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Deep eutectic solvents towards green polymeric materials

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Solvents are essential for chemical synthesis and material preparation; however, traditional solvents 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 promising alternatives owing to their eco-friendly attributes. In this review, we summarize studies on this novel solvent system in a broad range of applications, where DESs play 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 and nanofibers to membranes, films, and complex architectures generated from various techniques such as 3D printing, electrospinning, and self-assembly, together with their properties. Moreover, we discuss the green credentials through sustainability analysis and life-cycle assessment of DES-based polymeric materials. We believe this review will inspire more investigation into the use of DESs for functional green polymeric materials towards a sustainable future.

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 forms 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 researchers to seek environmentally responsible pathways when designing products and processes. Polymer materials have attracted much attraction from their inception by virtue of their unique properties to support daily life. However, the excessive production and consumption of synthetic polymer materials has resulted in diverse global issues with severe impacts on ecosystems. In addressing both scenarios while acknowledging the wide demand for polymer materials due to their durability and adaptivity, researchers have focused on ways to cater to this requirement with the development of environmentally friendly approaches.

The conventional synthesis approaches for polymer materials have various limitations due to the need for harsh conditions (*e.g.* concentrated solvents), high energy requirements (high heat, pressure), high cost, need to maintain a strict environment (anaerobic), use of toxic and/or volatile solvents and catalysts, and high waste generation coupled with an inability to reuse materials and difficulties in recycling. Deep eutectic solvents (DESs) come into play in this instance for generating a multitude of solvent systems for novel polymeric materials. DESs were first reported by Abbott *et al.* in 2001[1] and have been proven to have vast areas of applications in subsequent research. DESs are categorized as green solvents in the current era, whereby they can serve as valuable alternatives to conventional solvents due to their extremely low vapor pressure and non-flammability. Even though more than two decades have passed since the first report of this solvent class, there exist many possibilities for the exploration of DESs in polymer science owing to their low toxicity and natural degradability (Fig. 1). Apart from simply using DESs as a solvent replacement, their ability to act as a solvent as well as a monomer simultaneously generates more inroads towards green polymeric materials, even surpassing conventional polymer synthesis methods. Moreover, DESs present benefits in allowing for milder conditions to be used in polymer synthesis and lead to enhanced thermal and mechanical properties of the resulting polymeric materials. Besides their func-

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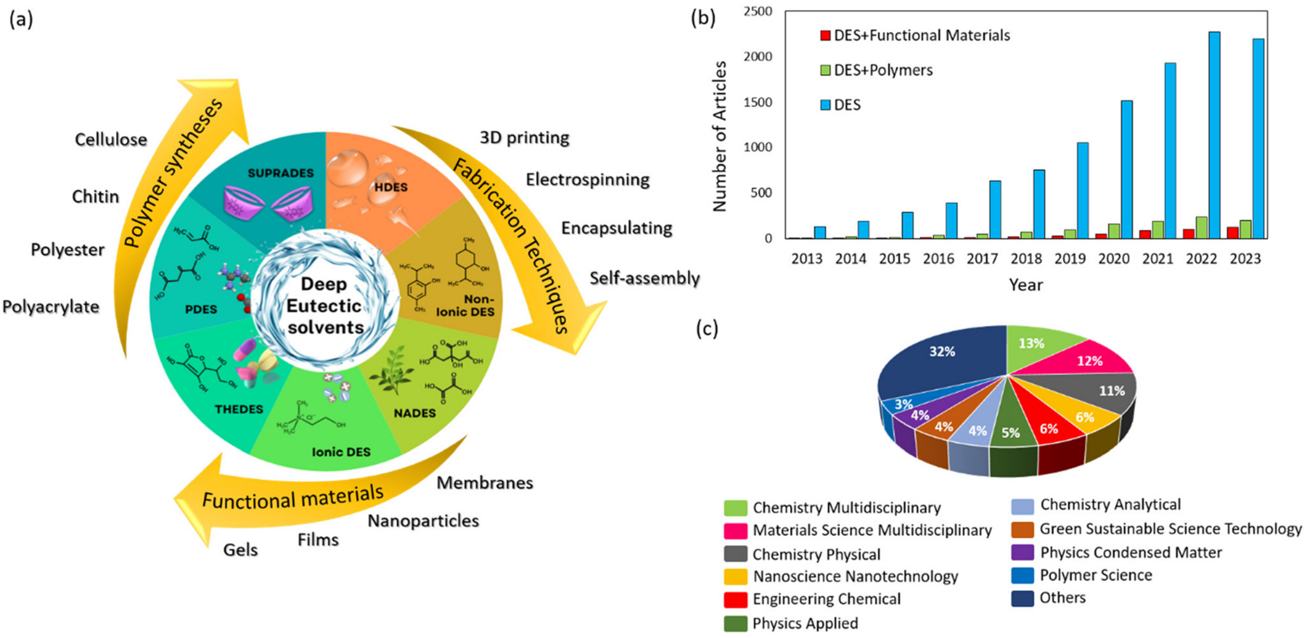

Fig. 1 (a) Different DES types (circle): supramolecular DES (SUPRADES), hydrophobic DES (HDES), non-ionic DES, natural DES (NADES), ionic DES, therapeutic DES (THEDES), polymerizable DES (PDES), and various polymers, functional materials, and fabrication methods involving DESs. (b) Number of DES-related publications over the years. (c) Percentage of DES-based functional materials-related publications in each field. The data were obtained from the Web of Science, 22 January 2024.

tion in the synthesis of polymers and related materials, the use of DESs for biopolymer treatment and corresponding material engineering has been widely investigated, in which DESs can overcome the recalcitrance and structural complexity of biomass, facilitating subsequent functional biopolymer material engineering.

This review aimed to identify the current trends in using DESs for green polymer synthesis and related functional polymeric materials, while outlining their green credentials and performing a sustainability evaluation of DES-based materials. Even though various applications of DESs have been discussed in previous studies, a compilation of the data and findings to address the needs of functional green polymeric materials has not been performed yet. Here, not only are the uses and advantages of DESs as a solvent or monomer discussed, but also the applications harnessing their unique properties are reported in emerging areas and technologies, such as efficient biomass extraction, stimuli-responsive materials, membrane science, nanofibers, and 3D printing, highlighting their future potential for helping drive society towards a green economy.

2. Background and properties of DESs

"Eutectic", originating from the Greek language, is a term used to describe substances that are readily melted, which can be interpreted in another way by considering the melting point depression of two components. With the discovery of a preparation process for ChCl and urea (1 : 2) that could occur at ambient temperature by Abbott *et al.*,[2] the aforementioned word gained greater significance in chemistry, and its use has increased over the past two decades. Deep eutectic solvents (DESs), as the name implies, represent the combination of two or more Lewis or Brønsted 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 in the liquid phases of the pure substances (Fig. 2a).[3]

Some researchers consider this solvent category as a subclass of ionic liquids, representing a class of ionic fluids generated at temperatures less than 100 °C.[4] However, a clear distinction of this class with DESs was eventually generated that considers the chemical nature of the two starting materials, the synthesis methods, the bonding nature, and greenness. The main constituents of ionic liquids are anions (organic heterocyclic) and cations (organic or inorganic), whereas the emphasis in DESs is to the hydrogen-bond donor and acceptor abilities.[5] This gives rise to differences in the intermolecular attractions, with ionic liquids having Coulomb forces as the main driving force for the ionic interactions with DESs having hydrogen bonds. Additionally, the preparation of ionic liquids involves several steps and reagents, apart from the main constituents for dilution of the compounds and purification to remove by-products, which can give rise to the generation of

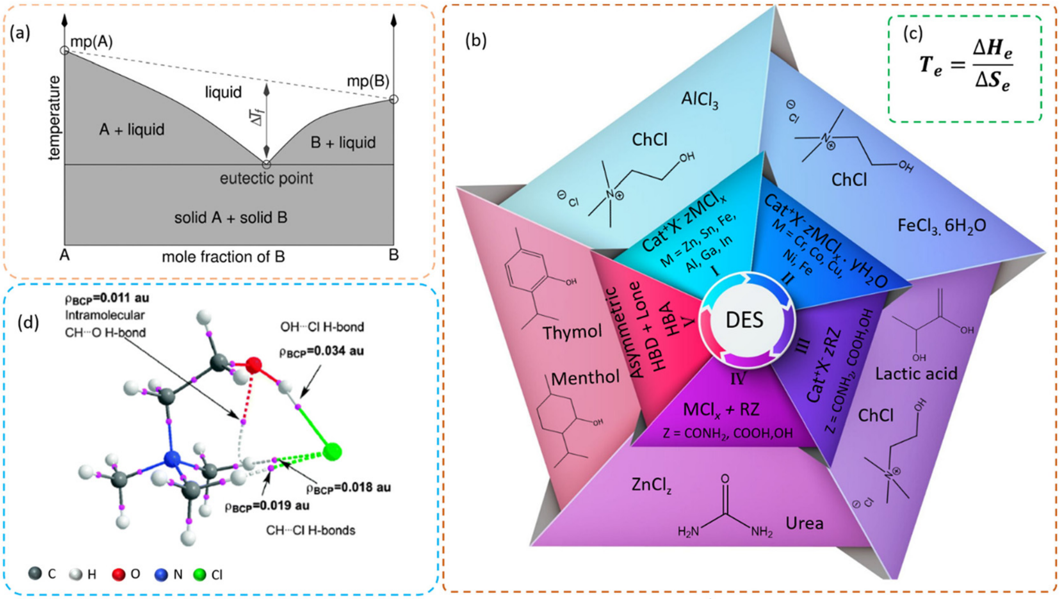

Fig. 2 (a) Two-component solid–liquid phase diagram showing the eutectic point.[4] Copyright 2014, American Chemical Society. (b) Schematic illustration of the classification of DESs (Cat^+ and X^- represent ammonium, phosphonium or sulfonium cations, and Lewis base, respectively). (c) Gibbs equation. (d) Non-conventional intramolecular hydrogen bonds generated from H in the methyl groups (CH···Cl, CH···OH) with the bond critical points (BCP) calculated by quantum theory of atoms in molecules (QTAIM) molecular graphs.[8] Copyright 2016, Royal Society of Chemistry.

waste, while DESs only requires simple steps (mixing the starting materials and applying heat, until the DES forms a transparent and viscous liquid). As for the components (starting materials), the initial components of the DESs are often non-toxic, cheap, and environmentally friendly. Compared to DESs, the starting materials of ionic liquids cannot be regarded as green and sustainable, whereby the environmental impact of ionic liquid systems strongly depend 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 similarities.

The initial studies based on DESs were focused on the extensive hydrogen bonding between the constituents, which was used to categorize the components as a hydrogen-bond acceptor (HBA) or hydrogen-bond donor (HBD). Afterward, with further investigations on the thermodynamic aspects of eutectic mixtures, it was 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 over 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 lower than the change in entropy. This can be derived by the Gibbs equation (Fig. 2c), where T_e, ΔH_e, and ΔS_e represent the eutectic temperature, enthalpy change, and entropy change, respectively.

Over time, the utilization of molecular simulations further facilitated visualization of the atomic level interactions within DES systems, whereby new approaches for hydrogen bonds generated were observed. In one instance, this was termed as an "alphabet soup", where novel noncovalent type interactions in the ChCl:urea system were observed, representing a deviation from the conventional hydrogen bonding definition (Fig. 2d).[8] In this study, the HBD ability of C–H bonds was stated to be one of the stronger interactions than traditional N–H or O–H bonding, leading to a high number of hydrogen bonds within the system. However, even though, DESs were introduced a few decades ago, studies on their interactions are still in a nascent state. Also, 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 their chemical environment.

2.1 Categories of DESs

The classification of DESs is mainly based on the HBDs and HBAs, whereby initially four main types of DESs were defined based on the ionic components[4] (Fig. 2b). Here, type I DESs represent quaternary halides (with an ammonium, phosphonium, or sulfonium cation) and metal chloride (Lewis base) as the main constituents, which were first discovered in 2001.[1] The scope of these was further improved with the incorporation of hydrated metal halides in type II, which results in a further reduction of the eutectic point compared to the analogous anhydrous compounds. Type III DESs were introduced after the discovery of the ChCl:urea system representing quaternary salts[2] and HBDs, where a vast number of possible compounds were suggested afterward as potential HBDs. A combination of metal halides and HBDs led to type IV DESs. With the quest for the meeting the requirements for non-ionic applications and the availability of strong negative deviations, type V DES have been defined recently.[9]

Great attention has been given to quaternary ammonium salts for the defined types I–III, and among these, the most commonly used HBA for type III DESs is considered to be choline chloride (ChCl) with the chemical formula $[HOC_2H_4N^+(CH_3)_3Cl^-]$. However, following 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 DESs have drawn greater attention among the stated categories.

