Electrospinning from room temperature ionic liquids for biopolymer fiber formation

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Polymer electrospinning has emerged as a powerful technique for the fabrication of nanofibrous materials with high specific surface areas, controllable compositions, and high porosities for a wide range of applications. The electrospinning of biopolymers for fiber formation is of particular interest not only because the resources are renewable, but also because of the desirable characteristics of these biomacromolecules, including biocompatibility, biodegradability, and exquisite specificity. Electrospinning has routinely relied on organic solvents for the dissolution of polymeric materials, which are evaporated in the course of nanofiber formation. Most biopolymers, however, are insoluble in organic solvents so they cannot be electrospun using conventional approaches. Room temperature ionic liquids (RTILs) offer a solution to overcome these difficulties due to their exceptional solvent properties, allowing the electrospinning of recalcitrant biopolymers like cellulose. Moreover, non-volatile RTILs can provide a 'greener' processing alternative by preventing the release of harmful volatile compounds to the environment. This review provides an overview of the advantages and challenges of polymer electrospinning from highly conductive, non-volatile RTIL solutions, emphasizing the utility of RTILs in the dissolution of biopolymers, and the fabrication of advanced functional biopolymer composite fibers.

1. Introduction

1.1 Biopolymer fibers

A major path toward sustainable development involves the use of biomass for the production of energy, as well as chemicals and materials. Biopolymers are derived from living organisms, and represent an invaluable renewable resource. While their sustainability is clearly an important factor for many applications, biopolymers are often the basis of functional materials and composites because of their desirable, and in many cases unique, properties, such as biocompatibility, biodegradability, and exquisite specificity. Biopolymer fibers, for example, have been used as active materials in a wide range of biomedical applications where their biological properties play a key role in their functionality. They are used as carriers for drug delivery and controlled released, as vascular grafts and as scaffolds for tissue engineering, as supports for biocatalysis, multifunctional membranes, sutures, and in biosensors.[1–4] Their use has also moved beyond the scope of biomedicine into membrane filtration, protective textiles, optical and (bio)chemical sensors, electrochemical cells (as membranes or as electrode material), nanoscale reinforcements, and catalysis.[5–7]

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One of the simplest ways of preparing continuous and uniform polymer fibers of varied composition is through electrospinning. Electrospun fibers have many properties that make them ideal materials for the aforementioned applications, including high specific surface areas (10–1000 m^2 g^{-1}),[8] high aspect ratios, high porosities (up to 80%),[7] and controllable diameters that range from nanometres to microns. Three-dimensional fibrous structures of electrospun fibers are malleable and can thus be manufactured into different shapes. Moreover, electrospinning is amenable to control of fiber composition and surface chemistry through blending, encapsulation, and immobilization of biological and other material components.[3] This allows the manipulation of chemical, physical, biological, and surface properties of the electrospun fibers to fit desired applications. Moreover, fibers in the nanometre range are subject to confinement effects that can lead to an enhancement of certain properties, such as surface energy, glass transition, thermal and electrical conductivity, and surface reactivity.[9] Finally, electrospun fibers are probably one of the safest nanomaterials currently used, since they are unlikely to become airborne and penetrate the body because of their length.[7]

1.2 Polymer electrospinning

The most basic electrospinning setup consists of a high-voltage power supply connected to a spinneret containing the polymer solution and to a grounded conductive collector (Fig. 1). The spinneret is often a syringe, controlled by a pump through which solution can be fed at a specific rate to form a pendant droplet at the needle tip. As a voltage difference is applied between the spinneret and the collector, electrical charge accumulates in the surface of the liquid droplet. When the electrostatic repulsion within the droplet exceeds the liquid surface tension,

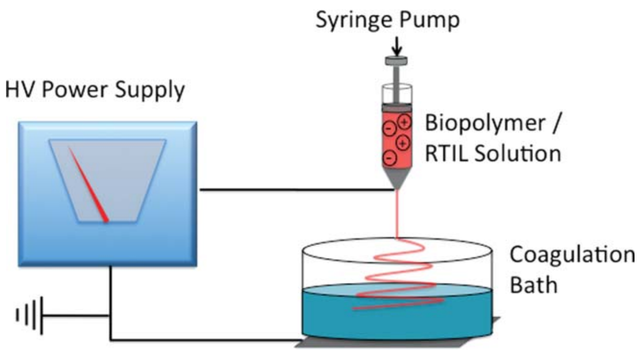

Fig. 1 Schematic diagram of an electrospinning apparatus with a coagulation bath collector for non-volatile solvent removal.

