system has been able to withstand a temperature ranging -30 °C to 100 °C and C_2Cl_4 which is widely used for dry cleaning of fabrics. The AA based DESs have been initially formed followed by a photo polymerization after inserting into the tube. Another study carried out by Lim et al.[113] probed the use of ChCl:AA PDES as a screen printable conductive ink. In this study, they have used a supramolecular assembly of poly(3,4ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT:PSS) to support the system which generated a conductivity of 1.3 mS cm^{-1} (sevenfold higher than the normal ChCl:AA gel). This conductivity was further improved tremendously to 130 mS cm^{-1} with the addition of H_2SO_4 to the system. The author attributed this observation to structural transformations of the supramolecules to a linearly ordered manner which facilitated the conductivity thereby improving the signal response rate. The prepared gel material showed self-healability, stretchable, and high fatigue resistant properties. Another double network PDES with the same DES system has been generated with robust mechanical properties (strain up to 1373%, stress up to 3.14 MPa) by Wang et al. with the use of polyacrylamide hydrogel consisting of acrylamide and hyper-branched polyester H20P.[116] Here the availability of a high number of hydrogen bonds as well as the covalent crosslinks enhanced the mechanical strength. The optimal conductivity of the hydrogel was approximately 0.21 mS cm^{-1}.

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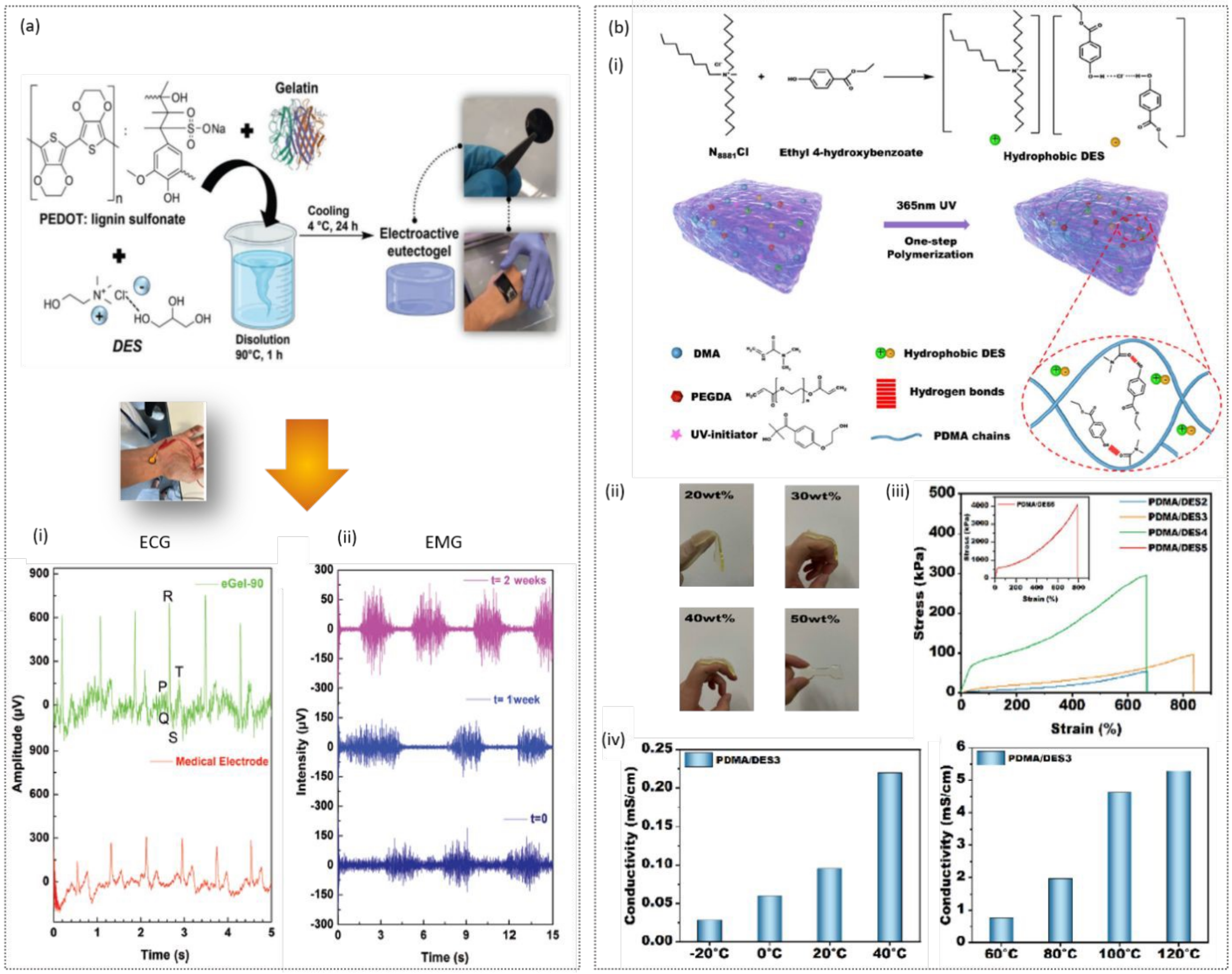

Figure 6. (a) Use of gelatin based eutectogels for medical applications. (i) ECG comparison with commercial medical electrode, (ii) time evolution EMG signals of thigh contraction/relaxation.[118] Copyright 2022, Wiley. (b) Hydrophobic DES-based gel. (i) Schematic illustration of hydrophobic DES based gel synthesis. (ii) Photographs of PDMA-DES gels with different polymer contents (20 to 50 wt%). (iii) Tensile stress-strain curves of PDMA-DES gels with highest tensile strength for 50 wt% polymer loading (4092.63 kPa). (iv) Conductivity of gel with 30 wt% polymer loading (PDMA/DES3) at different temperatures from -20 °C to 120 °C.[119] Copyright 2022, Wiley.

5.1.1.2 DES as medium

The other approach of generating stimuli responsive gels is the utilization of polymers (mainly AA and its derivatives) as the support for double network gels. A study carried out by Wu et al. investigated the effect of self-assembly of biopolymer agar in the DES system of ChCl:urea:water with Al^{3+}crosslinked polyAA.[120] A room temperature ionic conductivity of 2.1 mS cm^{-1} has been achieved in this study and it was reported that the effect of Al^{3+} may adversely affect the

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conductivity owing to the high amount of dynamic crosslinking even though it enhances the mechanical strength (stretchability up to 1595%) of the of the gel system.

A hydrophobic strain sensing eutectogel has been investigated by Gao et al. with N,N-dimethylacrylamide (DMA) polymer base (Figure 6b).[119] Here, the traditional ChCl was not used as the HBA to facilitate the conductivity, instead methyltrioctylammonium chloride:ethyl 4-hydroxybenzoate (1:2) has been chosen to enhance hydrophobicity. A stretchability of 900%, toughness of 341.14 kJ m^{-3} with a tensile strength of 97.58 kPa has been achieved owing to the reversible hydrogen bond interaction between the DES and the polymer in the gel with 30 wt% polymer scaffolds. The greatest strength has been observed in the gel with 50 wt% polymer (tensile strength of 4092.63 kPa, toughness of 13502.90 kJ m^{-3}). Another interesting approach on strain sensing with the use of DESs has been probed in harsh conditions for underwater communications.[121] Here, the team used both hydrophilic and hydrophobic DESs as well as polymer systems to achieve the intended properties with high level of interactions. ChCl:ethylene glycol has been utilized as hydrophilic DESs whereas thymol:decanoic acid as hydrophobic counterpart. For the polymers, AA and 2,2,2-trifluoroethyl methacrylate was copolymerized as hydrophilic and hydrophobic ends respectively. The team was able to generate stimuli responsive eutectogels with 0.93 mS cm^{-1} conductivity along with fast response time (1 s), immune to pH ranging from 3-9 with low swelling and low drying properties.