Apart from the stated classification, various sub-categories have evolved too, namely polymerizable DESs (PDESs), natural DESs (NADESs), therapeutic DESs (THEDESs), hydrophobic DESs (HDESs), and supramolecular DESs (SUPRADESs), indicating the plethora of combinations of different chemical species with HBA and HBD properties (Fig. 1a). The NADESs comprise bio-derived compounds that use nature's building blocks to generate eutectic mixtures. This type has attracted great attention from scientists owing to their nontoxic, biodegradable, and sustainable aspects. The eutectic mixtures of this kind comprise bio-derived compounds, mainly sugars, amino acids, and organic acids.[10] Further, the fine-tuning of the HBD and HBA towards biocompatible molecules can enable their pharmaceutical applications. This is where the THEDESs come into play, which highlights the biocompatibility, non-volatility, solubility, retention, and controlled release of therapeutic, bioactive 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 are explored in greater detail in subsequent sections.

2.2 Physicochemical properties of DESs

Identifying the properties of a 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 their 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. For instance, Omar *et al.* set up a database of existing DESs in 2023 together with their physical properties during the period from 2003 to 2021, which may be remarkably beneficial for researchers looking to scale up the applications of these DESs.[15]

A great number of explanations regarding the physicochemical properties of DESs have been given in past publications, such as hole theory to explain the interdiffusion and motion,[16] the Kamlet–Taft equation representing the strength of noncovalent interactions,[17] and the entropy of the system.[7] Below, we discuss some of the core observations of the past studies conducted that could have an effect on the performance of polymeric materials generated using these systems.

2.2.1 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 Brønsted acids and bases, giving rise to different pH values. In most studies, the HBD character has been considered as the determining factor for the DESs' pH value.[18]

2.2.2 Viscosity. The viscosity of a solution, in simple terms, is defined as the resistance to the movement of a fluid. This property plays a pivotal role in a solvent acting as an efficient solvent that can substitute for harmful solvents. Compared to conventional volatile solvents, it has been observed that DESs cover a high range of viscosities, with the lowest viscosity DES (6.6 mPa s) constituting a molar ratio 1 : 1 of trimethylsulfonium bis[trifluoromethylsulfonyl]imide : formamide and the highest (75 000 mPa s at 40 °C) being a 1 : 2 molar ratio of $ChCl : ZnCl_2$.[15] These values show the tunability of the viscosity in DES systems. This can be dependent on many factors, such as the molar ratio, temperature, interactions between the HBA/HBD, and the molar mass. According to hole theory, with the rise in temperature, the mobility of molecules increases by the generation of large voids, whereas at lower temperature, smaller voids are available, which, coupled with the larger sizes of ionic components, hinder molecular mobility, resulting in high viscosity, as represented by eqn (1), where r, k, T, and γ represent the radius of an average-sized void, the Boltzmann constant, absolute temperature, and the surface tension of the liquid, respectively.[19]

$$4\pi r^2 = \frac{3.5kT}{\gamma} \tag{1}$$

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 and HBAs, the polar functional groups, anions of the HBA present (RCl:HBD < RBr:HBD < RI:HBD),[15] and steric hindrance provided by longer chain alkyl groups in the system have a crucial impact. Also, the effect of the impurities should not be ignored as these can have an effect on the interactions. Additionally, for solvent-based applications, hydrophobic DESs with viscosities less than 20 mPa s are considered as attractive alternatives to conventional organic solvents (*e.g.*, heptane, octane, nonane, hexyl benzene).[20]

2.2.3 Density. Past studies have revealed that a variation of densities are possible, ranging from 0.8–1.5 g cm^{-3}. The vast majority of DESs exhibit densities higher than water, but certain hydrophobic DESs have lower values.[15,20,21] The density of a DES depends on similar aforementioned factors as for viscosity, such as temperature, water content, composition of the 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 separation.[20]

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

2.2.5 **Ionic conductivity.** DESs are widely studied for their conductive properties owing to the ionic species present in the media (types I–IV), which will be further discussed in the Sensor-based applications section. Considering their diffusion dynamics, most DESs, especially choline-based DESs, provide 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.[15,23] The low viscosity exhibited by most DESs hinders the ionic conductivity of the system. However, different approaches can be adopted to improve this property to obtain the desired output. The addition of water molecules up to a certain extent in a DES is considered a favorable approach to improve the ionic conductivity.[22]

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

3. DESs for green polymer synthesis

The use of DESs is considered a crucial requirement for polymer synthesis by virtue of the environmental concerns over hazardous solvents and their ease of processing. DESs can be used either as a solvent to facilitate the polymerization process, as the monomer participating in the final polymer synthesis, or both simultaneously. In whichever case, a basic understanding and careful selection of the constituents of the corresponding DES system is vital to generate the desired valuable outputs for the polymer synthesis. The understanding of the properties of DES systems, such as polarity of both the DES and polymer (using the Kamlet–Taft parameters) and the boiling point of the prepared DES, allows determining the maximum usable limit of the system.[17] In this part, the function of DESs as a reaction medium is summarized based on different polymerization processes.

3.1 DESs as a solvent for polymerization

3.1.1 **Radical polymerization.** The use of DESs as solvents for acrylic acid (AA) and acrylic amide derivatives polymerization is 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 hydroxyethyl-methacrylate (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] A few other enzymatic free radical polymerization studies have been carried out by several groups where the careful selection of the DES system is a prominent way to avoid deactivation of the enzyme used for the polymerization process.[25–27] Catalysis by the laccase enzyme has drawn wide attention owing to its high selectivity, ambient conditions, and non-toxicity. Altundağ *et al.* studied the inhibition of the laccase enzyme by a DES system consisting of D,L-menthol : decanoic acid (1 : 1) in a template-based polymerization of aniline. This study revealed that both the selected DES and aniline had 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 Khlupova *et al.* was able to generate oligomers with six monomer units of dihydroquercetin (Taxifolin) in a betanin:glycerol DES system. Here, the selection of betanin as a HBA was specifically considered as it would not inhibit the activity of the laccase enzyme, like ChCl. The resultant oligomers had an average molecular weight of 1800 g mol^{-1} with a polydispersity index of 1.09 and obtained a yield of 58 ± 7%.[27] The same approach was utilized by another set of researchers with an aim to produce conductive polyanilines by polymerization and copolymerization. In both cases, the DES facilitated a favorable environment for the enzyme at a DES : buffer 60 : 40 ratio.[26]

RAFT (Reversible Addition–Fragmentation Chain Transfer) and ATRP (Atom Transfer Radical Polymerization) can be considered as emerging radical-based polymerization approaches for achieving more controlled outputs. The polymerization of HEMA and block copolymerization with methyl methacrylate were studied by Kumar *et al.* using ChCl:urea.[28] The study revealed that higher molecular weight polymers (up to 40 700 g mol^{-1}) could be synthesized using this DES, with a conversion percentage of up to 90%. Additionally, the team suggested this DES as a non-aqueous solvent system for the polymerization-induced self-assembly (PISA) of block copolymers. Another more convenient RAFT polymerization was revealed by Li and

Yu, who proposed a polymerization environment under visible light and in the open air in the presence of DES.[29] Here, the authors used a tetrabutylammonium chloride:ethylene glycol DES to prompt the polymerization of methyl methacrylate, methyl acrylate, dimethyl acrylamide, and styrene. During this study, they observed that the DES medium provided for photostability through a "protected radical effect" on the chain transfer agents used (trithiocarbonate) compared to DMSO. This enhanced stability of the chain transfer agents enabled better control over the 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 the DES facilitated polymerization when carried out in confined spaces (mainly generated by long-chain RAFT agents), with high concentrations of monomers and radicals, leading to improved polymerization rates compared to conventional solvents.[28,29] A study carried out by Mendonça *et al.* involved 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 reported on the room-temperature polymerization (30 °C) with polymers having a polydispersity of less than 1.2 throughout the process.[30] Another group compared three ChCl-based DES systems (glycerol/urea/ethylene glycol) for the generation of poly(methyl methacrylate) with ATRP.[31] The team studied homogeneous and heterogeneous Cu(II) catalysis in DES media, which resulted in polymer synthesis with polydispersity index values of approximately 1.2 in both catalytic systems.

Overall, DESs as polymerization solvents have been shown to facilitate faster polymerization rates, allow maintaining mild reaction conditions, and enable controlled polymerizations compared to conventional solvents, primarily attributed to improved monomer dissolution, interactions with propagating radicals, controlled terminations due to their high viscosity, and a radical protection effect on chain transfer agents, therefore optimizing their use. However, studies on the interactions between DESs and the monomers that lead to these properties are required for further exploration in this area to identify the effect of the DESs 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 a ubiquitous approach over the past few years (Fig. 3a and b). However, the control of the species is a great challenge for scientists to ensure they can obtain the expected polymer products with fewer obstacles, with challenges mainly due to the high reactivity of the systems due to the significant polarity differences in Li–C bonds. 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 offer a more convenient approach to facilitate polymerization under aerobic conditions, owing to their 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 and 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 to proceed with greater yields of up to 90% and with low polydispersity indexes (1.1–1.3), with greater stability for the organolithium species compared to those obtained with conventional solvents (Fig. 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 the factors beyond the selection of the DES system, such as the reaction conditions, including the viscosity of the DES, the initiator concentration, and the duration of mechanical treatment (ultrasonication), all of which could significantly affect the resulting polymer properties (Fig. 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 a ball mill and twin-screw extruder for the synthesis of a water-soluble biopolymer and a crosslinked polymer (Fig. 3c). The authors pointed out there were differences in the polymer yield, noting that the inability to remove water from the system when using the ball mill resulted in a decreased product yield due to a shift in the equilibrium towards the product side.

3.2 DESs as monomers

Apart from acting as a medium for polymerization reactions to facilitate a favorable environment, the DES components (HBA or HBD) can actively participate in the reaction for the generation of polymer materials (also termed as polymerizable DESs or PDESs). The main requirements of the monomer component in PDESs 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 the polymerizability. These limit the number of candidates applicable for PDESs compared to the vast number of conventional monomers available. Primarily, research in this area has focused on the incorporation of one or more vinyl groups as the HBD or HBA, which then 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 then eventual removal of the inert solvent. However, the utilization of PDES has demonstrated a better solubility of the selected monomers *via* hydrogen bonding with a higher polymer conversion rate and percentage over those of traditional solvents. In a recent study, Lin *et al.* investigated the effect of a PDES (consisting of quaternary ammonium salts as the HBAs and AA as the HBD) on the polymerization kinetics of the monomer component (AA) compared to the utilization of the inert sol-