which strives to minimize the droplet's surface area, the droplet deforms forming a conical protrusion known as a Taylor cone.[10] After a certain threshold voltage is reached, a thin, charged, liquid jet is ejected from the tip of the cone and it is drawn towards the grounded collector. Initially, the jet follows a straight path. However, this stage is soon followed by the onset and growth of three possible jet instabilities;[11] two of these are axis-symmetric modes, where jet fluctuations occur around the main axis, and one is a non-axis-symmetric mode (Fig. 2). The first of these modes is the classical Rayleigh instability, which is dominated by surface tension and is suppressed at high electric fields. This mode leads to droplet formation (electrospraying). There is also an axis-symmetric, conductive mode typically occurring in highly viscous fluids that can result in beaded fibers. Finally, there is a non-axis-symmetric conductive mode responsible for a whipping motion of the jet. This bending motion is promoted at high surface charge densities and high fluid flow rates and is responsible for the thinning of the jet, allowing the formation of nanofibers. In electrospinning from aqueous and organic solvents, the solvent gradually evaporates during the jet's course and polymer fibers accumulate in the grounded electrode forming non-woven mats.[11–12]

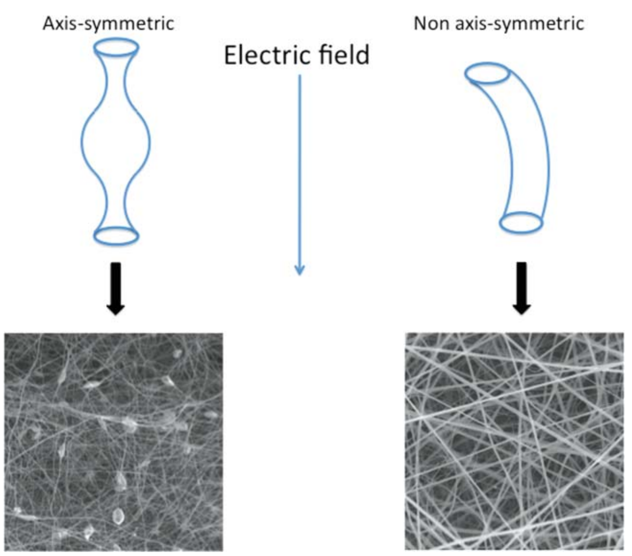

Fig. 2 Axis-symmetric and non axis-symmetric bending instability modes leading to different fiber quality (beaded or smooth fibers) depending on the predominant mode. The diagrams are adapted from reference 11.

The properties of the fibers obtained can be easily manipulated using a host of spinning and solution parameters.[13–15] The most relevant spinning parameters include the field strength, feed rate, and distance between collector and spinneret. Important solution parameters are the viscosity, surface tension, conductivity, vapor pressure, concentration, and polymer molecular weight, polydispersity, and architecture. These last four parameters impact chain entanglement density, the primary property that determines the spinnability of a given polymer solution.[16]

Novel electrospinning approaches can be used alter the morphology of the individual fibers and mats. For example, the spinneret can have double, concentric needles to allow formation of core-sheath morphologies,[17] where the core and the sheath are made of different materials. Multiple arrays of spinnerets have been used to generate co-mingled fibers.[18] Blow-assisted electrospinning can be used to control temperature, broaden operating conditions, or improve the production throughput, depending on the velocity of the gas stream.[7] In some cases, fiber morphology can be modified by constructing chambers that allow control of temperature and humidity.[19] Finally, by adjusting the geometry of the collector it is possible to form uniaxially aligned fibers, stacked arrays, or bundles of fibers.[20–22]

The properties of electrospun fibers largely depend on the chemical composition of the polymer solution. Thus, both the morphology and the properties of the electrospun fibers can be manipulated by spinning miscible and immiscible polymer blends, block copolymers, emulsions, or organic-inorganic composites.[3,5]

Electrospinning typically employs volatile organic solvents to prepare the polymeric spinning solution, which evaporate in the course of fiber formation. This process can release high levels of harmful volatile compounds to the environment, and it is unsuitable for effective recovery and recycling of the solvents.[5] Electrospinning from room temperature ionic liquids (RTILs) represents an interesting solution to this problem since these non-volatile solvents remain in the fibers as they are cast and are removed by means of a coagulation/washing bath, allowing their effective recovery using an array of strategies.[23] It is necessary to understand the characteristic properties of ionic liquids, their use as solvents in macromolecular science, and their role in polymer/RTIL composites. This review is focused on the application of RTILs as solvents for biopolymers, highlighting their utility in the dissolution of a wide range of recalcitrant but sustainable biopolymers.