A supramolecular assembly of D-gluconic acetal gelator has been utilized for a N-(2-Hydroxyethyl)acrylamide polymer based dual network hydrogel with ChCl:monoethylene glycol.[122] The results suggested that the increasing loading of DES led to an increase in conductivity (up to 3.74 mS cm^{-1}) accompanied with mechanical properties of elongation at break over 4300 %, tensile fracture strain of 0.21 MPa, and stability over -20 °C to 100 °C. Additionally,

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with the strong intermolecular interactions of the gelator G18 high level of adhesion on different substrates has been observed. Apart from the strain and pressure sensing ability, this eutectogel showcased temperature sensing properties as well, owing to the reduction in resistance at higher temperatures. Additionally, the reversible non-covalent interactions within the double network system has been demonstrated in this study by the overlapped front and rear hysteresis loops indicating rapid partial self-recovery.

Prasad et al. reported number of ionic gels based on polysaccharides which were responsive to pH, heat, solvent, and shear changes in 2018.[123] In this work, the team has presented the use of self polymerizable HEMA for pH responsive drug release (indomethacin) in ChCl:fructose (2:1). Another use of HEMA was presented in the same paper using ChCl:orcinol (1:1.5) for highly stretchable and good capacitance behavior. Fan et al. introduced an eutectogel with the polymerization of 1-viniylimidazole in ChCl:glycerol with a high stretchability (2300% elongation), self healability, and ionic conductivity in a wide temperature range (-30 °C to 60 °C).[124] The generated eutectogel demonstrated adhesion to different substrates with the highest adhesive strength of approximately 70 kPa with a glass substrate.

5.1.1.3 Self-assembly within DES for supramolecular eutectogels

Self-assemblies in deep eutectic solvents represent an emerging frontier in materials science, offering a versatile platform for the creation of intricate supramolecular structures. Several systems, including PEDOT:PSS, cyclodextrins, DNA, and gelatin, have gathered significant attention in this context. Among these systems, gelatin has emerged as a particularly prominent candidate for the development of stimuli-responsive materials over the past few years, which will be covered in detail in this section.

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Gelatin is a widely produced protein based natural biopolymer which finds its ubiquitous applications in food and pharmaceutical industry by virtue of its non-toxic nature. The availability of polar groups within the structure makes gelatin a perfect candidate for the fabrication of eutectogels with greater stability than conventional hydrogels (loss of water content). The study on the effect of DES on the interaction of gelatin triple helices has been probed by number of research groups when fabricating sensors.

A study carried out by Qin et al. pointed out the use of gelatin in 22 wt% loading for a ChCl:ethylene glycol DES to generate a nonvolatile transparent gel electrolyte for strain and pressure sensing applications. The prepared eutectogel showed pressure sensing ability at 1 kPa levels and ability to withstand a strain at 320% (tensile stress 67 kPa) with a conductivity of 2.5 mS cm^{-1} at room temperature.[125] Here, both ChCl and ethylene glycol played vital roles in mechanical stability of the gel where the kosmotropic nature coupled with high ion density of ChCl helps the assembly of gelatin chain bundles with higher intermolecular attractions (lowering intramolecular interactions within triple helices), while ethylene glycol promoted the formation of fewer number of gelatin triple helices with larger diameters which provided more flexibility.

Owyeung et al.studied the effect of HBDs on gelatin-DES based hydrogels using three main HBDs ethylene glycol, glycerol, and 1,2-propanediol.[126] Interestingly, this study revealed that the careful addition of little amount of water (5-6 wt%) to the gelatin supported (20 wt%) DES system enabled to improve not only the conductivity but also the toughness of the resultant eutectogel. The Young's modulus changed with respect to the HBDs indicating lowest value of 7 kPa from 1,2-propanediol to a highest value of 42 kPa for glycerol. The incorporation of water to the ethylene glycol based DES increased the toughness value by 195% while increasing the conductivity by 58% (to 5.2 mS cm^{-1}). The authors highlighted the formation of shorter triple helices of gelatin

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with the presence of glycerol and ethylene glycol in virtue of the steric hindrance generated compared to water molecules. The generated shorter helices facilitate greater amount of crosslinks in a selected volume resulting in a higher stretchability of the material. Additionally, the carefully added water molecules helped to build up interaction between non helical inter-chain bonding which then leads to higher toughness values synergistically.

Another class of electron conductive eutectogel was generated by Picchio et al. using gelatin matrix with the addition of PEDOT:lignin sulfonate with gelatin and DES (ChCl:glycerol). The resultant eutectogel showed high ionic and electronic conductivity values of 7.3 and 8.7 mS cm^{-1} [118] which was suggested as a possible candidate for strain sensors as well as a bio electrode for ECG and EMG recordings (Figure 6a).

The self healability and recyclability of gelatin/polyvinyl alcohol/dialdehyde carboxymethyl cellulose (DCMC) based composite eutectogels (ChCl:glycerin) has been studied with the potential applications for strain, humid, temperature sensitivity.[127] Here, the self-healing and mechanical properties (tensile strength ~1.25MPa, elongation 1400%) were enhanced by the synergistic effects gained through the imine and hydrogen bonds within the system. Each of the constituent play a vital role of the overall performance of the resultant material where, the DES contribute to the ion conductivity, self-healing properties, durability on wide operating temperatures, while polyvinyl alcohol/DCMC acts as water capturing agents during humidity changes and structural transition of gelatin effects the temperature sensing ability.

Recently, Mercadal et al. developed non-cyto toxic bio based eutectogel with strain sensing abilities and 3D printability with the use of ChCl:ethylene glycol, porcine gelatin.[128] Here, Tannic acid coated CNC has been utilized as the reinforcing agent at low concentrations (1-2 wt%) and the resultant gel indicated a strength of 30 kPa and 180% elongation. A time-dependent adhesive

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performance has been incorporated into the underwater adhesives from the silane-based PDES (Lauric acid:diethylaminoethyl methacrylate:(3-Amino-propyl)trimethoxysilane).[129] Here the authors were able to introduce the controllability of the gel adhesive remotely with the use of laser beam.

5.1.2 Aerogels and Xerogels

The preparation of light weight functional polymeric materials such as aerogels and xerogels are attracting greater attention nowadays. DES plays different roles in generating these materials owing to its tunable functionalities discussed in previous sections. Here the DES can play several roles such as, (1) DES acting as a solvent medium for generation of porous structures; (2) PDES for the generation of polymer structure within the porous gel; (3) Pretreatment of biomass by DES in light of functionalization.

The use of DES as a solvent has been primarily employed for the phenol-formaldehyde polycondensations. Chen et al. reported ChCl:urea-based DES system for CO_2 capture using xerogels, with the DES system serving multiple functions, including acting as a structure-directing agent, providing a source of nitrogen for the carbons, apart from functioning as a solvent.[130] Another use of similar polymer system has been generated for capacitor applications where $ZnCl_2$ and urea DES has facilitated the generation of carbon-based aerogels with a high surface area (1238.81 $m^2\ g^{-1}$).[131] Additionally, iron-based DES system for xerogel-based super capacitor applications has been studied by Chen et al. which has delivered a capacitance of 209 $F\ g^{-1}$ at a current density of 0.5 $A\ g^{-1}$. Here, the authors highlighted advantages gained by the DES assisted resorcinol-formaldehyde polycondensation by eliminating costly supercritical CO_2 drying processes incorporated in traditional xerogel preparation.[132] Itaconic acid[133] and anilinium chloride[134] has been used as PDESs for the generation of xerogels. Further the pretreatment of