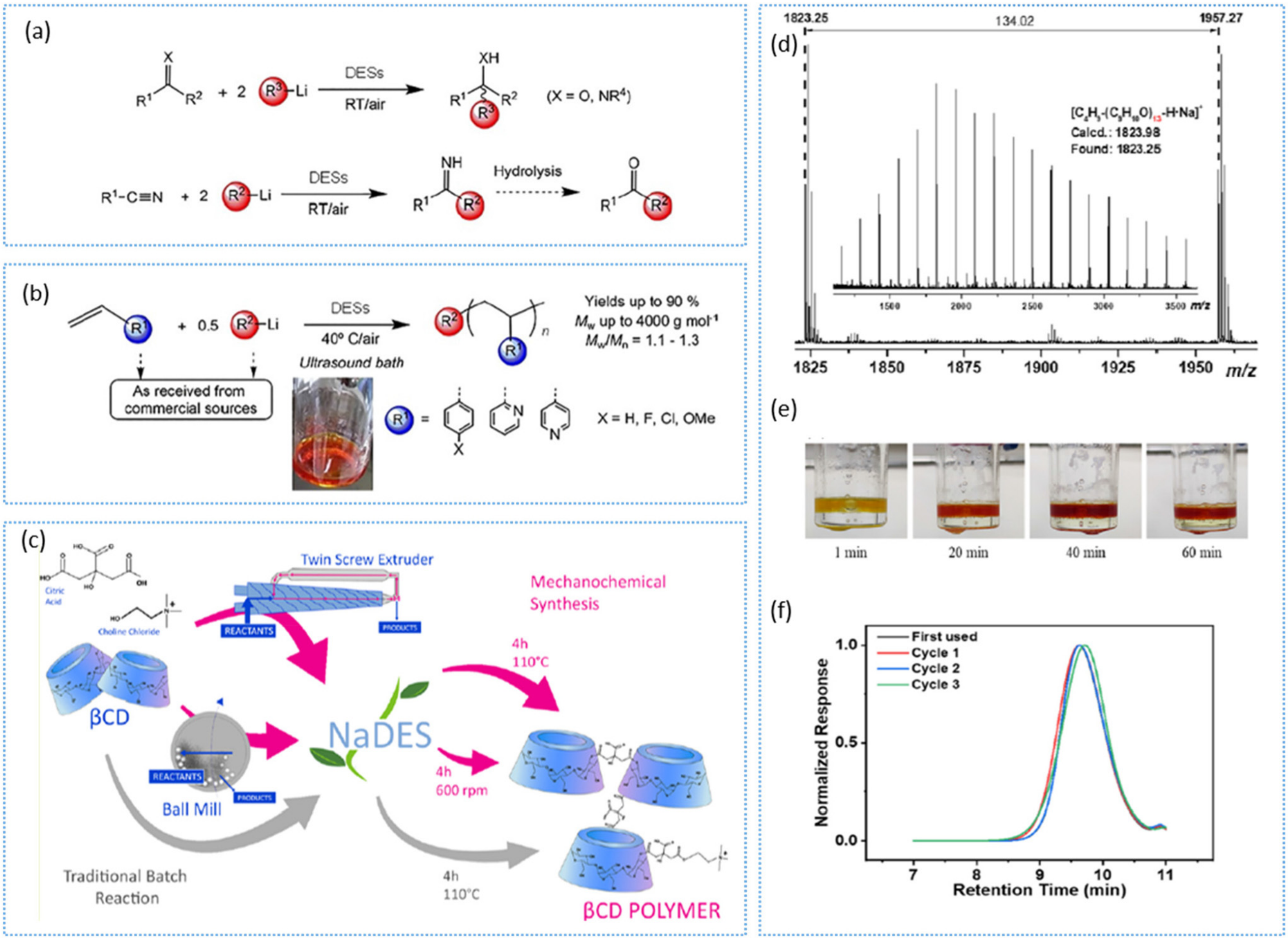

Fig. 3 (a) Nucleophilic addition reaction of the organolithium compound (R–Li) to carbonyl compounds in DES media; (b) anionic polymerization of olefins promoted by organolithium compounds and different ChCl-based DESs.[32] Copyright 2019, Wiley. (c) Polycondensation of β-cyclodextrin using NADES using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

vents DMF, DMSO, and methanol.[35] The authors reported a significantly high C=C conversion (~99%) in PDES medium as opposed to with traditional solvents (less than 30% conversion), besides the high rate of conversion. The main reason for this was attributed to the increased C=C bond activity of the AA monomer (which acted as the HBD) resulting from the hydrogen bonding with the quaternary ammonium salt-based HBAs. Additionally, a vast tunability of the physicomechanical properties of the PDES-based ionic gels was demonstrated by probing the hydrogen bonding levels between the different HBAs and the AA HBD. Here, one of the main advantage was the utilization of all the components of the DES system, even after the complete conversion of the monomers into the final polymer product, unlike in the traditional approach where the solvents are evaporated off. This reduces waste generation by eliminating the solvent evaporation step, while allowing for the tuning of the physicomechanical properties through varying the hydrogen-bond energies within the system.

Following 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 DESs as solvents, and the polymerizable components. The team utilized a polymerizable DES (ChCl as the HBA, and AA, methacrylic acid as the HBD monomers), comparing it with the polymerization of methyl methacrylate in the presence of a nonpolymerizable DES (ChCl:isobutyric acid).[37] In this context, the authors proposed that an increase in rate could be observed in both systems, whether the monomer was a part of the DES or not. Even though increased viscosity is seen as an unfavorable property in certain applications, for radical polymerization processes several studies have 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.[36–38] Jablonský *et al.* highlighted an enhancement of the monomer reactivity in polar media compared to in non-polar ones and the ability of the DESs (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 through the use of both experimental and simulation studies. The team used different molar ratios from 1 : 1 to 1 : 4. A reduction in the viscosity of the DES with the increased AA concentration was attributed primarily to the size disparity between the choline ions and AA, as well as the balance of the interactions between the 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 included in the systems. Wang *et al.* suggested the use of liquid metal nanodroplets (specifically, a mixture of indium and gallium), which could act as a substitute for the initiators and crosslinkers in the ChCl:AA PDES.[40] Here, the stabilization of the liquid metal nanodroplets by the viscosity of the PDES medium was reported. While AA served as the polymerizable component in the DES system, ChCl contributed to the system's non-covalent interactions, including hydrogen bonding and ionic bonding with Ga^{3+} ions, as well as its conductive properties. The polymerization demonstrated a fast curing (6 min), with high transparency (94.1%), and high stretchability (2600%), coupled with other desirable properties, such as ionic conductivity, self-healing, and resistance to freezing and drying.[40] Another group generated a polymer matrix with antimicrobial properties by incorporating benzalkonium chloride as an HBA to AA and methacrylic acid-based HBDs.[41]

In addition to the widely recognized AA and methacrylic acid-based HBDs, there is a growing interest in researching renewable monomers, such as itaconic acid and caffeic acid, and thermoresponsive monomers, such as *N*-isopropylacrylamide (NIPAM), as PDESs for specific applications. Additionally, in most of the stated polymerizations, higher reaction rates and crosslinking densities were achieved than in the synthesis in water.[17,38,42–45] Further, the use of HBAs with vinyl groups in an organic salt unit has been reported as PDESs. HBAs with quaternary ammonium monomers, such as 2-cholinium bromide methacrylate and 3-acrylamidopropyl trimethylammonium chloride, have 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, and 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 conditions).[46]

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

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

4. DESs with biomass functional materials

Besides their use as a solvent or monomer in synthetic polymers, DESs are widely utilized as a solvent for biomass pretreatment or bioactive compound extraction, due to their ability to disrupt the noncovalent 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 (see Table 1).

4.1 Lignocellulose

Lignocellulose biomass is the most abundant natural biopolymer and primarily comprises three sub-units: cellulose (35–83% of dry mass), lignin (0–43%), and hemicellulose (0–30%) combined in a 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 homopolymer containing D-glucose monomers linked by β-1,4-glycosidic bonds with strong hydrogen-bond attachments among the polymer chains, leading to crystalline and amorphous regions within the structure (Fig. 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, and *p*-hydroxyphenyl alcohol units. The availability of the aromatic groups (mainly linked with β-O-4 aryl-ether bonds) generates hydrophobic characteristics in lignin. Owing to the recalcitrant nature of these lignocellulose biomasses, pretreatment is essential to generate value-added functional polymers. The utilization of DESs for this purpose has emerged during the last two decades, mainly due to factors such as recyclability/low waste generation, ease of preparation, and non-toxicity. Vast numbers of studies have been conducted aiming for the isolation of lignin and cellulose biopolymers, whereas research on the isolation of hemicellulose is still in its infancy.[83]

The fractionation efficiency of biomass using DESs depends on various factors, including for the DES itself (molar ratio,

Table 1 Summary of studies attempting the conversion of biomass into nanomaterials using DESs

Feedstock/resource	Materials generated	DES	Major treatment conditions	Features		Application demonstration	Ref.
				Yield	Size/M_w/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 : $FeCl_3 \cdot 6H_2O$, 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%	20 × 100 × 700 nm	Reinforcing filler/ reinforcing fillers for chitosan films plasticized with DES	50
Bleached rice straw pulp	CNC	ChCl : OA, 1 : 1	80 °C for 4 h	55.1%	Average particle size of 69.3 ± 22.8 nm	—	51
Kraft pulp from poplar wood	CNC, CNF	ChCl : OAd, 1 : 1 with 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 8 h, 16 h	CNF urea: 85–89%, formic acid: 82–87%, CNC urea: 7–10%, formic acid: 7–13%	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
Microcrystalline cellulose	CNC, CNF	ChCl : OA, 1 : 1 with ultrapure 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 3 h, 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 °C,90 °C, 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

Table 1 *(Contd.)*

Feedstock/resource	Materials generated	DES	Major treatment conditions	Features		Application demonstration	Ref.
				Yield	Size/M_w/PDI/CRI		
Thermomechanical pulp	LCNC	ChCl : OA, 1 : 1, ChCl : OA : *p*-toluenesulfonic acid, 2 : 1 : 1	80 °C for 3 h	—	Width: ~6.0 nm, thickness: ~3.3 nm	Nano-composites reinforcement, cement additives, and packaging materials	61
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 3 h, 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 60–90 nm, 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 for 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 123.6–140.7 nm	Nanocomposite gel beads using a sodium alginate (SA) matrix to remove methylene blue (MB) from 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 18 h) 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 3 h	—	60–110 nm, M_w 1130–8500	Drug delivery, biomedical and tissue engineering applications	72

Table 1 *(Contd.)*

Feedstock/resource	Materials generated	DES	Major treatment conditions	Features		Application demonstration	Ref.
				Yield	Size/M_w/PDI/CRI		
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 3 h	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 16 h, pH 6, 4, 2	1.2–7.8%	200–700 nm	—	74
Bamboo powder	LNP, LCNF, carbon quantum dots	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, carbon quantum dots: 9.8 nm	Drug delivery, water treatment, and nano-fillers	75
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%, M_w: ~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 3 h	Average diameter: 42–49 nm, average length: 257–670 nm, mass yield ranging from 78–87.5%	Emulsifiers for Pickering emulsions	78
Alpha (α)-chitin from shrimp shells	Chitin nanocrystals	Betaine chloride : ferric chloride hexahydrate, 1 : 1	70–100 °C, 1–4 h, 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), M_w highest (0.5 h): 1.8 ± 0.4 Da, lowest (2 h): 0.3 ± 0.1 Da, CRI highest (0.5 h): 28.1 ± 0.4%, lowest (2 h): 25.2 ± 0.4%	Food and pharmaceutical industry; film enhancer, rheological modifier, Pickering emulsion stabilizer	81

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; M_w, molecular weight; CRI, crystallinity index; PDI, polydispersity index.