1.3 Ionic liquids

Over the past decade RTILs have emerged as a unique class of solvents for chemical transformations and processing. RTILs are low-temperature molten salts composed of large molecular ions that often posses some level of asymmetry and charge delocalization resulting in low lattice energies and melting points, often below room temperature.[24] These ionic solvents have exceptionally high ionic conductivities, wide electrochemical windows with extremely low vapor pressures, and high decomposition temperatures that lead to wide usable liquid ranges.[25–26] They are often referred to as "designer solvents" since their constitutive organic cations can undergo nearly unlimited structural transformations. The resulting combination of the various cations and anions can, in principle, generate up to 10^{18} different RTILs.[27] This yields exquisite tunability of physical and chemical properties, such as polarity, solubility, and miscibility. For example, RTIL/water miscibility can be finely adjusted to process requirements by a simple switch of the anion. Chemical separations also tend to be simplified in RTILs since the desired products can usually be easily extracted with other organic solvents or water, or distilled off, enabling efficient recycling of the RTILs.[28] Their inherent low vapor pressure and recyclability has won RTILs the epithet of "green solvents".

Despite the growing and now widespread use of RTILs in organic synthesis, the interest of RTILs in macromolecular science is fairly recent. Within this field, RTILs have been used in synthesis as reaction media for the generation of homopolymers and block copolymers,[29–30] or as organic catalysts for ring-opening polymerization to produce polymers such as polylactide.[31] They can be used in biomass modification of polysaccharides like cellulose,[32–33] and in chemical separations where block copolymer micelles with well-defined polar and non-polar nanodomains can act as selective carriers of valuable cargo from an RTIL phase to another solvent, such as water.[34] Their exceptional electrochemical properties, rapid response to external stimuli, and high ionic conductivity have been coupled with the favorable mechanical properties and the structure of polymers to yield functional composites.[35] These active materials have potential applications as ion conduction media for batteries, fuel cells, and sensors,[36] as membranes for gas separation,[37] as electroelastic materials for actuators and artificial muscles,[38] or as conductors or gate dielectrics in plastic electronics.[39]

1.4 Biopolymers and ionic liquids

The versatility of RTILs as solvents has been shown to be an invaluable tool for the dissolution of biopolymers that tend to be insoluble in most organic solvents. Perhaps the most significant example of this is the dissolution of cellulose in RTILs (up to 25 wt% in 1-butyl-3-methylimidazolium chloride),[40] since this biomaterial is an important target for energy conversion. RTILs that are hydrogen bond acceptors have been shown to dissolve the linear polysaccharide by disrupting the extensive network of hydrogen bonds present in this crystalline polymer.[32] RTILs are also of use in separating lignin from lignocellulosic biomass by selective dissolution, facilitating cellulose degradability after lignin removal.[41] Many other polysaccharides such as chitin,[42] amylose,[43] pectin,[44] and agarose;[45] keratins such as those in wool[46] and silk;[47] and several glycoproteins, including glucose oxidase, have also been solubilized in a variety of RTILs.[45] Moreover, some amide-enriched glycolipids dissolved in ether-containing RTILs self-assembled and formed ionogels at certain concentrations.[45] Highly sulfated glycosaminoglycans that are only soluble in water and highly polar solvents (*e.g.*, heparin or chondroitin sulfate), were shown to be soluble in benzoate-based RTILs.[48] Even DNA, which is soluble in a limited number of nonaqueous solvents, has been dissolved in a wide array of imidazolium-containing RTILs.[49] In fact, Ohno and coworkers[50] demonstrated the formation of so-called 'ionic liquidized DNA' through neutralization of the nucleic acid bases with suitable acids, like tetrafluoroboric acid, ultimately obtaining highly ion conductive DNA-based films. Table 1 shows solubility data of various biopolymers in RTILs.

Biopolymers can be chemically or enzymatically modified either prior to or following their dissolution. Enzymes generally have very limited solubility in RTILs and tend to remain suspended as powders. Those enzymes that dissolve in RTILs are typically inactivated due to a loss of enzyme tertiary structure.[51] Strategies, such as chemical functionalization of the enzyme or cosolvent dissolution, can be undertaken to preserve the activity of dissolved enzymes. Cytochrome c, for example, is soluble and active in chloride-containing RTILs,[52] as well as in hydrated choline dihydrogen phosphate.[53] However, in most cases enzymes act as heterogeneous catalysts in RTIL media. In particular, hydrolases and oxidoreductases have been shown to retain their activity when suspended in these polar solvents.[54] This feature is surprising since organic solvents with a similar polarity range tend to denature enzymes by disrupting their intramolecular hydrogen bonds. RTILs containing anions with low hydrogen bonding basicity are generally enzyme-compatible since they are thought to create less interference with the internal hydrogen bonds of the enzyme.[55] Several comprehensive reviews have been published on biocatalysis in RTILs.[51,54,56–57]

The unique solvent capabilities of RTILs described above can be exploited to create functional biomaterials, such as the RTIL-cast, blood-compatible heparin/cellulose membranes prepared for kidney dialysis applications.[58] In other applications, the RTIL can actually become an active component of the biomaterial. For example, RTIL-doped, chitosan-based membranes with enhanced ionic conductivity have been used as electrolyte membranes for dye-sensitized solar cells.[59] Flexible energy-storage devices based on cellulose/multi-wall carbon nanotube (MWNT) nanocomposites that function as an integrated electrode/spacer/electrolyte unit were also recently demonstrated.[36] Specifically, [BMIM][Cl] was used both as a solvent for cellulose dissolution and as an electrolyte in the resulting nanocomposite-based "paper" supercapacitors.