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biomass has been studied giving rise to the separation of oil, organic molecules, water, and dye. Glucose and ChCl DES treated CNF has been utilized by Long et al. in the generation of carbon aerogel with recycling ability up to 100 cycles (Figure 7b).[135] Peng et al. documented a top-down approach of utilizing cornstalk pith for the aerogels with oil/organic solvent sorption ability (Figure 7a). Here, they used DES for selective delignification and removal of hemicellulose to generate hydrophobic aerogel by further modifications.[136] Recently, Zhu et al. generated a composite aerogel with DES (ChCl:lactic acid) treated lignin from grapevine with chitosan for the removal of dyes (methylene blue, congo red), catechin, and epicatechin where the π orbit interactions of lignin and the samples have played a prominent role.[137]

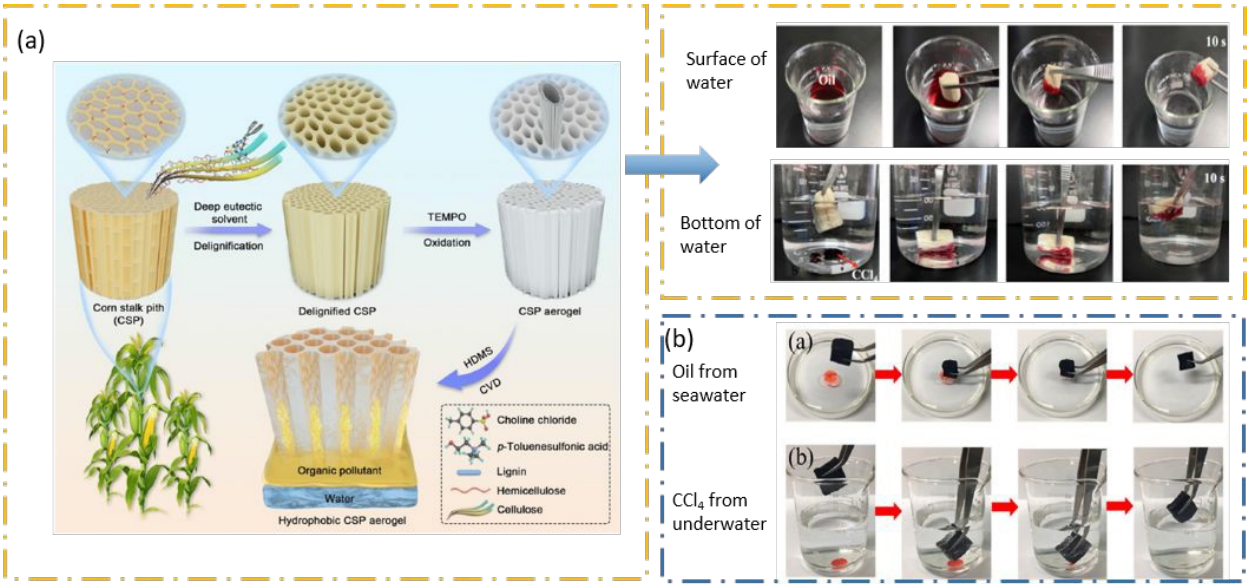

Figure 7. (a) Top down approach on generating hydrophobic aerogel from corn-stalk pith demonstrating good oil/water separation capability.[136] Copyright 2023, Elsevier. (b) Absorption of oil from sea water and CCl_4 from underwater using carbon aerogel derived from DES modified CNF.[135] Copyright 2021, Elsevier.

5.2 Fibers

The exploratory research efforts of DES open a myriad of possibilities for material fabrication. The use of these green alternative solvents would not only be environmentally conscious but also

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cost effective. To further demonstrate the potential of DES materials, various research works have been done to exploit the potential of their usage resulting nanofibers. These nanofibers coupled with electrospinning techniques can be applied to fields such as biomedical and agriculture. Sousa et al. first reported the use of DES as a solvent for electrospinning to produce agar nanofibers for potential biomedical applications.[138] The alternative solvent for electrospinning was prepared with DES ChCl:urea. The different blends of polyvinyl alcohol/agar and DES conditions resulted in various characteristics of the fibers in terms of the surface roughness, diameter size, and all blends exhibited good spinnability and mechanical resistance. Additionally, Mano et al. had approach the fabrication of electrospun polyvinyl alcohol fibers with NADES.[139] The main advantage of NADES in the fabrication of polyvinyl alcohol biopolymers is the acceptable toxicity profile and biocompatibility. As DES and NADES are hygroscopic liquids, it prevents premature evaporation of the solvent during fiber fabrication. The benefits of DES in terms of recyclability, lower cost, and suitable compatibility, puts it in the spotlight for alternatives to regular volatile solvents and its more expensive counterpart, ionic liquids.

However, adverse effects from residual DES could be detrimental to the integrity of the biopolymer fibers. A wet electrospinning strategy with the use of ChCl:lactic acid DES had been explored to prepare lignin fiber aerogels. The electrospun fibers were reported to coagulate in the water bath setup to sufficiently coagulate and remove the DES residues.[140] The resulting lignin fiber aerogel was carbonized and exhibited excellent electrochemical stability as a super capacitor electrode, as compared to the commercial counterpart. This demonstrates that DES is a greener solvent alternative to produce quality electrospun fibers to further build into aerogels. The compatibility of DES as a better solvent in electrospinning as compared to volatile ones such ethanol, and DMF extends to the production of protein-based electrospun nanofibers as well. Zein

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nanofibers are difficult to be electrospun directly due to other conditions such as temperature and UV-light exposure.[141] Mouro et al. fabricated nanofibers from electrospinning polymeric blend of polyvinyl alcohol and regenerated wool keratin from wool waste in different DES mixtures of ChCl:urea and L-Cysteine:lactic acid.[142] The nanofibrous membrane exhibited good antioxidative and anti-microbial properties to be valorized in other industrial applications. As the choice of solvents impacts the quality and outcome of the fibers, DES can facilitate the fabrication of these nanofibers due to its non-volatility.

On another hand, DES can be incorporated directly into the polymers for electrospun nanofibers. Sereshti et al. synthesized polyamide 6 (PA6)/[polymerized HEMA:1-tetradecanol] based electrospun nanofibers to extract residual pesticides from cereal flour analysis.[143] At higher DES content, the increase in viscosity of the polymer blend becomes a hindrance, whereas too low results in droplet formation. An optimal range of polymeric DES nanofibers resulted in satisfactory recovery of pesticide, demonstrating a fast and green alternative to multiclass pesticide analysis. Furthermore, NADES integrated poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) electrospun nanofibers were successfully fabricated for air filtration and resulted in a unique rugose morphology (Figure 8a).[144]

Electrospinning with DESs or DES containing polymers creates unique nanofibers with a promising avenue in healthcare, particularly in drug delivery systems. The DES, ChCl:mannose was used to dissolve polyvinyl alcohol and combined with honey or acetylsalicylic acid (ASA) to fabricated nanofibers through electrospinning (Figure 8b).[145] In the different blends of polymeric nanofibers, polyvinyl alcohol-DES demonstrated fast release drug delivery, polyvinyl alcohol-DES-honey exhibited excellent properties for wound healing and polyvinyl alcohol-DES-ASA can potentially be used in rapid drug release in oral mucosal systems.