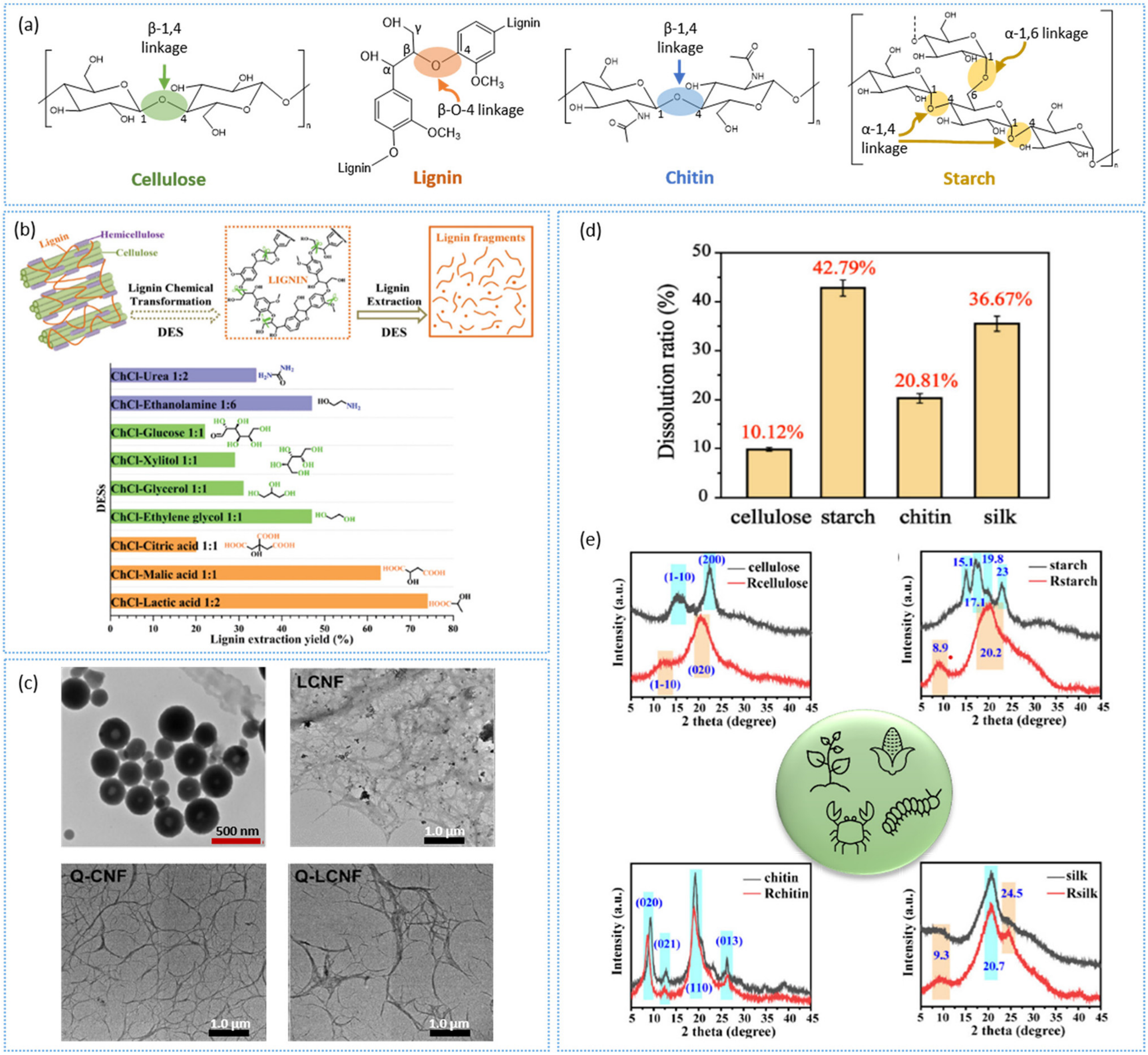

Fig. 4 (a) Main chemical linkages of cellulose, lignin, chitin, and starch. (b) Lignin fractionation using a DES and the extraction yield.[88] Copyright 2020, Royal Society of Chemistry. (c) TEM image of lignin nanospheres, LCNF, quaternized CNF (Q-CNF), and LCNF (Q-LCNF).[76] Copyright 2023, Elsevier.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

temperature, viscosity, acidity/basicity) and the bonding nature within the lignocellulose biomass (number of cleavable bonds available). DESs are widely popular for their specific ability to promote the dissolution of hemicellulose and lignin without disturbing cellulose, as first reported in 2012.[84,85] The main reason for this was attributed to the strong cohesive energy existing within the cellulose structure preventing its dissociation in the presence of DESs. Further, the formation of robust hydrogen bonds between the DES and cellulose stabilizes the DES–cellulose system, simultaneously selectively disrupting other noncovalent 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 this to date (Fig. 4b).

Apart from the fractionation of lignocellulose biomass, DESs can reduce the size of these natural polymeric materials towards the nanoscale, including cellulose nanocrystals (CNCs),[48,51,52,54,85] cellulose nanofibers (CNFs),[57,58,63] lignin nanoparticles (LNPs),[66,69,70] and lignin-containing CNCs/CNFs[61,62,64,86] (Fig. 4c). Even though it was stated that DESs can selectively dissociate the bonds of lignin to promote detachment from the lignocellulose biomass structure, the studies of the actions of DESs on cellulose as a starting material in the microscale have revealed an 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 together 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).[76,87–89] Luo *et al.* explored the use of different DES systems to develop stable and uniform LNPs, and incorporated these into a polyvinyl alcohol matrix as a nanocomposite material for medical and food-packaging applications.[90] The addition of LNPs increased the tensile strength and thermal stability of the matrix, 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, namely hemicellulose-derived activated nanocarbon, lignin nanospheres, and lignin containing CNFs (Fig. 4c).[76]

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

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

4.2 Chitin

Chitin is the second-most-abundant polysaccharide biopolymer consisting of *N*-acetyl-glucosamine and *N*-glucosamine units, and 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 of cellulose and it exists mainly in three configurations, namely α-, β-, and γ-chitin, based on the molecular arrangement. The *N*-deacetylation process (at least 50%) leads to the generation of chitosan, which is considered an alternative biopolymer derived from chitin.[100]

The extraction of chitin consists of two main steps, namely demineralization and deproteinization, where the former involves 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 have applied their knowledge of DESs to process this biomaterial, with the first attempt at this conducted in 2017.[100] Since then, numerous studies have been published in this area over the past years owing to the ease of processing (one step) and the attractive properties of DESs. The highly organized nature of chitin demands strong DES systems mainly consisting of acidic HBDs.[99–101] Here, the utilization of type III DESs with carboxylic acids as HBDs has enabled 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 have displayed a specific ability to reduce the particle size into the nanoscale. For instance, Yuan *et al.* highlighted the dual role of the aforementioned DES as a hydrolysation and acylation reagent.[78] Among the different acidic systems used, ChCl:malonic acid has demonstrated remarkable outcomes in terms of both the purity and yield, with the effective removal of proteins and minerals.[99–103]

Li *et al.* reported the detailed mechanism of chitin extraction, with 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 can depend on various factors, such as temperature, acidic nature, and reaction time within the system and process.[102] Additionally, numerous nanomaterials, including nanocrystals and nanofibers, have been isolated by chitin with the use of DESs coupled with mechanical treatments, which enable removing the amorphous zones in raw chitin.[103] The synthesis of chitin nanomaterials has been reported with diameters ranging from 20–80, 12–44, and 42–49 nm with the use of ChCl:$ZnCl_2$,[80] ChCl:*p*-toluenesulfonic acid,[77] and ChCl:carboxylic acids (oxalic acid dihydrate, lactic acid, malonic acid, citric acid monohydrate, DL-malic acid)[78] based DESs respectively. In the latter study, when comparing 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 the DES in those systems was identified as the enhancement of the mechanical properties and plasticity of chitosan-based films.[101] Additionally the chemical property variance between chitin and chitosan leads to different solubilities in the 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 the green credentials, several researchers have tried to utilize DESs to unveil the structural transition of starch. The use of DES-based starch treatment can be categorized into two main parts: dissolution and plasticizisation.[107]

The solubility of starch with the use of different DESs has been studied, and in many studies a maximum solubility up to 10% has been observed.[108] A study carried out by Zdanowicz and Spychaj indicated that the treatment of a carboxylic acid-based DES on potato starch led to starch degradation. As a result, most researchers tend to probe ways to utilize this polysaccharide with the use of non-destructive constituents of DESs, mostly containing substituents such as imidazole, urea, and glycerol, with no chemical structure alterations 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 that the DES with glycerol displayed better performance over sorbitol, and also that the urea content of the system affected the dissolution temperature of starch.[107] In the current stage where the synthesis of starch nanoparticles using DESs 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 the crystalline and amorphous regions of the starch, with DES treatment for 2 h generating aggregated nanoplatelets sized 38–117 nm (Fig. 5b). Further, esterification of the nanoparticles due to the effect of oxalic acid in the DES has been observed with increased treatment time.

DESs are usually popular for their plasticizing ability when it comes to starch-based applications. The plasticization of starch takes place when the DES constituents disrupt the granular structure of starch *via* hydrogen bonding, resulting in swelling.[108] The main factors affecting the plasticizing include the temperature, force, water content, and chemical constituents.[108,109] Zdanowicz compared different DESs and ionic liquids with the conventional plasticizer glycerol to treat potato starch, and revealed that urea-based DESs and ionic liquids generated a better dissolving capacity while having lower viscosity values compared to glycerol, which is a beneficial property for thermoplastic starch processing (Fig. 5a).[110]

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 a DES can enhance the surface properties of starch when compared to conventional plasticizers, such as glycerol and urea.[107] The effects of sugar-alcohol-based DESs were studied by Zdanowicz *et al.*, who revealed that a sorbitol-based DES provided attractive mechanical properties (tensile strength of 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 in the production of flexible films with a highest elongation at break greater than 200% with a urea:glycerol system.[107] The plasticizing ability of DESs can depend on several factors, such as temperature and force applied, as well as the technique used (*e.g.*, extrusion, thermocompression).[108] A study carried out by Deng *et al.* discussed the importance of the use of a ChCl:ethylene glycol DES on corn starch for non-destructive starch processing and also carried out a structural analysis.[106]

Utilizing renewable feedstocks (in accordance with the seventh principle of green chemistry) to produce value-added functional materials with the help of DESs can open an avenue for environmentally friendly alternative ways to synthesize materials. Here, the effect of hydrogen bonding in the dissociation of biomasses plays a prominent role, while the plasticizing effect of DESs on starch provides attractive physico-mechanical properties in the subsequent composite materials. The utilization of DESs for the treatment of biomass materials discussed herein has the ability to generate nanomaterials with high purity levels compared to the harsh conditions needed with conventional approaches. The most common chemical modification arises with the acylation of the abundant hydroxyl groups of the biomasses, especially esterification with carboxylic acid-based DES treatment. This functionalization is deemed to be favorable owing to the improved dispersibility of the regenerated biopolymers and their high storage stability, which ensures their effective utilization for most applications.

5. Functional materials engineered utilizing DESs

In the above two chapters, we summarized how DESs facilitate the polymerization of synthetic polymers as monomers or solvents and the use of DESs in 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, besides an improved mechani-

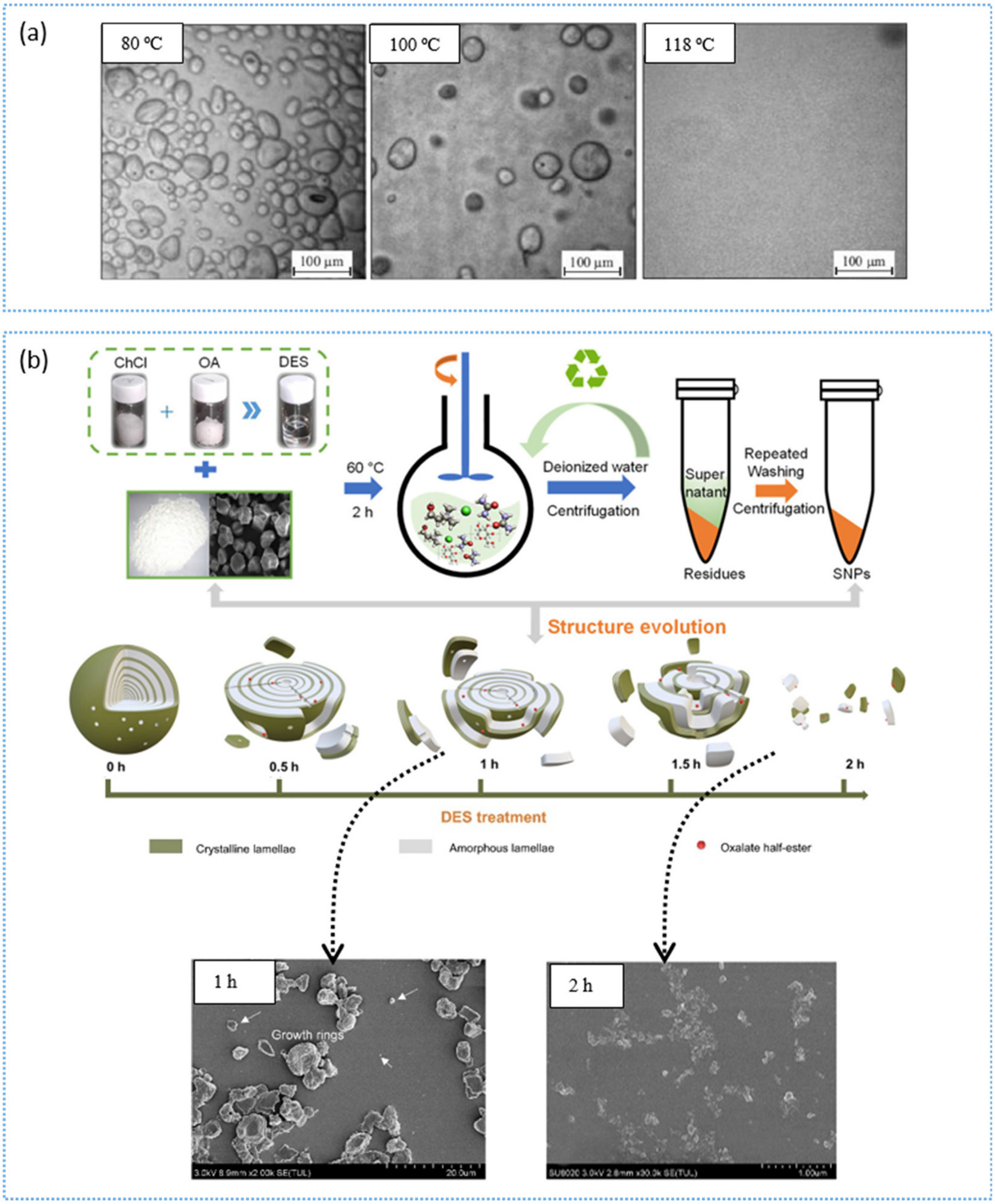

Fig. 5 (a) Plasticization effect of ChCl:urea DES on dried potato starch at 80 °C, 100 °C, and 118 °C.[109] Copyright 2018, Elsevier. (b) Illustration of the formation of starch nanoparticles: DES treatment (ChCl:oxalic acid dihydrate) on waxy maize starch for 1 h and 2 h.[81] Copyright 2022, Elsevier.