2. Electrospun fibers from ionic liquids

The main driving force for using RTILs in electrospinning is to obtain nanoscale and microscopic fibrous materials with high surface areas and high aspect ratios from recalcitrant biopolymers; an enticing possibility that remains vastly unexplored (see Table 2 for a list of synthetic and natural polymers that have been electrospun from ionic liquids). Not surprisingly, most efforts have focused on cellulose because of its solubility in RTILs that are hydrogen bond acceptors, as well as its natural abundance, renewability, and widespread use of cellulose fibers in a variety of commercial applications. Due to the insolubility of cellulose in organic solvents and its inability to melt, electrospinning of cellulose has typically relied on the use of cellulose derivatives, most commonly cellulose acetate, having higher solubility in organic solvents.[60] Unfortunately, fibers obtained from cellulose derivatives are more susceptible to degradation and tend to have reduced thermal stability when compared to native cellulose.[9] There are only a few non-RTIL solvent systems that allow the direct electrospinning of cellulose; n-methylmorpholine n-oxide/water (NMMO/H_2O), ethylene

Table 1 Solubility of biopolymers in ionic liquids

Biopolymer	RTIL[a,b]	Solubility	$T/°C$	Ref.
Polysaccharides				
Agarose	[MOEMIM][Br]	20 mg mL^{-1}	nd	45
	[MOMMIM][Br]	10 mg mL^{-1}	nd	45
Amylopectin	[BMIM][Cl]	5 wt%	70	84
Amylose	[AMIM][HCOO]	4, 19 wt%	30, 60	44
	[BMIM][N(CN)$_2$]	4 g L^{-1}	25	43
	[MOEMIM][Br]	30 mg mL^{-1}	nd	45
	[MOMMIM][Br]	30 mg mL^{-1}	nd	45
Cellulose[c]	[AMIM][HCOO]	10 wt%	60	44
	[AMIM][Cl]	10 wt%	100	44
	[BMIM][Cl]	25 wt%	microwave heating	40
	[BMPY][Cl]	12–39 wt%	105	85
Chitin	[BMIM][CH$_3$COO]	3–7 wt%	110	86
	[AMIM][Br]	10 wt%	100	87
	[BMIM][Cl]	10 wt%	110	42
Chitosan	[AMIM][Cl]	8 wt%	110	86
	[BMIM][[CH$_3$COO]	12 wt%	110	86
	[BMIM][Cl]	10 wt%	110	86
Chondroitin 6 sulfate, IM[d]	[EMIM][Ba]	>9 mg mL^{-1}	35	48
	[BMIM][Ba]	>5 mg mL^{-1}	35	48
Chondroitin 6 sulfate, Na[e]	[EMIM][Ba]	>1 mg mL^{-1}	35	48
	[BMIM][Ba]	0.5 mg mL^{-1}	35	48
Dextran	[BMIM][Cl]	15 wt%	90	88 86
	[BMIM][CH$_3$COO]	20 wt%	90	2
Dextrin	[AMIM][HCOO]	25 wt%	~46	44
Heparan sulfate, IM[d]	[EMIM][Ba]	3 mg mL^{-1}	35	48
	[BMIM][Ba]	3 mg mL^{-1}	35	48
Heparin, IM[d]	[EMIM][Ba]	7 mg mL^{-1}	35	48
	[BMIM][Ba]	7 mg mL^{-1}	35	48
Hyaluronic acid, IM[d]	[EMIM][Ba]	>10 mg mL^{-1}	35	48
	[BMIM][Ba]	10 mg mL^{-1}	35	48
	[BMIM][BF$_4$]	>3 mg mL^{-1}	35	48
	[BMIM][PF$_6$]	>2 mg mL^{-1}	35	48
Hyaluronic acid, Na[e]	[EMIM][Ba]	9 mg mL^{-1}	35	48
	[BMIM][Ba]	5 mg mL^{-1}	35	48
	[BMIM][PF$_6$]	1 mg mL^{-1}	35	48
Inulin	[AMIM][HCOO]	2, 25 wt%	30, 55	44
Lignin	[MMIM][MeSO$_4$]	>500 g kg^{-1}	90	41
	[BMIM][CF$_3$SO$_3$]	>500 g kg^{-1}	90	41
	[EMIM][CH$_3$COO]	>300 g kg^{-1}	90	41
	[AMIM][Cl]	>300 g kg^{-1}	90	41
	[BMIM][Cl]	>100 g kg^{-1}	90	41
	[BZMIM][Cl]	>100 g kg^{-1}	90	41
Pectin	[AMIM][HCOO]	1.5, 2.5 wt%	65, 80	44
Starch	[AMIM][Cl]	15, 20 wt%	80, 100	89
	[BMIM][Cl]	10 wt%	80	90
	[BMIM][N(CN)$_2$]	10 wt%	90	90
Xylan	[AMIM][HCOO]	21 wt%	95	44
	[AMIM][HCOO]	1.5 wt%	45	44
Proteins (non-catalytic)				
Bovine serum albumin	[BMIM][Cl]	10 wt%	90	2 86
	[BMIM][CH$_3$COO]	20 wt%	90	2
Collagen	[EMIM][Cl]	1.3 wt%	100	91
Elastin	[EMIM][Cl]	6.0 wt%	100	91
Silk (*B. mori*)	[BMIM][Cl]	13.2 wt%	100	47
	[BMiM][Br]	0.7 wt%	100	47
	[BMIM][I]	0.2 wt%	100	47
	[DMBIM][Cl]	8.3 wt%	100	47
	[EMIM][Cl]	23.3 wt%	100	47
	[EMIM][Ser]	>20 wt%	100	91
	[EMIM][Ala]	>20 wt%	100	91
	[EMIM][Gly]	26.3 wt%	100	77
	1 : 1 [EMIM][Cl]/[BMIM][Cl]	7.4 wt%	100	77
	1 : 1 [EMIM][Cl]/[DMBI][Cl]	10.3 wt%	100	77
Wool keratin	[BMIM][Cl]	4 wt%	100	92
	[BMIM][Cl]	11 wt%	130	92
	[BMIM][Br]	2 wt%	130	92
	[AMIM][Cl]	8 wt%	130	92
Zein	[BMIM][Cl]	15 wt%	80	90