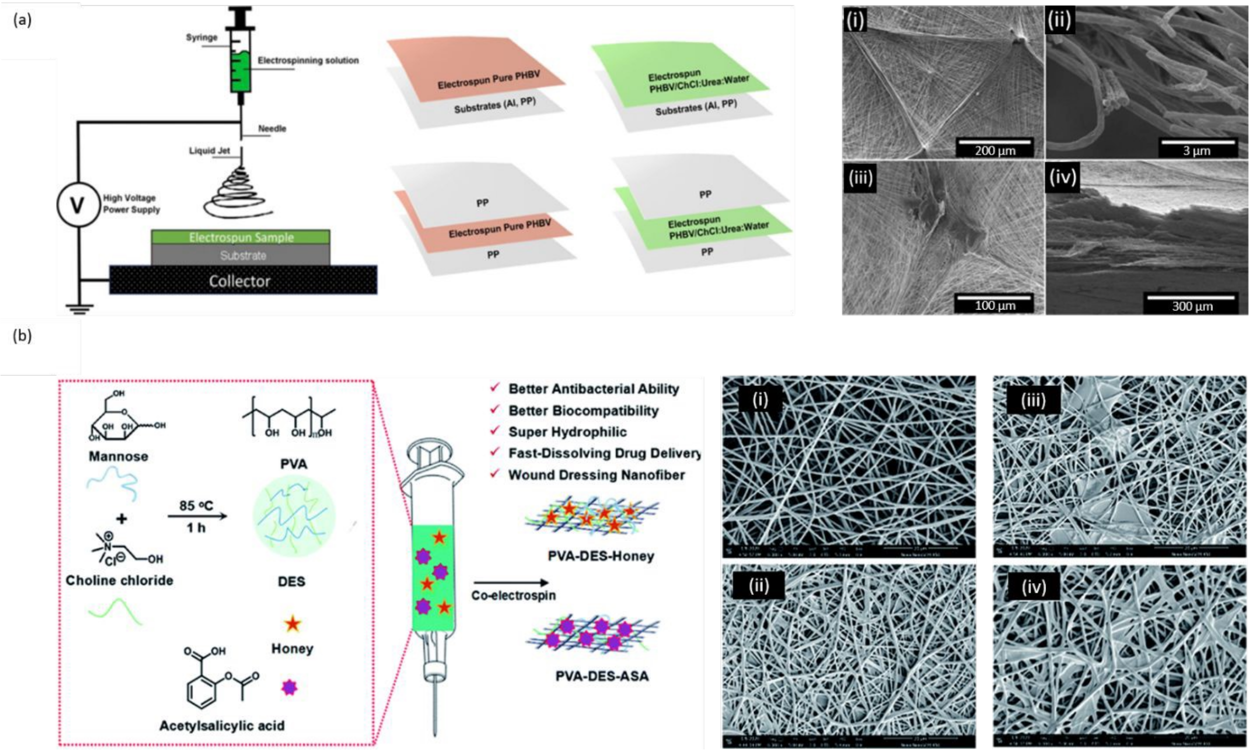

Figure 8. (a) Schematic diagram of sample preparation via electrospinning and its subsequent morphology of (i) pure PHBV on Al foil, (ii) PHBV/DES on polypropylene (PP), (iii) pure PHBV on PP, and (iv) PHBV/DES on PP.[144] Copyright 2023, American Chemical Society. (b) A Schematic diagram of the fabrication of polyvinyl alcohol-DES, polyvinyl alcohol-DES-honey, polyvinyl alcohol-DES-ASA by electrospinning and its subsequent morphology in (i) pure polyvinyl alcohol nanofibers, (ii) polyvinyl alcohol-DES, (iii) polyvinyl alcohol-DES-honey and (iv) polyvinyl alcohol-DES-ASA.[145] Copyright 2021, Royal Society of Chemistry.

Drug release can be optimized with the correct morphology, porosity, and interaction between the active agent and the polymeric nanofibers. Generally, electrospun drug systems deliver small molecules such as proteins or small drugs by surface interaction with the nanofibers. The smooth surface characteristics of the nanofibers can be achieved with the help of DES additives as well. Polycaprolactone fibers containing DES1 (ChCl:acetic acid) and DES2 (ChCl:glycerol) were electrospun for the release of ibuprofen and was found to have hydrophilic behavior which had an effect on the drug release profile.[146] The application of DES in electrospinning techniques and polymeric nanofibers minimizes the use of hazardous, volatile solvents with an option to recycle

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residual DES. The properties and morphologies of nanofibers derived from DES can be tuned to the level of DES in the system.

5.3 3D printing

With the improvement of fast paced scientific advancements additive manufacturing has gained a greater interest over the past few years. Researchers are continuously searching for ways to develop novel printable materials which can be used for range of applications. DES being a non-volatile, environmentally friendly material has proven to cater this demand in several studies and this area of research is evolving rapidly owing to its vast tunability of properties by fine tuning the bonding nature with polymers and other constituents.

5.3.1 Physical blending in DES system

DES systems with ethylene glycol or glycerol have been studied by several researchers for 3D printing applications. Lai et al. used ChCl:ethylene glycol based system for 3D printing application with ionically crosslinked AA by Al^{3+}.[147] Here, the authors used CNC to generate the shear thinning behavior of the ink generated for direct ink writing (DIW) and observed a high storage modulus (approximately 60 kPa) and yield stress (2.5 Pa) in return at a CNC loading of 22.5 wt%. The same team eventually studied ChCl:glycerol based system in AA and acrylamide based polymer system and found out that the effect of thermally induced gelation of CNC can reduce the loading to 10-14 wt% owing to the solvolysis of sulfate half ester of the CNC structure.[148] Another 3D printing ink generated by Pal et al. utilized Zr based metal organic framework crystals (MOFs) apart from CNC fillers into a system with acrylamide polymers and DES (ChCl:ethylene glycol), which enhanced not only the rheology, mechanical strength, and conductivity of the materials but

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also colorimetric sensing ability when exposed to acidic compounds for DIW of sensor fabrication.[149]

Several applications of the use of gelatin for non-cytotoxic sensor based applications has already been discussed in the section 5.1.1.3 in detail.[118, 128] These studies also probed the ability of the gels for 3D printing applications via hot extrusion processes at mild temperature conditions (37 °C to 42 °C) where the printed articles were able to preserve the shape and pattern of the printed articles. Sheikhi et al. suggested the use of DES for a radically distinct approach for the 3D printing of jammed microgels.[150] Here, the authors used the DES in the final step to coat the 3D printed jammed article to ensure the strength of the material, which ended up generating self-standing structures. The team used L-arginine and glycerol (1:2) based DES system for this purpose with a polymer network consisting of vinyl-functionalized gelatin, AA, and glycidyl methacrylate. The distinct role of amino acids and 1,2-diols based DES as an activator in covalent bond formation to make epoxy functional group for nucleophilic reactions at ambient conditions has been highlighted in this study.

Aguzin et al. studied the use of PEDOT:PSS in DES systems to enhance the ionic electronic conductivity and observed a supramolecular assembly and gelification in the system accompanied by DESs. The group studied several DES systems with differing HBDs such as aliphatic polyols, organic acids to aromatic compounds and the suggested PEDOT:PSS/DES ratio of 30 wt% provided the gel-like textures. Here, p-toluenesulfonic acid and pyrogallol containing DESs presented the highest storage modulus values (160 Pa and 120 Pa respectively) and the author attributed this phenomenon to the π-π interactions between the phenolic moieties of PEDOT, PSS, and HBDs. Furthermore, system with ChCl:lactic acid was used for the DIW application owing to

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the biocompatibility with annealing process at 50 °C for 16 hours for the fabrication of conductive patterns.[151]

The generation of 3D printing ink using lactic acid and maleic acid based DES systems in a one pot strategy has been suggested by Wang et al. with the addition of glycidyl methacrylate polymer system and CNCs.[152] In this research the team observed a higher strength in the maleic acid based DES system due to the presence of the additional chemical crosslinks generated by the unsaturation present in the structure of maleic acid.