cal strength. The versatility of DESs enable them to play an important role in this context as a green alternative to conventional approaches, thus they are the subject of increasing research as an emerging area of interest (Fig. 1b). In this section, we reveal the strategies and properties of the functional materials generated by the application of DESs in a range of categories.

5.1 Gels

5.1.1 Eutectogels. The study on DES-based gels has received considerable attention from the scientific community over the past decade with the evolution of developments related to ionic liquids and then work striving for more stable, eco-friendly approaches. This class of gel materials has also been termed as "Eutectogels" with the development of various applications to distinguish their chemical behavior. The preparation of eutectogels can be classified into three main approaches according to the chemical constituents: (1) the polymerization of one constituent of the DES, especially HBDs with unsaturation (PDESs); (2) where DESs act as a solvent/medium for polymerization reactions of the constituents present in the medium; (3) the self-assembly of the components within DESs to generate supramolecular solids, which lead to gel-like structures.[112] The ability to fine-tune a DES by changing the HBAs and HBDs has enabled researchers to move further towards sensor-based applications of DESs in recent years, where ionic DESs can participate in conductive pathways. As ChCl is the most widely used nontoxic and economical ionic HBA, the use of it to generate polymeric eutectogels is of high interest for researchers.

5.1.1.1 Eutectogels using PDESs. The application of DESs in gel materials has shown beneficial results over conventional hydrogels and ionic liquid gels mainly owing to their non-volatility, non-toxicity, and ease of preparation. The utilization of PDESs further enhances the properties through noncovalent ionic and hydrogen bonding within the DES components and polymer chain, besides from the covalent bonds with the polymer backbone of the HBD or HBA. This leads to enhanced mechanical properties of the system, together with high fatigue resistance.[113] The vast tunability of DESs enables an effective dissolution of organic and inorganic additives, thereby enabling their use in diverse applications.[114] The low or no water within the eutectogel system further overcomes the drawbacks associated with conventional hydrogels due to the evaporation of water at high temperatures and freezing at lower temperatures.[114–116] The self-healing effect arising from the abundant hydrogen bonding is also another added advantage of DESs in gel-based systems, which enhances their robust nature. Collectively, these properties of DESs open up attractive avenues for the utilization of DES-based gel materials compared to traditional gel materials.

The utilization of the polymerizable, renewable itaconic acid for hydrogels was proposed by Bednarz *et al.*, who generated a poly(itaconic acid-*co*-bisacrylamide) hydrogel using a ChCl:itaconic acid PDES, highlighting the faster copolymerization in the DES medium than in water.[44] Another dual network eutectogel with more properties, including a visual strain-sensing ability, was developed recently by Liu *et al.*[114] utilizing a ternary DES ChCl:glycerol:*N*-acryloyl glycinamide (NAGA) with a conductivity of 0.7405 mS cm^{-1} and temperature tolerance of −20 °C to 60 °C. Here, the incorporation of photonic crystals into the gel led to colour changes at different strains, while the polymerized NAGA provided mechanical stability. Most of the gel-based applications reported to date have used AA, acrylamide, and acrylic acid derivatives in a DES medium.[117]

In 2021, Wang *et al.* suggested a different approach to incorporate a 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 was able to withstand a temperature range from −30 °C to 100 °C and C_2Cl_4, which is widely used for the dry cleaning of fabrics. The AA-based DES was initially formed, followed by photopolymerization after being inserted into the tube. Another study carried out by Lim *et al.*[113] probed the use of a ChCl:AA PDES as a screen-printable conductive ink. In their study, they used a supramolecular assembly of poly(3,4-ethylenedioxythiophene)/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 tremendously improved to 130 mS cm^{-1} with the addition of H_2SO_4 in to the system. The authors attributed this observation to structural transformations of the supramolecules into a linearly ordered manner, which facilitated the conductivity, thereby improving the signal response rate. The prepared gel material showed self-healing, stretchable, and high fatigue-resistance properties. Another double network PDES with the same DES system was generated with robust mechanical properties (strain up to 1373%, stress up to 3.14 MPa) by Wang *et al.* utilizing a 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 reported to be approximately 0.21 mS cm^{-1}.

5.1.1.2 DESs as a medium. The other approach of generating stimuli-responsive gels is the utilization of polymers (mainly AA and its derivatives) as a support for double network gels. A study carried out by Wu *et al.* investigated the effect of the 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} was achieved in this study, and it was also reported that the effect of Al^{3+} may adversely affect the conductivity owing to the high amount of dynamic crosslinking, even though it enhanced the mechanical strength (stretchability of up to 1595%) of the gel system.

A hydrophobic strain-sensing eutectogel was investigated by Gao *et al.* with a *N*,*N*-dimethylacrylamide (DMA) polymer base (Fig. 6b).[119] Here, the traditional ChCl was not used as the HBA to facilitate the conductivity, instead methyltrioctylammonium chloride : ethyl 4-hydroxybenzoate (1 : 2) was chosen to enhance the hydrophobicity. A stretchability of 900%, toughness of 341.14 kJ m^{-3}, and tensile strength of 97.58 kPa were achieved owing to the reversible hydrogen-bond interactions between the DES and the polymer in the gel with 30 wt% polymer scaffolds. The greatest strength was observed in the gel with 50 wt% polymer (tensile strength of 4092.63 kPa, toughness of 13 502.90 kJ m^{-3}). Another interesting approach for strain sensing with the use of DESs was probed under harsh conditions for underwater communication.[121] Here, the team used both hydrophilic and hydrophobic DESs as well as polymer systems to achieve the intended properties with a high level of interactions. ChCl:ethylene glycol was utilized as the hydrophilic DES system, whereas thymol:decanoic acid was its hydrophobic counterpart. For the polymers, AA and 2,2,2-trifluoroethyl methacrylate were copolymerized as the hydrophilic and hydrophobic ends, respectively. The team was able to generate stimuli-responsive eutectogels with 0.93 mS cm^{-1} conductivity along with a fast response time (1 s), and immunity to pH ranging from 3–9, together with low swelling and low drying properties.

A supramolecular assembly for a D-gluconic acetal gelator was utilized for a *N*-(2-hydroxyethyl)acrylamide polymer-based

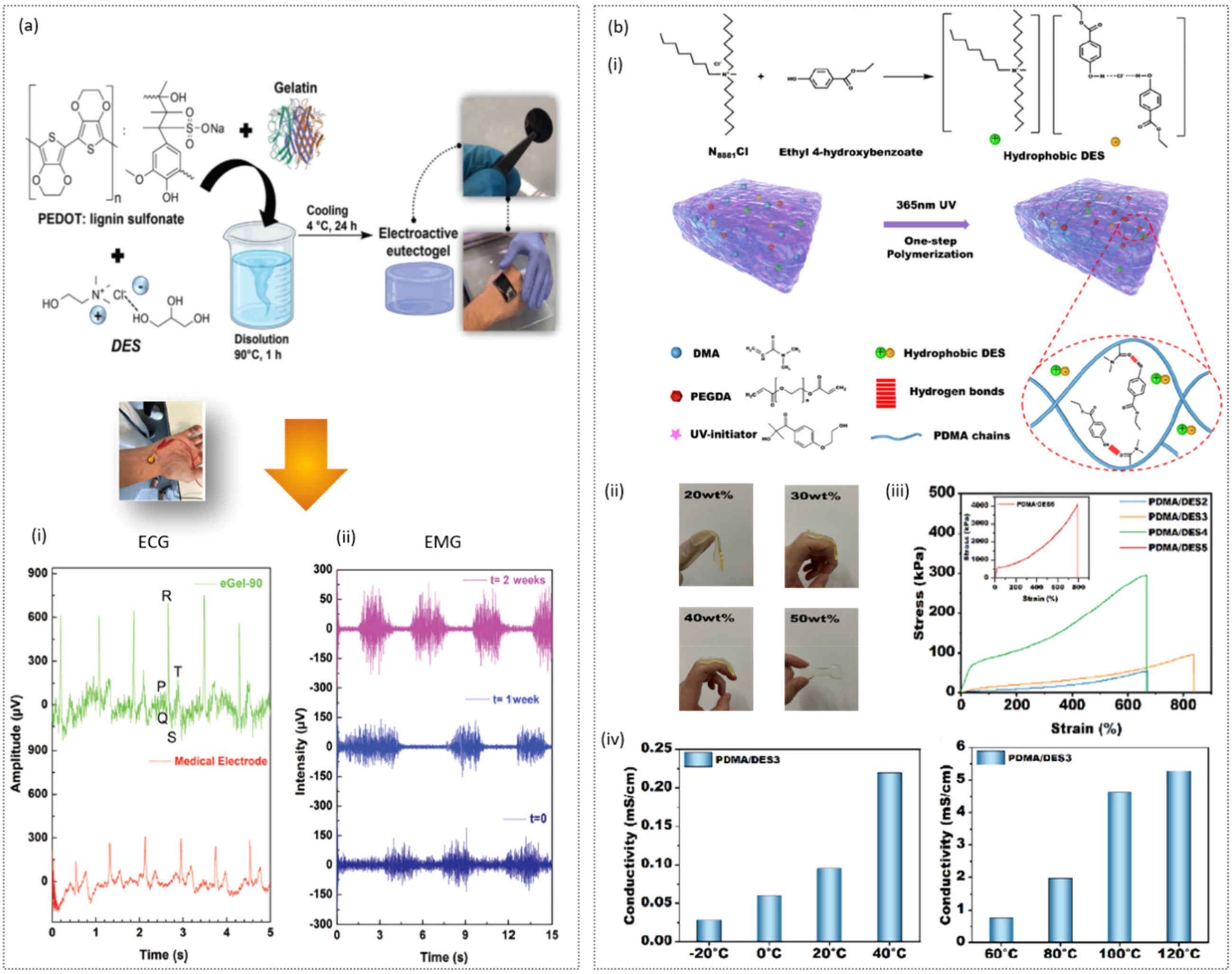

Fig. 6 (a) Use of gelatin based eutectogels for medical applications. (i) ECG comparison with a commercial medical electrode, (ii) time evolution EMG signals for thigh contraction/relaxation.[118] Copyright 2022, Wiley. (b) Hydrophobic DES-based gel. (i) Schematic illustration of hydrophobic DES-based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

dual network hydrogel with ChCl:monoethylene glycol.[122] The results suggested that increasing the loading of the DES led to an increase in conductivity (up to 3.74 mS cm^{-1}), accompanied with improved mechanical properties, including an elongation at break of over 4300%, tensile fracture strain of 0.21 MPa, and stability over the range of −20 °C to 100 °C. Additionally, with the strong intermolecular interactions of the gelator G18 a high level of adhesion on different substrates was 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, reversible noncovalent interactions within the double network system were demonstrated in this study by the overlapping front and rear hysteresis loops, indicating a rapid partial self-recovery.