Table 1 *(Contd.)*

Biopolymer	RTIL[a,b]	Solubility	T/°C	Ref.
Enzymes				
C. antarctica lipase B	[TEMA][$MeSO_4$]	3 mg mL^{-1}	40	93
Cytochrome C[f]	[BMPYR][H_2PO_4]	37 mg mL^{-1}	nd	94
	[Ch] [H_2PO_4]	~ 37 mg mL^{-1}	nd	94
	[BMIM][H_2PO_4]	~ 37 mg ml^{-1}	nd	94
Glucose oxidase	[MOEMIM][Br]	1 mg mL^{-1}	nd	45
	[MOMMIM][Br]	1 mg mL^{-1}	nd	45
Thermolysin	[BMIM][PF_6]	3.2 mg mL^{-1}	37	95
Nucleic acids				
DNA	[HMIM][Cl]	1 wt%	85	49
	[MPYR][BF_4]	1 wt%	100	49
	[EMIM][ClO_4]	1 wt%	107	49

[a] List of cation abbreviations: [AMIM] – 1-allyl-3-methylimidazolium; [BMIM] – 1-butyl-3-methylimidazolium; [BMPL] – n-butyl-n-methylpyrrolidinium; [BMPY] – 1-butyl-3-methylprydinium; [BZMIM] – 1-benzyl-3-methylimidazolium; [Ch] – choline; [DMBIM] – 1-butyl-2,3-dimethylimidazolium chloride; [EMIM] – 1-ethyl-3-methylimidazolium; [HMIM] – 1-hexyl-3-methylimidazolium chloride; [MMIM] – 1,3-dimethylimidazolium; [MOEMIM][Br] – 1-methoxyethyl-3-methylimidazolium; [MOMMIM][Br] – 1-methoxymethyl-3-methylimidazolium; [MPYR] – 1-methylpyrazolium; [TEMA] – triethylmethylammonium. [b] List of anion abbreviations: [Ala] – alanine; [Ba] – benzoate; [BF_4] – tetrafluorborate; [Br] – bromide; [CF_3SO_3] – trifluoromethanesulfonate ; [CH_3COO] – acetate; [Cl] – chloride; [ClO_4] – perclorate; [Gly] – glycine; [H_2PO_4] – dihydrogen phosphate; [HCOO] – formate; [I] – iodide;[$MeSO_4$] – methylsulfate; [$N(CN)_2$] – dicyanamide; [PF_6] – hexafluorphosphate; [Ser] – serine. [c] A complete list of the solubility of cellulose in RTILs can be found in reference 32. [d] Imidazolium salt. [e] Sodium salt. [f] 10–20 wt% water content.