5.3.2 3D printing with PDES systems

Numerous efforts have been conducted for the utilization of polymerizable DESs to generate 3D printable inks. Among these AA and acrylamide based DESs has been vastly studied.[153,154, 155, 156, 157,158,159,160,161] DIW based 3D printing has been studied in several instances with the use of different rheological modifiers. Vorobiov et al. compared the use of sulfated CNC and ChCl:urea treated CNCs with the loading of 6-15 wt% in the system and concluded that the presence of charged groups (in sulfated CNC) indicated a greater stabilization in ChCl:AA based system.[157] Additionally a stabilization of bacterial cellulose nanofibers using same DES system (ChCl:AA) has been proposed by Prosvirnina et al. by highlighting the formation of a polysiloxane shell on the surface of cellulose which resulted in lowering of agglomeration and printed structures with smooth surfaces.[158] Further a comparison conducted with imidazolium based ionic liquid and ChCl with AA DES revealed that the low viscosity level of choline based DES provides more favorable results in DIW printing than the imidazolium ones.[155] The properties have been further enhanced by grafting polyAA to the surface of CNF incorporated when fabricating the ink. Carbopol has been suggested as an alternative rheological modifier to CNC and CNFs by Vo et al. with a use of

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ternary PDES of ChCl:ethylene glycol:AA (1:1:2) which resulted in an enhanced stretchability (300%) and high sensitivity (gauge factor 3.1) in the 3D printed structures.[160]

In addition to the commonly employed DIW printing method, other techniques such as Stereo lithography (SLA), Digital Light Processing (DLP), and Liquid Crystal Display (LCD) have also been explored in conjunction with DES systems. The rapid curing time is a significant factor in most of these printing approaches, surpassing the importance of viscosity adjustments. Up to the present time, researchers have investigated numerous combinations of PDESs to address this aspect.

Su et al. suggested the fabrication of transparent antistatic 3D printed materials using SLA method. The group utilized PDES system consisting of ChCl:AA (1:2) which contributed to the enhancement of antistatic property and 2-hydroxyethyl acrylate for the strength requirements. The photo polymerization of this system indicated fast curing speed (10 s) and the highest mechanical strength has been observed at 20% DES loading with a 90% polymer conversion rate.[153] Cai et al. worked on a similar DES system with SLA technique to fine-tune the printing structure as interlocked pyramid type for pressure sensing applications.[154] A ternary PDES with acrylamide:ChCl:maleic acid (1:1:2) has been studied with this printing technique which resulted in highly transparent objects (95.6%) coupled faster curing time of 6 s (24 W UV light 410 nm) has been reported by the same team (Figure 9a).[156] Here, the team suggested that the strength of the material was comprised of soft monomer system (maleic acid/ChCl) and a hard system (acrylamide/ChCl) which resulted in the generation of copolymer product of poly (acrylamide/ChCl-co-maleic acid/ChCl). Furthermore, they emphasized that an elevation in photo initiator concentration resulted in higher conductivity due to the decrease in molecular weights of the polymers. Conversely, an increase in crosslinking agents led to a reduction in conductivity.

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The same group investigated the application of this PDES system in DLP based printing technique highlighted the temperature stability of the printed material over a wide temperature range (-70 °C to 120 °C) while maintaining its properties (conductive, compressible, and transparent) on the generation of capacitive ionic skins.[159]

Lacalle et al. suggested a novel DES system probing the interconnections between methacrylic and acrylic quaternary ammonium monomers with phenolic derivatives. Here, unlike conventional approaches the authors used the polymerization of the HBA for the PDES for 3D printing based on DLP method. The work highlighted the metal complexation ability, fast processability, and antibacterial properties of the suggested PDES while providing more inputs on the adhesive properties on the pyrogallol and hydrocaffeic acid-derived ionic polymers, and ultra-tough nature of tannic acid, gallic acid derived polymers (strength ~3 MPa).[162]

A study conducted by Zhu et al. utilized LCD based printing technique to generate printable material with ChCl:HEMA PDES (Figure 9b). The addition of tannic acid (10-40 wt%) not only enhanced the antibacterial properties of the printed item but also improved the homogeneity of the generated ink by interconnecting via noncovalent bonds with the DES system.[163] An interesting study on the 3D printing of sacrificial mold coupled with reprocessing study of the ink has been conducted by Li and co-workers utilizing a ternary PDES (ChCl:acrylamide:4-acryloylmorpholine) with LCD (Figure 9c). The solubility parameters of the final products have been tuned by adjusting the ratios of the PDES components and the authors highlighted that the 4-acryloylmorpholine monomer played a vital role in lowering the viscosity at ambient temperature. The studies conducted on the recycling of the printed material indicated a recovery efficiency exceeding 65% in tensile strength, strain at break, and young's modulus.[161]

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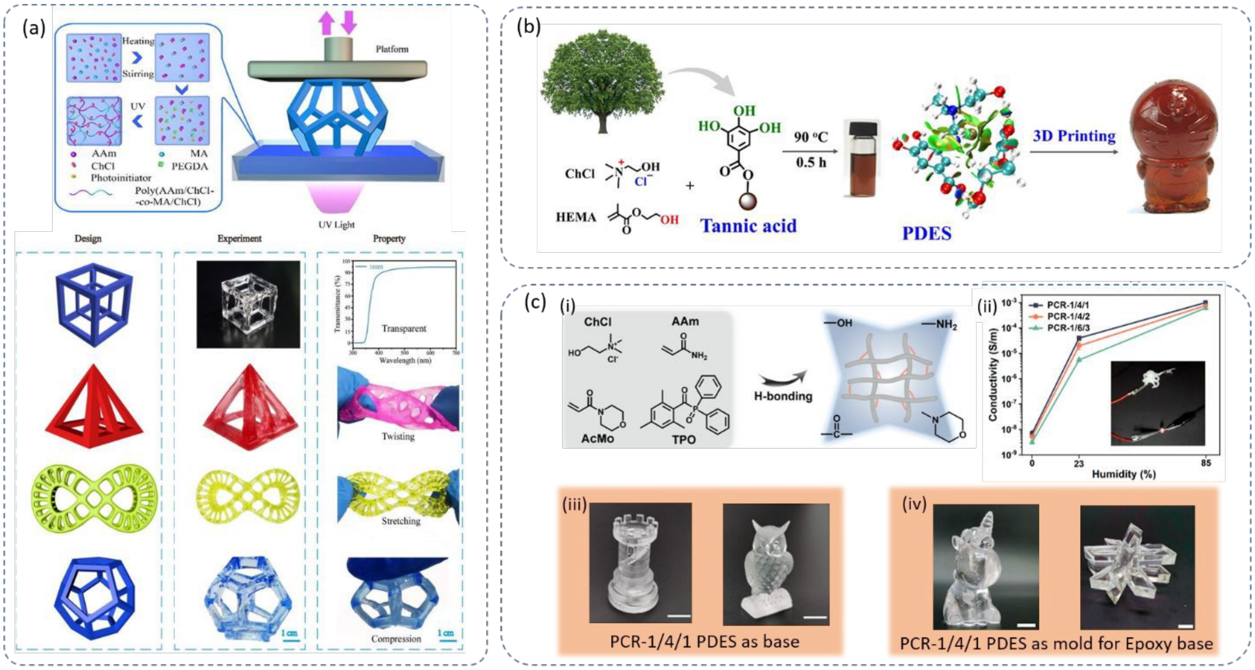

Figure 9. Photocurable resins generated by PDES for 3D printing applications (a) Schematic illustration of SLA printing of PDES (acrylamide:ChCl:maleic acid) and 3D printed models for conductive elastomeric sensors.[156] Copyright 2021, Elsevier. (b) LCD 3D printing of bio-based PDES (ChCl:HEMA).[163] Copyright 2023, American Chemical Society. (c) (i) Composition and hydrogen bonding in the PDES (ChCl: acrylamide:4-acryloylmorpholine). (ii) Conductivity variations with respect to humidity from 0-85%. (iii) Structures generated by LCD 3D printing of PCR 1/4/1 (ChCl:acrylamide:4-acryloylmorpholine 1:4:1). (iv) Epoxy structures generated by 3D printed PCR 1/4/1 sacrificial molds.[161] Copyright 2023, American Chemical Society.