Prasad *et al.* reported in 2018 a number of ionic gels based on polysaccharides that were responsive to pH, heat, solvent, and shear changes.[123] In their work, the team investigated 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 achieving a highly stretchable and good capacitance behavior. Fan *et al.* introduced a eutectogel through the polymerization of 1-viniylimidazole in ChCl:glycerol, which demonstrated high stretchability (2300% elongation at break), self-healability, and ionic conductivity in a wide temperature range (−30 °C to 60 °C).[124] The generated eutectogel also demonstrated good adhesion to different substrates, with the highest adhesive strength of approximately 70 kPa with a glass substrate.

5.1.1.3 Self-assembly within DESs for supramolecular eutectogels. Self-assembly in deep eutectic solvents represents 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 attracted 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, and is covered in detail in this section.

Gelatin is a widely produced protein-based natural biopolymer that has been ubiquitously applied in the food and pharmaceutical industry thanks to its nontoxic 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). Studies on the effects of DESs on the interaction of gelatin's triple helices have been performed by a number of research groups when fabricating sensors.

A study carried out by Qin *et al.* utilized gelatin as a 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 a pressure-sensing ability around 1 kPa levels and the ability to withstand a strain of 320% (tensile stress of 67 kPa) with a conductivity of 2.5 mS cm^{-1} at room temperature.[125] Here, both the ChCl and ethylene glycol played vital roles in the mechanical stability of the gel, where the kosmotropic nature coupled with high ion density of ChCl facilitated the assembly of gelatin chain bundles with higher intermolecular attractions (lowering the intramolecular interactions within the triple helices), while ethylene glycol promoted the formation of a fewer number of gelatin triple helices with larger diameters, thus providing greater 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 a small amount of water (5–6 wt%) to the gelatin supported (20 wt%)-DES system enabled an improvement not only in the conductivity but also in the toughness of the resultant eutectogel. The Young's modulus was also changed with respect to the HBDs, indicating a lowest value of 7 kPa with 1,2-propanediol to a highest value of 42 kPa for glycerol. The incorporation of water in to the ethylene glycol-based DES increased the toughness value by 195%, while also increasing the conductivity by 58% (to 5.2 mS cm^{-1}). The authors highlighted the formation of shorter triple helices of gelatin with the presence of glycerol and ethylene glycol by virtue of the steric hindrance they generated compared to water molecules. The generated shorter helices facilitated a 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 led to higher toughness values synergistically.

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

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

Recently, Mercadal *et al.* developed a non-cytotoxic bio-based eutectogel with strain-sensing abilities and 3D printability through the use of ChCl:ethylene glycol, porcine gelatin.[128] Here, tannic acid-coated CNC was utilized as a reinforcing agent at low concentrations (1–2 wt%) and the resultant gel revealed a strength of 30 kPa and elongation at break of 180%. A time-dependent adhesive performance was 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 controllability of the gel adhesive remotely with the use of a laser beam.

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

The use of DESs as solvents has been primarily applied for phenol–formaldehyde polycondensations. Chen *et al.* reported a 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, and providing a source of nitrogen for the carbon, besides functioning as a solvent.[130] Another use of a similar polymer system was generated for capacitor applications, where a $ZnCl_2$ and urea DES was used to facilitate the generation of carbon-based aerogels with a high surface area (1238.81 m^2 g^{-1}).[131] Additionally, an iron-based DES system for xerogel-based supercapacitor applications was studied by Chen *et al.*, which delivered a capacitance of 209 F g^{-1} at a current density of 0.5 A g^{-1}. Here, the authors highlighted the advantages gained by using DES-assisted resorcinol–formaldehyde polycondensation by eliminating the costly supercritical CO_2 drying processes incorporated in traditional xerogel preparation.[132] Itaconic acid[133] and anilinium chloride[134] have been used as PDESs for the generation of xerogels. Further the pretreatment of biomass has been studied for the separation of oil, organic molecules, water, and dyes. Glucose and ChCl DES-treated CNFs were utilized by Long *et al.* for the generation of carbon aerogel with a recycling ability of up to 100 cycles (Fig. 7b).[135] Peng *et al.* documented a top-down approach utilizing cornstalk pith for aerogels with an oil/organic solvent sorption ability (Fig. 7a). Here, they used a DES for the selective delignification and removal of hemicellulose to generate a hydrophobic aerogel through 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 played a prominent role.[137]

5.2 Fibers

The exploratory research efforts of DESs has opened up a myriad of possibilities for material fabrication. The use of these green alternative solvents would not only be an environmentally conscious approach but also cost effective. To further demonstrate the potential of DES materials, various research works have been done to exploit the potential of their usage in nanofibers. These nanofibers coupled with electrospinning techniques can be applied to diverse fields, such as biomedical and agriculture. Sousa *et al.* first reported the use of a DES as a solvent for electrospinning to produce agar nanofibers for potential biomedical applications.[138] The alternative solvent for electrospinning was prepared with the DES ChCl:urea. Different blends of polyvinyl alcohol/agar and DES conditions resulted in varying the characteristics of the fibers, in terms of the surface roughness and diameter size, and all the blends exhibited good spinnability and mechanical resistance. Additionally, Mano *et al.* reported an approach for the fabrication of electrospun polyvinyl alcohol fibers with a NADES.[139] The main advantage of NADES in the fabrication of polyvinyl alcohol biopolymers is the acceptable toxicity profile and biocompatibility. As DESs and NADESs are hygroscopic liquids, they prevent premature evaporation of the solvent during fiber fabrication. The benefits of DESs in terms of recyclability, lower cost, and suitable compatibility have put them in the spotlight as possible alternatives to regular volatile solvents and their more expensive counterparts, ionic liquids.

However, there are some possible adverse effects from residual DES that could be detrimental to the integrity of the biopolymer fibers. A wet electrospinning strategy with the use of a ChCl:lactic acid DES was explored to prepare lignin fiber aerogels. The electrospun fibers were reported to coagulate in the water bath setup sufficiently enough to coagulate and remove the DES residues.[140] The resulting lignin fiber aerogel was carbonized and exhibited excellent electrochemical stability as a supercapacitor electrode, as compared to the commercial counterpart. This demonstrated that DESs can be a greener solvent alternative to produce quality electrospun fibers to further build into aerogels. The compatibility of DESs as better solvents in electrospinning compared to volatile solvents, such as ethanol and DMF, extends to the production of protein-based electrospun nanofibers as well. Zein nanofibers are difficult to be electrospun directly under certain conditions, such as temperature and UV-light exposure.[141] Mouro *et al.* fabricated nanofibers from electrospinning a polymeric

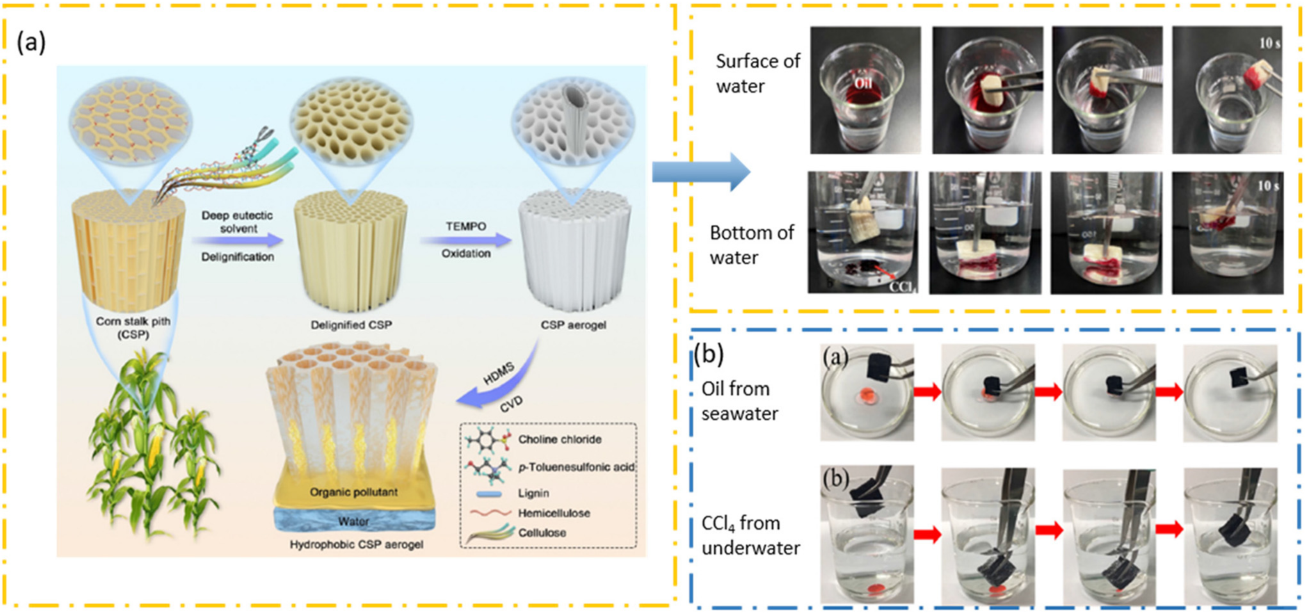

Fig. 7 (a) Top-down approach for generating a hydrophobic aerogel from cornstalk pith that demonstrated a good oil/water separation capability.[136] Copyright 2023, Elsevier. (b) Absorption of oil from sea water and CCl_4 from underwater using a carbon aerogel derived from DES-modified CNFs.[135] Copyright 2021, Elsevier.

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 antimicrobial properties that could be valorized in other industrial applications. As the choice of solvents impacts the quality and outcome of the fibers, DESs can facilitate the fabrication of these nanofibers due to their non-volatility.

On the other hand, DESs can be incorporated directly into polymers for obtaining electrospun nanofibers. Sereshti *et al.* synthesized polyamide 6 (PA6)/[polymerized HEMA:1-tetradecanol]-based electrospun nanofibers to extract residual pesticides for cereal flour analysis.[143] At a higher DES content, the increase in viscosity of the polymer blend becomes a hindrance, whereas too low a viscosity results in droplet formation. An optimal range of polymeric DES nanofibers was tested and resulted in a satisfactory recovery of pesticides, demonstrating their potential as a fast and green alternative for 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 (Fig. 8a).[144]

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

Drug release can be optimized with the correct morphology, porosity, and interactions between the active agent and the polymeric nanofibers. Generally, electrospun drug systems can 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 were found to have hydrophilic behaviors that could affect the drug-release profile.[146] The application of DESs in electrospinning techniques and polymeric nanofibers minimizes the use of hazardous, volatile solvents, together with providing an option to recycle the residual DES. The properties and morphologies of