Table 2 List of biopolymers and synthetic polymer electrospun from RTILs

Polymer	RTIL	Collector	Ref.
Biopolymers			
Cellulose	[BMIM][Cl]	Ethanol bath	65
Cellulose	[BMIM][Cl], [BMIM][Cl]/DMSO	Water bath	66
Cellulose	[AMIM][Cl], [AMIM][Cl]/DMSO	Rotating drum (Cu), high humidity	67
Cellulose/heparin IM	[BMIM][Cl]	Water bath	65
Silk (*B. mori*)	[BMIM][Cl]	Water bath	77
Synthetic polymers			
PMIA	[BMIM][BF_4]	Water bath	64
PS	[BMIM][PF_6]	Aluminium foil	71
PAN	[BMIM][Br]	Rotating drum (Dacron)	63
PLLA[a]	Chloroform/[HMIM][Cl]	Aluminium foil	70

[a] RTIL added as additive (0.039–0.254 mol kg^{-1}).

diamine/potassium thiocyanate (ED/KSCN), and lithium chloride/dimethylacetamide (LiCl/DMAc).[61] All of these systems contain non-volatile compounds that require adaptations to the electrospinning techniques to remove them from the fibers being formed. Incomplete removal of solvent can lead to polymer plasticization and ultimately to partial or complete fiber fusion. Moreover, electrical charge retention in the electrospinning of cellulose from LiCl/DMAc mixtures can result in fibers that arrange vertically in the collector against the gravitational force, and collapse and agglomerate once the electrical field is removed.[62] These are common challenges in the electrospinning of polymers from RTILs, where additional processes are required to preserve fiber morphology during collection.[63–64]

2.1 Strategies for fiber collection and RTIL removal

Nanometer-to-micrometre diameter cellulose fibers were first electrospun from an RTIL ([BMIM][Cl]) by our group.[65] The collection of fibers and removal of the ionic liquid was accomplished utilizing a grounded ethanol coagulation bath, confirming complete RTIL removal by elemental analysis. Later reports on the electrospinning of cellulose from the same ionic liquid used water as coagulant.[66] Ethanol is more effective than water in removing [BMIM][Cl] from cellulose fibers, but it has the drawback that it is highly flammable and can ignite easily. Water/ethanol mixtures can reduce the fire hazard significantly, while improving the kinetics of RTIL removal from the fibers. Stationary coagulation baths are often inefficient at removing non-volatile solvents from electrospun cellulose fibers that do not sink and immerse in the coagulant, as these fibers buildup on the surface of the liquid.[67] Incorporation of surfactants into aqueous coagulation baths and/or recirculation of the coagulant can prevent fiber buildup and agglomeration.[61]

Several other solutions have been developed for fiber collection and removal of non-volatile solvents from electrospun fibers, such as rotating collectors, usually in the form of disks or drums, which include intermittent immersion of fibers in a coagulation bath during rotation,[61] or collection and subsequent immersion in a bath.[63] When rotating drum collectors are used in conjunction with high relative humidity electrospinning environments, as in the case of the cellulose fibers electrospun from 1-allyl-3-methylimidazolium chloride ([AMIM][Cl]),[67] the water present helps rigidify and coagulate the fibers leading to skin formation. This skin maintains fiber shape, and prevents fiber contraction, adherence, and fusion. Some fiber fusion may be advantageous since a small degree of fiber interconnectivity could increase the overall mechanical stability of non-woven mats without significantly decreasing fiber surface area and porosity or increasing fiber diameter.

2.2. Control of fiber morphology through solution properties

While electrospinning is a relatively simple process, the prediction of fiber morphology can be challenging because of the complex relationships between solution properties and spinning parameters that impact fiber thinning. Mathematical models of the electrospinning process suggest that solution conductivity plays a key role in fiber morphology.[68] As mentioned earlier, highly conductive electrospinning solvents often produce ultra-thin, uniform fibers because of the predominance of non-axis-symmetric, whipping instabilities at high charge densities over the axis-symmetric instability modes, which promote droplet and bead formation. RTIL-based polymer solutions exhibit high conductivities because these solvents are composed solely of ions, and can thus facilitate the formation of thin, uniform fibers. For example, poly(*m*-phenylene isophthalamide) (PMIA) fibers electrospun from the RTIL,[BMIM][BF_4] display smaller, more narrowly distributed diameters than fibers formed from a less conductive DMAc/$CaCl_2$ solution.[64] However, RTILs also tend to have very high viscosities, with surface tensions that are typically between that of water and common organic solvents. Thus, droplets or beaded fibers can be formed when the surface tension and viscosity of the spinning solution are sufficiently high to favor axis-symmetric instability modes.[63,66] A way to circumvent this limitation is to decrease the viscosity and surface tension of the spinning solution by increasing its temperature. Temperature-controlled electrospinning is typically achieved by modifying the electrospinning setup with a constant temperature chamber surrounding the syringe.[63,66] This strategy can effectively control fiber morphology since the viscosity of RTILs tends to be a strong function of temperature. Moreover, since the temperature dependence of the viscosity of RTILs usually follows the Vogel-Fulcher-Tammann (VFT) equation,[69] a good prediction of the viscosity at the spinning temperatures can be obtained *a priori* from VFT parameters reported in the literature. For example, temperature control was employed by Wu and coworkers[63] in the electrospinning of polyacrylonitrile (PAN) from [BMIM][Br], observing stable jet formation and smooth and continuous fibers only upon increasing the temperature of the spinning solution to 70, 80, and 85 °C for 3, 4, and 5 wt% solutions, respectively. The increase in temperature led to a striking decrease in viscosity, a moderate decrease in surface tension, and an increase in the conductivity of the solutions. As expected, the lower concentrations exhibited reduced solution viscosities; however, solutions with concentrations below 3 wt% could not allow fiber formation because of insufficient chain entanglement density.