5.4 Membranes and Films

The escalating challenges associated with plastic waste have spurred significant research into environmentally friendly and biodegradable solutions for membrane and thin film based applications. The transition in membrane science from traditional size separation to selective filtration and plastic-based thin films to functional polymeric materials from natural substitutes has been developed with a notable focus on the application of DESs due to their unique ability to interact via hydrogen bonding, serving both as modifiers for structural enhancement and as key functional materials.

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Pulyalina et al. investigated a polymer composite using polyamide-imide (Torlon) and a DES comprising zinc chloride and acetamide. The optimal DES loading of 50% resulted in the generation of pores within the polyamide-imide Torlon membrane, enhancing surface hydrophilicity by 24.9%, and showcasing the role of DES as a plasticizer (Figure 10a).[164] Non-ionic DESs were employed by Ismail et al. to dissolve PVDF polymer, producing three different morphologies of resultant membranes with varying pore sizes and thickness values (Figure 10b).[165] The addition of polyvinylpyrrolidone resulted in a finger-like structure, and the membrane prepared with N-methylacetamide-acetamide and 2 wt% polyvinylpyrrolidone demonstrated superior performance with high water permeate flux (96.82 L m^{-2} h^{-1}) and 96.32% of bovine serum albumin separation. In the pursuit of sustainability, another study evaluated the performance of NADESs as solvents for polyvinylidene fluoride (PVDF) and poly(acrylonitrile) membranes, aiming to differentiate the structure of polymer membranes for water purification applications. The generated membranes exhibited diverse morphologies, pore sizes ranging from 0.03 ± 0.01 μm to 1.08 ± 0.01 μm, and an average porosity of 84 ± 1%, demonstrating potential in water purification processes.[166]

The exploration of DESs for plasticizer applications began a decade ago, with initial uses highlighted as a novel plasticizer for cellulose acetate-based applications in 2013. The plasticizing ability of DESs, particularly ChCl-based DESs with urea, was attributed to high electronegativity and charge delocalization, enhancing the ionic conductivity of cellulose esters.[167] Subsequent research has probed the plasticizing abilities of various DESs, using ChCl as the HBA and urea, citric acid, malonic acid, and glycerol as primary HBDs.[168]

Biopolymer-based films, including chitin,[101] chitosan,[169,170,171] cellulose,[172,173] lignin,[174] pectin,[175] agar, agarose,[168] starch,[176] and gelatin,[177] have been extensively explored using DESs for film

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formation, serving as solvents for size reduction and homogenization. The tensile properties of chitosan-based films were found to be dependent on the degree of deacetylation (DDA), with higher DDA (around 95%) levels resulting in increased mechanical strength.[101] Apart from the studies related to structural enhancement on the surface, pysicomechanical properties, and antibacterial activities in chitosan films, the antioxidant activity of such film has been reported by Jakubowska et al. with the inclusion of quercetin which is a naturally obtainable plant polyphenol for the application of the storage of rapeseed oil.[171] Yu et al. studied the effect of chitosan based films for food packaging with different combinations of DESs with ChCl and organic acids.[170] Here, the team has probed the anti-bacterial, antioxidant as well as UV-barrier properties of the prepared films and found out that the one prepared with ChCl and acetylsalicylic acid indicated the best performance (DPPH scavenging activity approximately 60%, inhibition of *E. coli* and *S. aureus*). Additionally, the team suggested that the enhancement of the antibacterial properties was due to the synergistic effects of the chitosan and chosen DESs.

Studies on plant-based derivatives such as cellulose, lignin, and pectin, have been explored for property enhancements in areas such as antioxidant and UV shielding.[178] Composite films from cellulose and modified lignin revealed that antioxidant and UV shielding performance depended heavily on lignin pretreatment methods. Cellulose-lignin-based films with enhanced UV protection properties were generated using ChCl:oxalic acid and ChCl:glycerol-based DES treatments.[174] Xia et al. generated recyclable lignocellulosic bioplastic film with ~128 MPa tensile strength and toughness of 2.8 MJ m^{-3} with DES treated (ChCl:oxalic acid) wood powder.[179] Pectin-based edible films, utilizing different DES ratios of ChCl, citric acid mono hydrate, exhibited diverse structural transitions and film properties, with the 3:1 DES treatment showing superior tensile strength (7.32 ± 0.50 MPa), melting temperature, and barrier properties (relative humidity

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and water vapor transmission rate).[175] The authors attributed this property to the entanglement of branch with the less plasticizing effect (Figure 10c).

Hydrophobic DES systems, such as thymol:octanoic acid, were studied for their water barrier properties on chitosan/gelatin films.[180] While water contact angle (above 90%) and water vapor transmission rate were improved at higher DES loadings (6-15%), tensile strength decreased. Nonetheless, the elongation at break increase (for DES above 6% loadings) was attributed to an increase in the free volume of the polymer matrix, making 9% DES-incorporated chitosan films recommended for food packaging applications. NADESs have been explored for achieving self-healing properties in polymer-based films.[169] Optimal loading of 67 wt% of NADES (ChCl:citric acid) in chitosan films exhibited 56% recovery on elongation at break and 72% original strength after breaking. Additionally, NADESs, particularly ChCl:vanillyl alcohol:gelatin, demonstrated superior adhesives strength (approximately 135 kPa) with shear thinning behavior for thin film applications.[181]

Recent studies on sodium acetate trihydrate/urea-based DES revealed enhanced thermal stability and crosslinking in gelatin/polyvinyl alcohol composite films.[177] Higher DES loadings (60%) prevented undesired gelation of gelatin at low temperatures, increased elongation at break of 631%, and accelerated crosslinking without the need for additional catalysts.

All the aforementioned applications provide evidence for the application of DES as solvent of vast majority of the polysaccharides and its use as the surface modification of the films as mainly plasticizers and others modifications such as hydrophobicity, UV-shielding, antioxidant, antibacterial, barrier properties as well as self-healing. Additionally, the use of DES extractants for property enhancement represents a novel and sustainable pathway, allowing for the recycling and re-use of extracted DES in functionalized polymer film formation. Various studies have

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explored the extraction of bioactive compounds, including polyphenols and anthocyanins, using DESs for modifying polymer films. Notably, DES-extracted anthocyanins exhibited superior antibacterial and antioxidant properties for edible films,[182] while carotenoids extracted by DES enhanced plasticity and served as a colorant antioxidant in corn starch-based films.[173] Additionally, specialized applications, such as generating chitosan-based bioactive polymer films with improved mechanical and anti-plasticity properties, were achieved through SUPRADES (β-cyclodextrin as the HBA and maleic acid, lactic acid, and citric acid as HBDs) extraction of polyphenols from bayberry.[183] Here, the effect of the ultrasound on the extraction of polyphenols has been accessed where it improved mechanical property of the chitosan based film, anti-plasticity ability as well as the adhesion property which enable the use of it for animal tissue based applications.