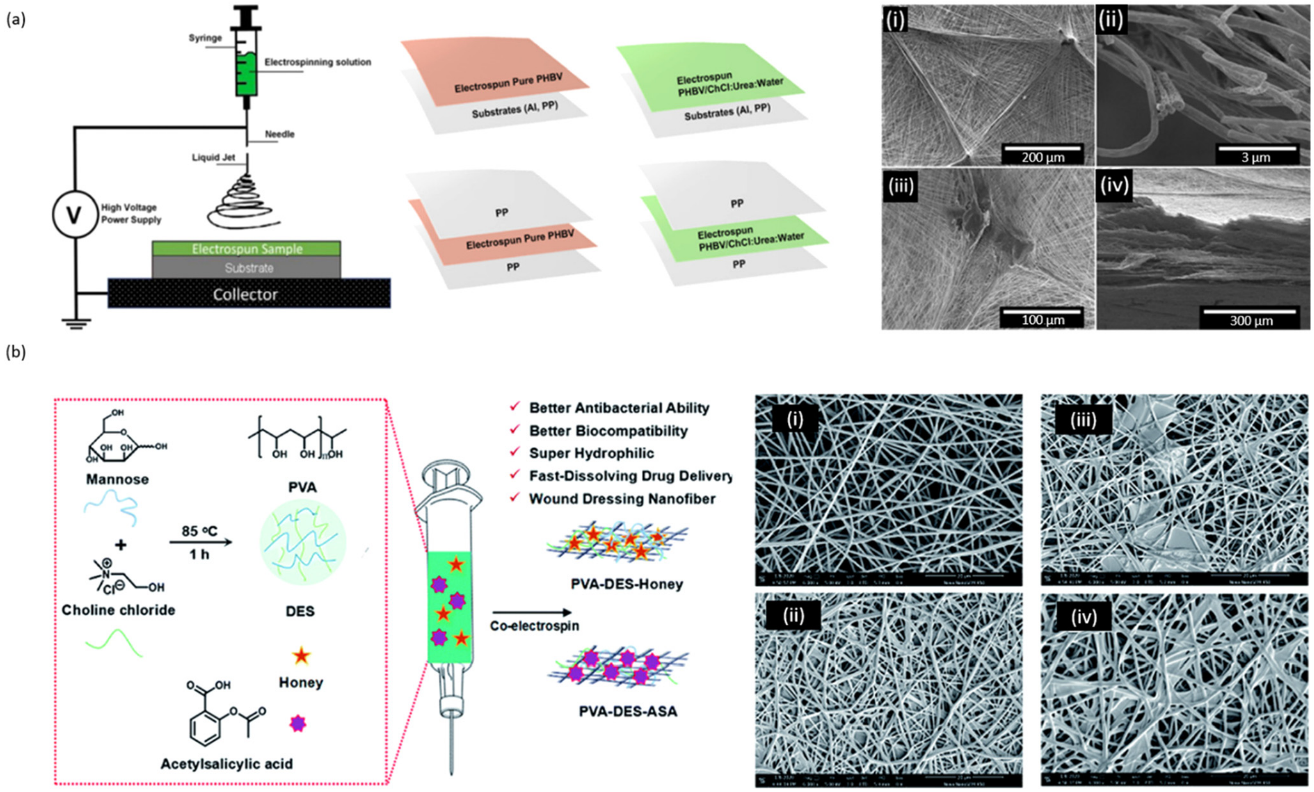

Fig. 8 (a) Schematic diagram of sample preparation *via* electrospinning and its subsequent morphology for (i) pure PHBV on Al foil, (ii) PHBV/DES on polypropylene (PP), (iii) pure PHBV on PP, and (iv) PHBV/DES on PP.[144] Copyright 2023, American Chemical Society. (b) Schematic diagram of the fabrication of polyvinyl alcohol–DES, polyvinyl alcohol–DES–honey, and polyvinyl alcohol–DES–ASA systems prepared by electrospinning, and their 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.

nanofibers derived from DESs can be tuned to the level of the DES in the system.

5.3 3D printing

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

5.3.1 Physical blending in DES systems. DES systems with ethylene glycol or glycerol have been studied by several researchers for 3D printing applications. Lai *et al.* used a ChCl:ethylene glycol-based system for a 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 for direct ink writing (DIW) and observed a high storage modulus (approximately 60 kPa) and yield stress (2.5 Pa) return at a CNC loading of 22.5 wt%. The same team eventually studied the ChCl:glycerol-based system in an AA and acrylamide-based polymer system and found that the effect of the thermally induced gelation of CNC could reduce the loading to 10–14 wt% owing to the solvolysis of the 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) besides CNC fillers in a system with acrylamide polymers and a DES (ChCl:ethylene glycol), which showed enhanced rheology, mechanical strength, and conductivity of the materials, as well as a colorimetric sensing ability when exposed to acidic compounds for DIW sensor fabrication.[149]

Several applications of the use of gelatin for non-cytotoxic sensor-based applications were already discussed in 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 under mild temperature conditions (37 °C to 42 °C), where the printed articles were able to preserve the original shape and pattern. Sheikhi *et al.* suggested the use of DESs for a radically distinct approach for the 3D printing of jammed microgels.[150] Here, the authors used a DES in the final step to coat a 3D printed jammed article to ensure the strength of the material, which ended up generating self-standing structures. The team used an 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 the amino acids and 1,2-diols-based DES as an activator in covalent bond formation to make epoxy functional groups for nucleophilic reactions under ambient conditions was 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 the DESs. The group studied several DES systems with differing HBDs, such as aliphatic polyols, and organic acids to aromatic compounds, and suggested the PEDOT:PSS/DES ratio of 30 wt% provided the desired 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 authors attributed this phenomenon to the π–π interactions between the phenolic moieties of PEDOT, PSS, and HBDs. Furthermore, a system with ChCl:lactic acid was used for a DIW application owing to its biocompatibility, with an annealing process at 50 °C for 16 h 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 was suggested by Wang *et al.* with the addition of a 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 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 have been vastly studied.[153–161] 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 loadings of 6–15 wt% in the system, and concluded that the presence of charged groups (in sulfated CNC) indicated a greater stabilization in the ChCl:AA-based system.[157] Additionally a stabilization of bacterial cellulose nanofibers using the same DES system (ChCl:AA) was proposed by Prosvirnina *et al.* by highlighting the formation of a polysiloxane shell on the surface of cellulose, which resulted in a lowering of agglomeration and allowed obtaining printed structures with smooth surfaces.[158] Further a comparison was conducted with an imidazolium-based ionic liquid and ChCl with AA DES and revealed that the low viscosity level of the choline-based DES provided more favorable results in DIW printing than the imidazolium ones.[155] The properties were further enhanced by grafting polyAA to the surface of the CNF incorporated when fabricating the ink. Carbopol was suggested as an alternative rheological modifier to CNCs and CNFs by Vo *et al.* with the use of a ternary PDES of ChCl : ethylene glycol : AA (1 : 1 : 2), which resulted in an enhanced stretchability (300%) and high sensitivity (gauge factor of 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 displays (LCDs), 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 the SLA method. The group utilized a PDES system consisting of ChCl : AA (1 : 2), which contributed to the enhancement of the antistatic property, and 2-hydroxyethyl acrylate for the strength requirements. The photopolymerization of this system indicated a fast curing speed (10 s) and the highest mechanical strength was observed at a 20% DES loading with a 90% polymer conversion rate.[153] Cai *et al.* worked on a similar DES system with the SLA technique to fine-tune the printing structure as an interlocked pyramid type for pressure-sensing applications.[154] A ternary PDES with acrylamide : ChCl : maleic acid (1 : 1 : 2) was studied with this printing technique, which resulted in highly transparent objects (95.6%) coupled with a faster curing time of 6 s (24 W UV light 410 nm), as reported by the same team (Fig. 9a).[156] Here, the team suggested that the strength of the material was due to its structure comprising a soft monomer system (maleic acid/ChCl) and a hard system (acrylamide/ChCl), which resulted in the generation of a copolymer product of poly(acrylamide/ChCl-*co*-maleic acid/ChCl). Furthermore, they emphasized that increasing the photoinitiator 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. The same group investigated the application of this PDES system in a DLP-based printing technique and 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 by 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 the DLP method. This 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 an increase in strength due to the ultratough nature of the tannic acid- and gallic acid-derived polymers (strength ~ 3 MPa).[162]

A study conducted by Zhu *et al.* utilized an LCD-based printing technique to generate printable materials with a ChCl:HEMA PDES (Fig. 9b). The addition of tannic acid (10–40 wt%) not only enhanced the antibacterial properties of the printed items but also improved the homogeneity of the generated inks by interconnecting *via* noncovalent bonds with the DES system.[163] An interesting study on the 3D printing of a sacrificial mold coupled with a reprocessing study of the ink was conducted by Li and co-workers utilizing a ternary PDES (ChCl:acrylamide:4-acryloylmorpholine) with an LCD (Fig. 9c). The solubility parameters of the final products could be tuned by adjusting the ratios of the PDES components, and the

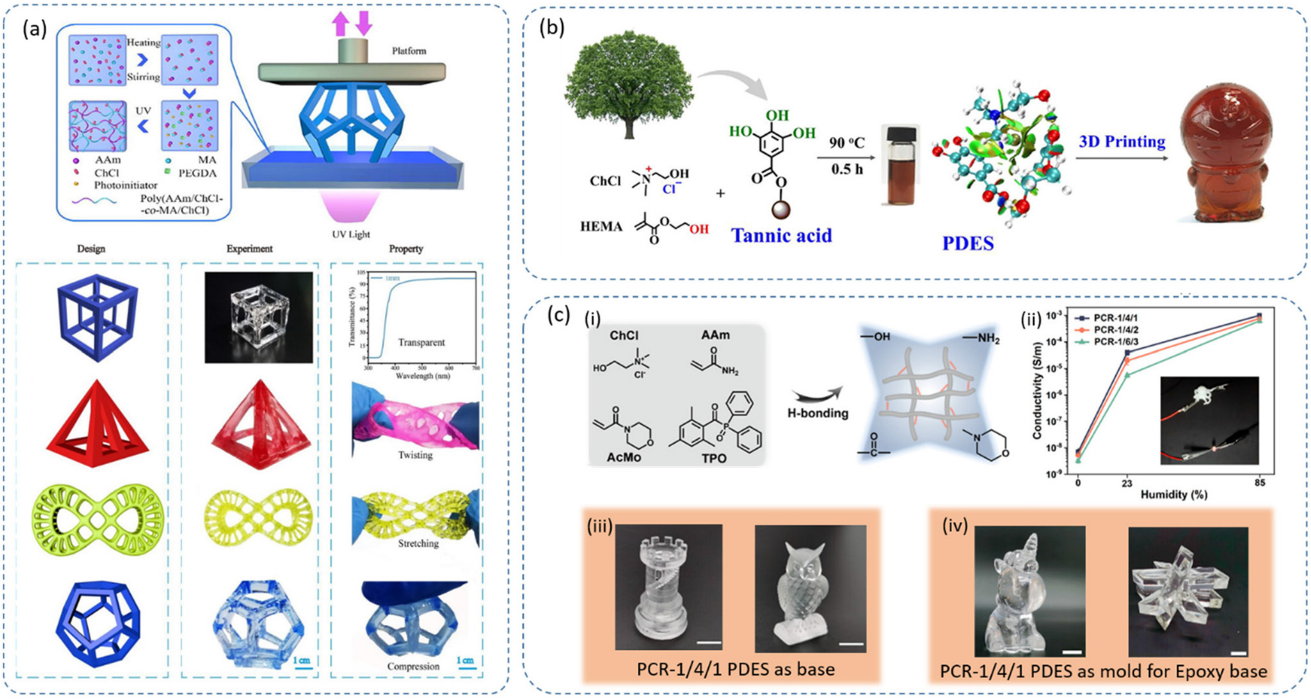

Fig. 9 Photocurable resins generated by PDESs for 3D printing applications. (a) Schematic illustration of SLA printing of a PDES (acrylamide:ChCl:maleic acid) and 3D printed models for conductive elastomeric sensors.[156] Copyright 2021, Elsevier. (b) LCD 3D printing of a bio-based PDES (ChCl:HEMA).[163]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

authors highlighted that the 4-acryloylmorpholine monomer played a vital role in lowering the viscosity at ambient temperature. 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]

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.