Another strategy is to use a co-solvent to reduce the viscosity and surface tension of the RTIL/polymer solution. For example, the viscosity and surface tension of [AMIM][Cl]/cellulose solutions were decreased by the gradual addition of dimethyl sulfoxide (DMSO), without observing any precipitation of the crystalline polymer even at high co-solvent concentrations.[67] Interestingly, the addition of DMSO also helped increase the conductivity of the spinning solution. Smooth cellulose fibers could be obtained within a range of polymer concentrations and co-solvent ratios when there was a balance between chain entanglement density (viscosity), surface tension, and conductivity that allowed axis-symmetric instabilities to be suppressed. As expected, a high conductivity, combined with low surface tension and viscosity led to decreased fiber diameter.

2.3 RTILs as additives

The important role that conductivity has on the spinnability of a polymer solution has led to the use of RTILs not only as the primary component of the spinning solution, but also as a dopant to enhance the ability of the electrospinning solution to carry charge. For example, small amounts of 1-hexa-3-methylimidazolium chloride ([HMIM][Cl]) were added to chloroform solutions of poly(L-lactic acid) (PLLA) to increase the conductivity of the spinning solutions.[70] The conductive additive led to decreases in the length of the jet and to an earlier onset of the bending stability, ultimately resulting in a five-fold decrease in fiber diameter, and a reduction in fiber polydispersity, as compared to those prepared from chloroform alone. Because the RTIL was not removed from the fibers after deposition, the fibers with higher additive contents were shown to aggregate, intertwine, and fuse, leading to large fiber diameters. The looping of fibers and extensive fusion observed were thought to be exacerbated by the back-building of charge closer to the needle in the highly conductive solutions.

2.4 Fiber crystallinity

Rapid solidification of a polymer in solution can have drastic effects on the polymer crystallinity and consequently on polymer thermal properties. Cellulose has a polymorphous crystalline structure that transforms from type-I to type-II upon native cellulose regeneration. Type-I cellulose has the highest degree of hydrogen bonding. Upon electrospinning cellulose from [BMIM][Cl], Quan *et al.*[66] demonstrated the formation of type-II polymorph fibers with lower crystallinity compared to native cellulose, but much higher crystallinity than present in a regenerated cellulose film. This is thought to be a result of the higher orientation of the cellulose chains in the fiber than in a film. However, thermogravimetric analysis reveals that the cellulose fibers have lower thermal stability than the regenerated films, which is attributable to partial cellulose degradation during the electrospinning process.

A decrease in the crystallinity and the heat resistance of PMIA fibers electrospun from [BMIM][BF_4] compared to the crystallinity of commercial wet-spun fibers has also been reported.[64] Changes in the crystallinity and thermal properties of these fibers are important since PMIA is widely used as a fire resistant material.

2.5 Electrospun composite fibers

Most studies have focused on improving the solubility and spinnability of polymer solutions using RTILs. Few studies have tried to prepare composite fibrous materials having increased functionality. A notable exception is the preparation of cellulose/heparin composite fibers electrospun from RTILs.[65] As mentioned earlier, glycosaminoglycans are insoluble in most organic solvents, but have been shown to be soluble in RTILs containing benzoate anions. Thus, an imidazolium salt of heparin was dissolved in 1-ethyl-3-methylimidazolium benzoate ([EMIM][BA] and mixed with a cellulose/[BMIM][Cl] solution. The fibers obtained from the electrospinning of this mixture showed anticoagulant activity, demonstrating that the high voltage employed in the electrospinning process did not affect the bioactivity of heparin. These composite fibers show promise in the construction of blood-compatible, artificial vessels.

Composite fibers from a synthetic polymer, polystyrene (PS), and an RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF_6]), have been obtained by electrospinning to produce conductive, superhydrophobic surfaces.[71] PS is rendered superhydrophobic due to both the fiber surface roughness and the hydrophobicity of the RTIL that swells it. Moreover, the conductivity imparted by the RTIL can effectively eliminate static-charge accumulation preventing potential fire hazards related to this charge accumulation.