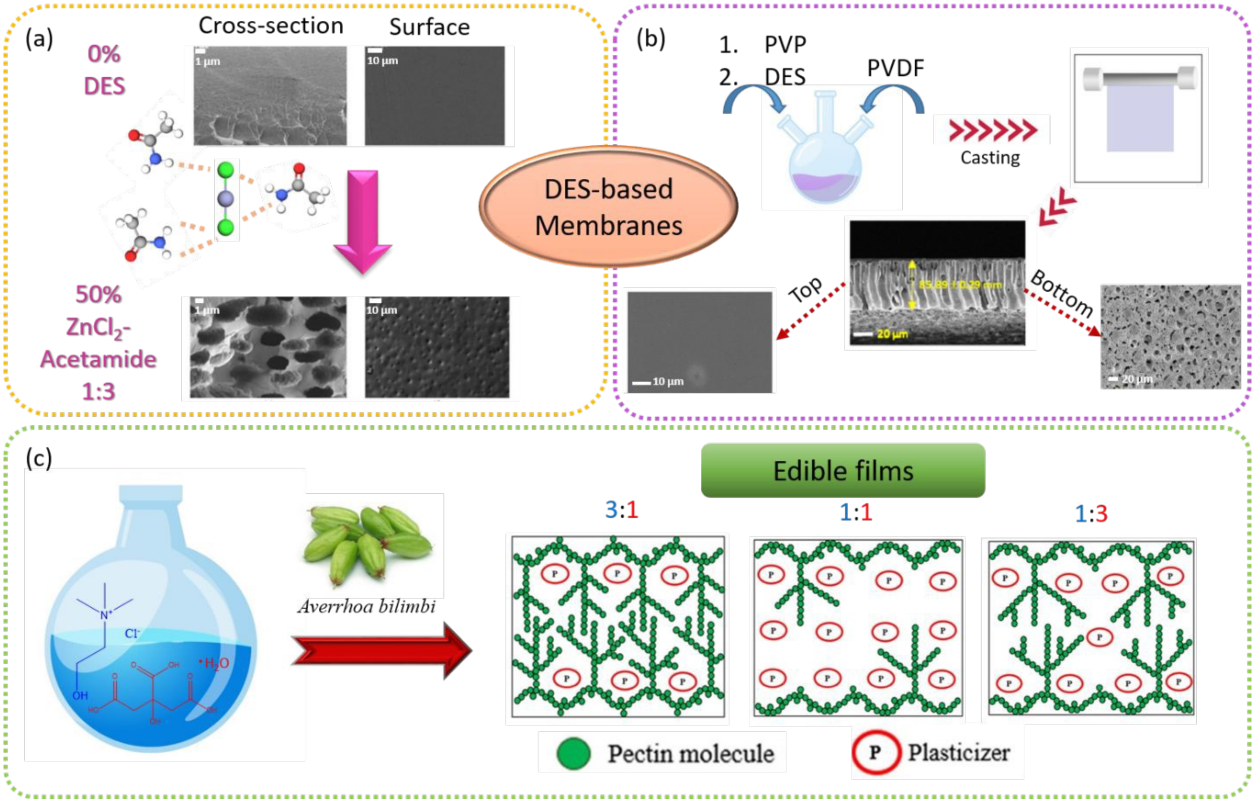

Figure 10. SEM images of generation of porous membranes (a) polyamide-imide membranes before and after incorporation of $ZnCl_2$:acetamide.[164] Copyright 2021, MDPI. (b) with non-ionic DES (N-methyl acetamide:N-methyl urea).[165] Copyright 2022, Elsevier. (c) Schematic illustration of plasticization effect of edible films generated by *Averrhoa bilimbi* pectins with DES.[175] Copyright 2020, Elsevier.

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All the above studies have demonstrated that DES can be used as green solvents to develop various types of functional materials with different properties. DES can also be integrated with advanced manufacturing methods, such as electrospinning and 3D printing. We believe that these studies can be further extended towards cutting-edge applications based on specialty and sustainable materials. The careful engineering of DES by balancing the hydrophilic/hydrophobic, polar/nonpolar ratios can also play a vital role for the generation of advanced polymeric nanomaterials. Additionally, the stabilization achieved in organolithium species in anionic polymerizations[32] and metal coordination ability in DES[162] suggest the potential for it to be used as coordination polymer materials.

6. Green credentials-sustainability evaluation of DES-based materials

Sustainability has been increasingly discussed and emphasized, be it at the government level or at the scientific community level, as an important issue to be prioritized, likely due to the climatic change experienced in recent years. The concept of sustainability identified by the United Nations in the 2030 Agenda for Sustainable Development comprises several aspects. To quote a few goals set by the United Nations are “ensure availability and sustainable management of water and sanitation for all”, “ensure sustainable consumption and production patterns”, “ensure healthy lives and promote well-being for all at all ages” and “protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss”.[184] In short, actions that can threaten human survivability and destroy nature in the long run are not sustainable.

It is not uncommon for DES to be considered as the green alternative to ionic liquids or other conventional solvents used for extraction and synthesis. In fact, this exact belief has seen the

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increasing research on DES[185] (Figure 1b-c). The basis of this confidence mainly comes from the idea that DES components are derived from natural sources. However, it is questionable whether being derived from natural sources is sufficient to view DES as the green alternative.

A way to assess is using the concept of life-cycle assessment (LCA). LCA is a well-known tool that has largely been used to evaluate the environmental impact of a technology or a product from cradle to grave. This tool has the advantage of capturing all the impacts without having the burden shift from one environmental impact to another. It comprises four stages, starting from setting the scope and the goals, followed by identifying the inputs and outputs as well as the possible impacts. Lastly, interpretation can be made with all the information gathered in the earlier steps (Figure 11).[186] As such, the accuracy and effectiveness of LCA depend primarily on the completeness of scope and knowledge for each step.

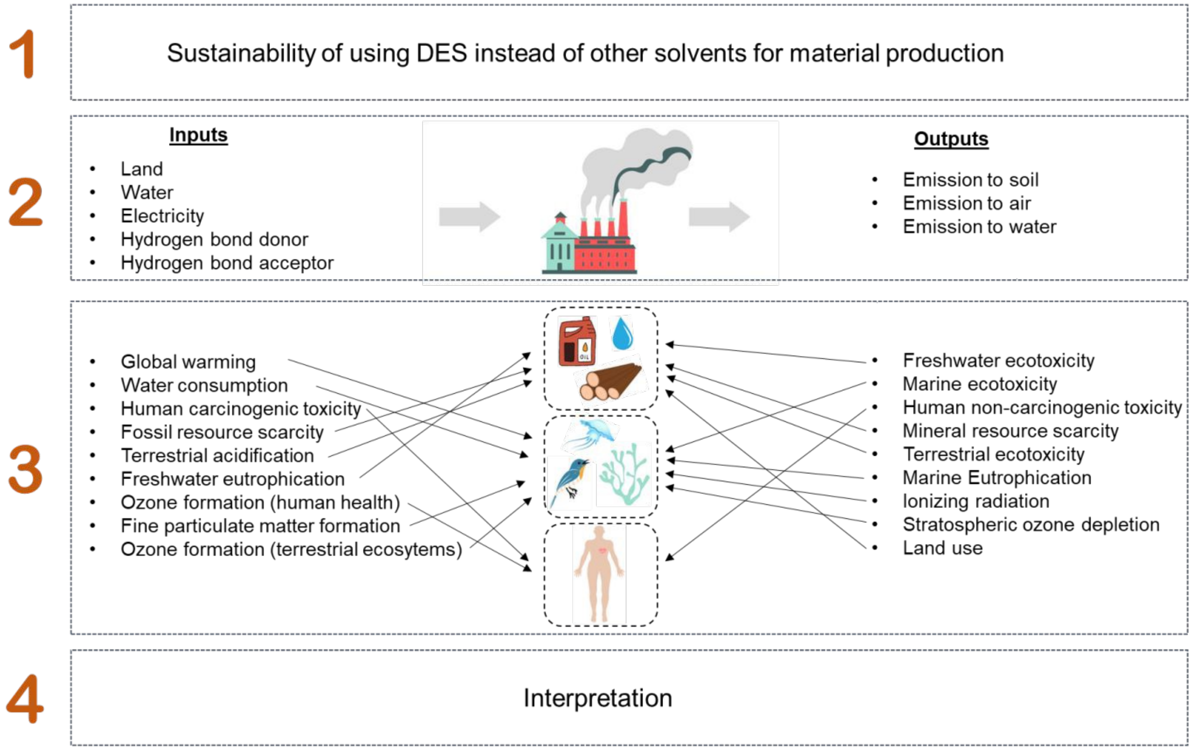

Figure 11. Different phases in the life cycle assessment for the example of DES-based materials.