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 the surface hydrophilicity by 24.9%, and showcasing the role of the DES as a plasticizer (Fig. 10a).[164] Non-ionic DESs were employed by Ismail *et al.* to dissolve PVDF polymer, producing three different morphologies of the resultant membranes with varying pore sizes and thickness values (Fig. 10b).[165] The addition of polyvinylpyrrolidone resulted in a finger-like structure, while the membrane prepared with *N*-methylacetamide–acetamide and 2 wt% polyvinylpyrrolidone demonstrated superior performance, with a high water permeate flux (96.82 L m^{-2} h^{-1}) and 96.32% 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 structures of the 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 the initial uses highlighting their potential 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 their high electronegativity and charge delocalization, which could enhance 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 the primary HBDs.[168]

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

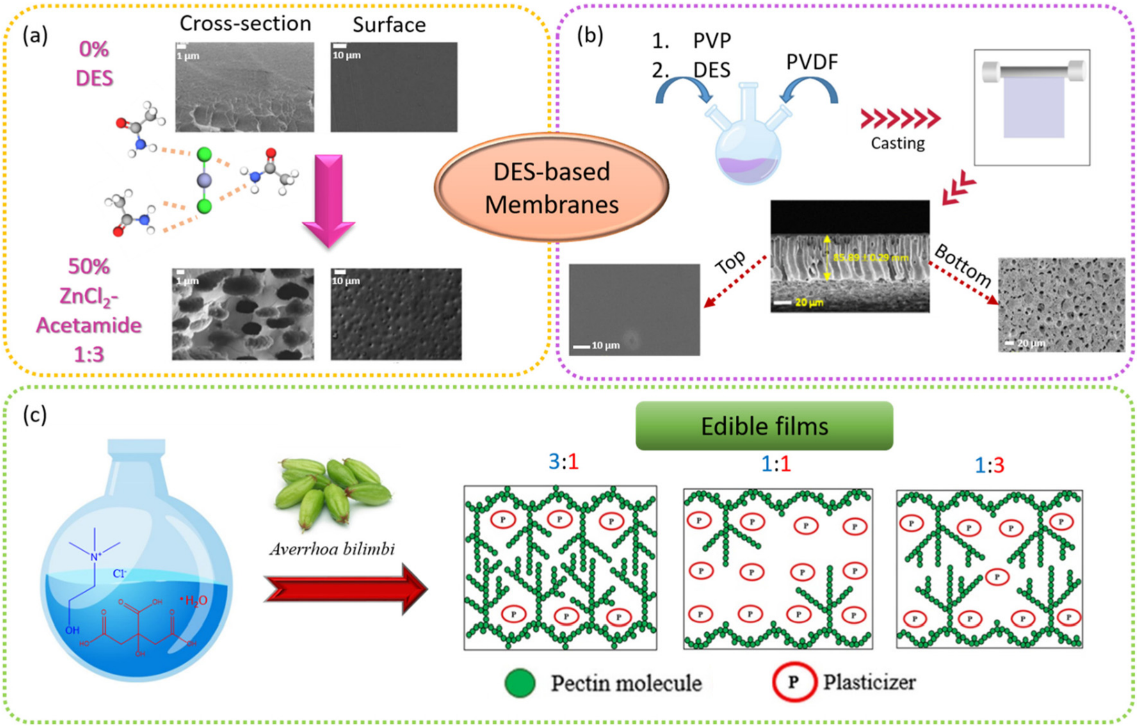

Fig. 10 Illustration of the generation of porous membranes and their SEM images. (a) Polyamide-imide membranes before and after incorporation of $ZnCl_2$: acetamide.[164] Copyright 2021, MDPI. (b) With non-ionic DES (*N*-methyl acetamide:*N*-methyl urea).[165] Copyright 2022, Elsevier. (c) Schematic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

with higher DDA (around 95%) levels resulting in increased mechanical strength.[101] Apart from the studies related to structural enhancement on the surface physicomechanical properties and antibacterial activities in chitosan films, the antioxidant activity of such films was reported by Jakubowska *et al.* with the inclusion of quercetin, which is a naturally obtainable plant polyphenol, for a storage application for 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 probed the antibacterial, antioxidant, as well as UV-barrier properties of the prepared films and found out that the one prepared with ChCl and acetylsalicylic acid had the best performance (DPPH scavenging activity of 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 performed with an aim to achieve property enhancements in areas such as antioxidant and UV shielding.[178] Composite films from cellulose and modified lignin revealed that the antioxidant and UV-shielding performances depended heavily on the 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 a DES-treated (ChCl:oxalic acid) wood powder.[179] Pectin-based edible films, utilizing different DES ratios of ChCl, and citric acid monohydrate, 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 and water vapor transmission rate).[175] The authors attributed this property to the entanglement of branches with a lower plasticizing effect (Fig. 10c).

Hydrophobic DES systems, such as thymol:octanoic acid, were studied for their water barrier properties on chitosan/gelatin films.[180] While the water contact angle (above 90%) and water vapor transmission rate were improved at higher DES loadings (6–15%), the tensile strength decreased. Nonetheless, the elongation at break increase (for DES systems with an 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] An optimal loading of 67 wt% NADES (ChCl:citric acid) in chitosan films exhibited a 56% recovery of the elongation at break and 72% of the original strength after breaking. Additionally, NADESs, particularly ChCl:vanillyl alcohol:gelatin, demonstrated superior adhesive strength (approximately 135 kPa) with shear-thinning behavior for thin-film applications.[181]

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

All the aforementioned applications provide evidence for the application of DESs as solvents for a vast majority of polysaccharides and their use for the surface modification of films as mainly plasticizers and for achieving other modifications, such as endowing systems with hydrophobicity, UV-shielding, antioxidant, antibacterial, and barrier properties as well as a self-healing property. Additionally, the use of DES extractants for property enhancement represents a novel and sustainable pathway, allowing for the recycling and reuse of the extracted DESs in functionalized polymer film formation. Various studies have explored the extraction of bioactive compounds, including polyphenols and anthocyanins, using DESs for modifying polymer films. Notably, DES-extracted anthocyanins have exhibited superior antibacterial and antioxidant properties for edible films,[182] while carotenoids extracted by DESs have shown enhanced plasticity and been used 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 ultrasound on the extraction of polyphenols was assessed and it was found to improve the mechanical properties of the chitosan-based film, including its anti-plasticity ability as well as adhesion property, which could enable its use in animal-tissue-based applications.

All the above studies have demonstrated that DESs can be used as green solvents to develop various types of functional materials with different properties. DESs 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 DESs by balancing the hydrophilic/hydrophobic, polar/nonpolar ratios can also play a vital role in the generation of advanced polymeric nanomaterials. Additionally, the stabilization achieved in organolithium species in anionic polymerizations[32] and the metal coordination ability in DESs[162] suggest the potential for them to be used as coordination polymer materials.

6. Green credentials and 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.[189–192] The concept of sustainability identified by the United Nations in the 2030 Agenda for Sustainable Development comprises several aspects. A few goals set by the United Nations are to "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 to "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 DESs to be considered as green alternatives to ionic liquids or other conventional solvents used for extraction and synthesis. In fact, this exact belief has fueled an increase in research on DESs[185] (Fig. 1b and 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 DESs as green alternatives without further assessment and proof.

A way to assess their green credentials is by 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 (Fig. 11).[186] As such, the accuracy and effectiveness of LCA depend primarily on the completeness of the scope and knowledge for each step.

Under LCA guidelines, the inputs and outputs are one of the main components to evaluate the green credentials of DES-based materials. First, the acid used to prepare DESs 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 due to its biodegradable and regenerable nature, making it a sustainable choice. Hence, it is expected that the combination of both reagents would be sustainable and green compared to conventional solvents. Unfortunately, it is not as green as it appears to be upon a deeper understanding of 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 preferred 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 ChCl synthesis to use with 1 g chitin powder. If malic acid is

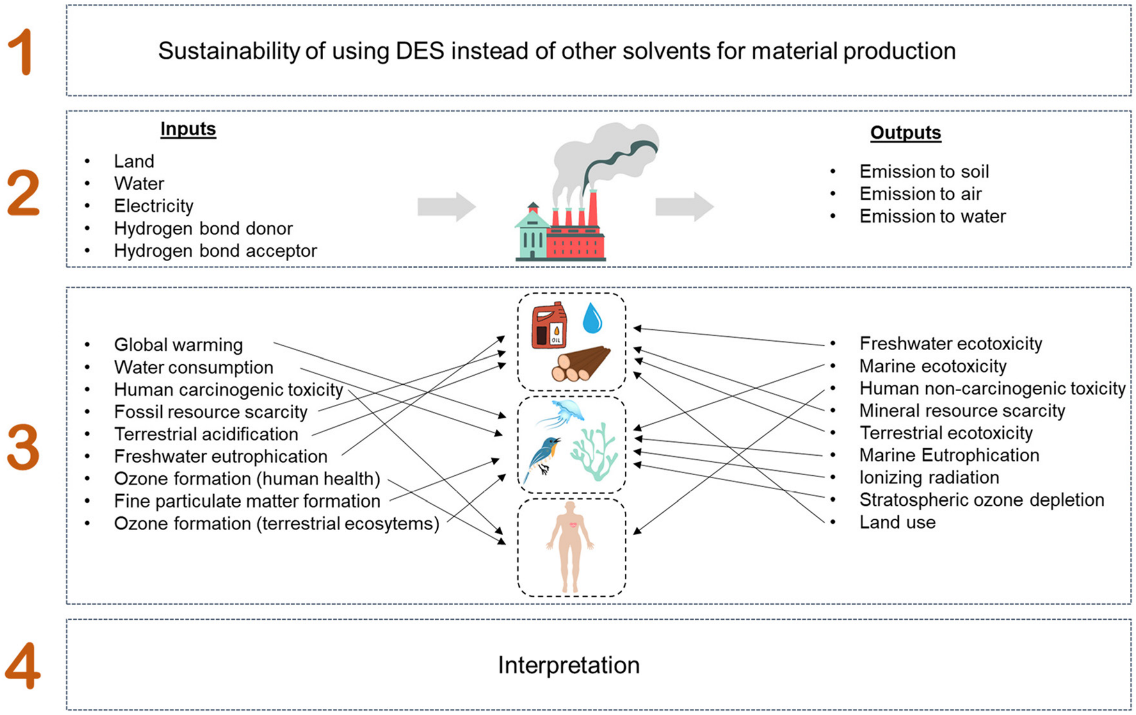

Fig. 11 Different phases in the life-cycle assessment for the example of DES-based materials.

used instead of lactic acid, the amount of HCl required for 1 g chitin powder is 1.50 g. This brief 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 a relative impact below 50% for all the fields, except for metal depletion potential, which displayed a slightly poorer performance (~60%). Among the tested solvents, ethyl acetate and dichloromethane fared the worst, as each topped the group in 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 a 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 could be recycled up to nine times.[179] These findings suggest that DESs are an even more attractive sustainable alternative 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 the DES or to extract and mix fresh DES? Additionally, one needs to determine the emissions and to see from which reaction they are lower? In summary, DES-based materials seem to be relatively green but more study is needed.

7. Conclusion and outlook

This review provided an overall summary and an update on the current trends in the utilization of DESs in green polymer synthesis and the construction of functional polymer materials, with eco-friendly nontoxic constituents. Regarding the synthesis and preparation of polymer materials, DESs can function as solvents, monomers, and can be used for biomass pretreatment, whereby variable functional polymer materials can be realized in the form of gels, nanofibers, films, and membranes. The various characteristics of DESs, such as the utilization of renewable feedstocks (*e.g.* NADESs), 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 a prevention of waste, demonstrating the capability of DESs for use in large-scale manufacturing in an environmentally sustainable manner. The unique hydrogen bonding existing within DESs coupled with their other properties, such as catalyst, plasticizer, pore generator, shear-thinning behavior, dispersant, and tunable hydrophilicity/hydrophobicity, provides numerous possibilities to probe more applications for polymeric materials in the future.

However, given that different extents of hydrogen bonding can significantly affect the generation of functional polymeric materials by DESs, the mechanism of the influence of hydrogen bonding is still unclear. More extensive computational simulations could be utilized in this aspect to visualize the molecular interactions, in this case, the hydrogen bonding. This approach would help to understand the bonding nature of the DES systems more distinctively while reducing unnecessary lab trials. Another aspect of interest involves how to investigate DESs' 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 in DESs has been emphasized in various cases as 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 DES systems.

There is still a great potential to exploit this comparatively new solvent system to use as a top-down approach for 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 could be more insightful.[98,196] The application of DESs in crafting polymeric items, like 3D printing, can facilitate the creation of customized structures for functional polymers, resulting in reduced waste generation. However, further inroads in this technology could be probed with the advancements in 4D printing and smart materials, especially given the stimuli-responsive materials generated *via* polymeric DESs owing to their responsiveness to external stimuli, such as temperature, pH, humidity, and electricity.

Currently, there is extensive discussion on sensor-related applications of DES-based polymeric material 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 DESs, which have been identified recently as a new sub-class.[197] We have summarized the multiple roles of DESs in different polymer materials. The integration of these multi-functions of DESs 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 still in the initial phases. Specifically, we evaluated the green credentials and sustainability of DES-based polymer materials. The economic evaluation of the recyclability of DESs and further utilization of the extractives generated during biomass pretreatment could be another focus area in the future.

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.

Conflicts of interest

The authors declare no conflict of interest.

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