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Under the guideline of LCA, the inputs and outputs are one of the main components to evaluate the green credentials of DES-based materials. Firstly, the acid used to prepare the DES is less harsh than those needed for acid hydrolysis. Choline chloride is a popular HBA perhaps due to it being an additive for domestic animal feed as well as biodegradable and regenerable nature, making it a sustainable choice. Hence, it is expected that the combination of both reagents to be sustainable and green as compared to conventional solvents. Unfortunately, it is not as green as it appears to be upon a deeper understanding on its synthesis process. The production of 539 kg ChCl requires 157 kg of 30% (w/w) hydrochloric acid (HCl), 99 kg of 30% (w/w) trimethylamine (TMA), 206 kg of DI water and 962 kg of 8% (w/w) ethylene oxide/steam mixture.[187] Despite so, its use is still prefered over the use of strong acids such as HCl. Using the example of nanochitin preparation, 3 M HCl aqueous solution (150 ml) was used for 5 g α-chitin powder.[195] This is equivalent to 3.29 g HCl required for 1 g chitin. In contrary, 50 g DESs (molar ratio of ChCl:organic acid is 1:2) was used for 2 g chitin powder to prepare chitin nanocrystals.[78] In the scenario that lactic acid is used as the hydrogen bond donor, 1.91 g HCl is needed for the ChCl synthesis to use with 1 g chitin powder. If malic acid is used instead of lactic acid, the amount of HCl required for 1 g chitin powder is 1.50 g. The comparison shows that the use of DES is indeed a greener approach.

Kyung et al. compared the potential environmental profiles of reline, a DES that is made up of ChCl and urea, to other common organic solvents such as ethanol, methanol, ethyl acetate, and dichloromethane for the process of synthesizing 0.2 kg acetophenone.[187] For the seven examined areas (global warming potential, freshwater eutrophication potential, metal depletion potential, freshwater ecotoxicity potential, human toxicity potential, terrestrial acidification potential, and water depletion potential), reline performed comparably well with relative impact below 50% for all the fields except for metal depletion potential, which displayed a slightly poorer performance

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(~60%). Among the tested solvents, ethyl acetate and dichloromethane fared the worst as each topped the group for the different areas.

In recent years, many studies have investigated recycling DES to enhance the sustainability of DES-based materials.[188,193,194] It was discovered that the reactivity of DES (i.e. choline chloride and oxalic acid) to deconstruct lignocellulosic material only dropped by ~3.2% after 5 rounds of recycling.[179] It was further estimated that the DES can be recycled up to nine times.[179] These information makes DES an even more attractive sustainable alternative as compared to conventional solvents. While the idea is promising, the inputs and the outputs for DES recycling must be cautiously weighed to determine if it is indeed more environmentally friendly than the act of using fresh DES for the reaction. For instance, resources such as electricity and solvents would be necessary to recycle the DES. Would it be more sustainable to channel these invaluable resources to recycle DES or to extract and mix fresh DES? Additionally, the emissions from which reaction is lower? In summary, the DES-based materials seem to be relatively green.

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7. Conclusion and outlook

This review provided an overall summary and current trends of the utilization of DES in green polymer synthesis and the building up of functional polymer materials, with eco-friendly non-toxic constituents. Regarding the synthesis and preparation of polymer materials, DES functions as solvents, monomers, and biomass pretreatments, where variable functional polymer materials were realized in the format of gels, nanofibers, films, and membranes. The various characteristics of DESs, such as the utilization of renewable feedstock (e.g. NADES), vast tunability, recyclability, and non-toxicity, align well with the twelve principles of green chemistry. Their all-in-one system approaches and mild reaction conditions ensure 100% atom efficiency with waste prevention, demonstrating the capability of DESs for large-scale manufacturing in an environmentally sustainable manner. The unique hydrogen bonding existing within DES coupled with other properties such as catalyst, plasticizer, pore generator, shear thinning behavior, dispersant, and tunable hydrophilicity/hydrophobicity provides numerous possibilities to probe more applications on polymeric materials in the future.

However, given that different extents of hydrogen bonding significantly affect the generation of functional polymeric materials by DES, the mechanism of the influence of hydrogen bonding is still unclear. More extensive computational simulations can be utilized in this aspect to visualize the molecular interactions, in this case, the hydrogen bonding. This approach will help to understand the bonding nature of the DES system more distinctively while reducing unnecessary lab trials. Another aspect of interest involves how to investigate DES's influences on the initiators employed in polymerization reactions. Moreover, it is essential to clearly differentiate between the presence of water molecules as an impurity, influenced by the hygroscopic properties of specific chemicals like ChCl, and the deliberate introduction of water into the system. The impact of water

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in DES has been emphasized in various cases, influencing the efficiency of polymer synthesis, depolymerization, or functionalization processes, as well as cost reduction. Further studies on the reaction rates can provide deeper insights into identifying the influences of water within the DES system.

There is still a great potential to exploit this comparatively new solvent system to use as a top-down approach to the valorization of unpopular biomasses (e.g. marine biomass, industrial waste, and food waste). Despite the passage of two decades, ChCl continues to be emphasized as the HBA in most applications. It is now opportune to investigate alternative HBAs that offer comparable performance while overcoming the hygroscopicity of ChCl. Additionally,research based on renewable or non-petroleum derived HBDs and HBAs (e.g. itaconic acid, caffeic acid, menthol, thymol) with room temperature DES pretreatment can be more insightful[98,196]. The application of DES in crafting polymeric items, like 3D printing facilitates the creation of customized structures for functional polymers, resulting in reduced waste generation. However, further inroads in this technology can be probed with the advancements in 4D printing and smart materials, especially given the stimuli-responsive materials generated via polymeric DES owing to its responsiveness to external stimuli such as temperature, pH, humidity, electricity, etc.

Currently, there is extensive discussion on sensor-related applications of DES-based polymeric materials technologies and the conductivity levels generated in DES media. Further exploration of these conductive DES-based polymer sensors could be expanded to the robotic field, incorporating the use of magnetic DES, which has been identified recently as a new sub-class.[197] We have summarized the multiple roles of DES in different polymer materials. The integration of these multi-functions of DES in one polymeric material is the most challenging part and worth more effort to investigate. Moreover, research on the longevity and LCA of these materials seems to be

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still in the initial phases. Specifically, we evaluated the green credentials and sustainability of DES-based polymer materials. The economy-wise evaluation of the recyclability of DES and further utilization of the extractives generated during biomass pretreatment can be another focus area.

This comprehensive review offers a detailed examination of the present patterns in the utilization of DESs for the synthesis of functional polymeric materials, showcasing their versatility across a wide range of applications and highlighting possible future pathways. These applications extend from the efficient use of biomass resources to the development of advanced sensor-based technologies. By exploring the diverse functionalities of DESs, the review seeks to inspire innovative thinking and strategic planning for the integration of these solvents in emerging areas of research and technology.

Acknowledgements

This Research is supported by the RIE2025 MTC Individual Research Grants (M22K2c0085), administered by the Agency of Science, Technology and Research (A*STAR), Singapore. This research is also supported by National Research Foundation (NRF) Singapore under its NRF Investigatorship (NRF-NRFI07–2021–0003). This work was also supported by the National Medical Research Council (NMRC), Singapore, under its Clinician Scientist-Individual Research Grant (MOH-001357-00). The first author would like to acknowledge the Agency for Science, Technology and Research (A*STAR) for providing the sponsorship for her Ph. D programme.

Conflict of Interest

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The authors declare no conflict of interest.

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