3. Outlook

Electrospinning of biopolymers from RTILs is still in its infancy. There are many opportunities for the RTIL-assisted electrospinning of intractable biopolymers. In addition to cellulose, other structural polysaccharides, including chitin and pectins; proteins, including gelatin, collagen, and enzymes; and nucleic acids, including DNA and RNA, are soluble in RTILs (Table 1). Thus, electrospinning of these biopolymers from RTILs should also be possible under certain conditions. Tunable solubility, a well-recognized property of RTILs, provides a clear advantage in biopolymer electrospinning. However, the versatility of RTILs could also be exploited for tailoring other solution properties relevant to electrospinning, such as viscosity and electrical conductivity. Similarly, the optimization of solution properties using mixtures of RTILs or mixtures of RTILs with common molecular solvents warrants further investigation. An improved fundamental understanding of how electrospinning proceeds in highly conductive, non-volatile solvents might help to explain differences in fiber morphologies observed as compared to the spinning of neutral polymers and polyelectrolytes from organic and aqueous solvents.[70,72–73] Perhaps the most exciting prospect in using RTILs as electrospinning solvents is for the fabrication of biodegradable, biocompatible, and biorenewable fiber composites.

In particular, electrospinning from RTILs offers many opportunities for the formation of hybrid fiber composites of biopolymers and inorganic nanomaterials. The excellent solvent properties of RTILs are not limited to polymers. Enhanced dispersions of several types of inorganic nanomaterials can be prepared in RTILs because their polar, electrolytic nature seems to reduce the tendency of nanoparticles to aggregate.[74] For instance, the organic cations in RTILs have favorable interactions with π-electron-rich compounds, such as single-wall carbon nanotubes (SWNTs), which can form stable gels in ammonium-containing RTILs.[75] Moreover, RTILs can improve the dispersion of certain nanoparticles, such as layered silicates and carbon nanotubes (CNTs), in polymer matrices.[76–77]

Nanoparticles can be incorporated into electrospun biopolymer fibers by direct dispersion in the polymer solution, coaxial spinning to form fibers with a nanoparticle core and a biopolymer sheath, and even by nanoparticle synthesis within the fiber after deposition by including the precursors (usually metal salts) within the polymer solution.

The potential applications for such nanocomposite fibrous materials are far-reaching, since they can combine the desirable properties of biopolymers, with the size-dependent properties of nanoparticles (*e.g.*, magnetic, photonic, chemical, mechanical, and electrical properties), in a high surface area template with characteristic dimensions in the nanoscale range. There are already several review articles that discuss in detail strategies for production of a wide array of functional nanocomposites, as well as their potential applications.[6,78–79] A few of examples of potential biopolymer-based composite fibers electrospun from RTILs, which are expected to provide enhanced functionality in specific applications, are provided below.

Natural silk fibers have outstanding mechanical properties, such as high strength, toughness, elasticity, and resistance to failure. Moreover, depending on their source, silk fibers can show excellent biocompatibility, biodegradability, and oxygen and water permeability. However, the crystalline regions of the fibroin cores in silk exhibit extensive hydrogen bonding and have a hydrophobic nature that makes their dissolution challenging.[47] Imidazolium-based RTILs, particularly those containing chloride and glycine anions, dissolve *Bombyx mori* (*B. mori*) silk.[47,77] Silk and silk-containing nanofibers have been electrospun from [BMIM][Cl],[77] as well as from a few organic solvents including formic acid.[80] Fibrous nanocomposites from *B. mori* silk and SWNTs have been obtained by electrospinning and show significant enhancement in Young's modulus (up to 460%) compared to the pristine electrospun silk fibers.[81] In addition to the impressive mechanical properties of membranes made from silk nanocomposite fibers, silk fibroin and silk fibroin/wool keratose fibers are also capable of binding heavy metal ions because of the presence of carboxylic, sulfonate, and amine groups.[82] Thus, reinforced, silk-containing, fibrous mats electrospun from RTILs should exhibit enhanced mechanical properties due to the presence of dispersed nanofiller together with high affinity towards toxic heavy metals. Such nanocomposite membranes should be ideally suited for filtration applications.

The electrospinning of cellulose composite fibers to obtain membranes suitable for separations, sensing, catalysis, and biomedical applications, is one of the key targets advancing the use of RTILs in this processing technique. Many hydrophobic dyes and complexants are soluble in RTILs and can be incorporated into electrospun, hydrophilic cellulose membranes for detection of contaminants and water treatment. These membranes could allow fast transport of species to active sites and may have improved water permeation and low gas porosities, as compared to synthetic polymer membranes.[74]

In the same manner, the biocompatibility, renewability, and availability of cellulose makes materials based on electrospun fibers ideal supports for enzymes. There are many examples in the literature of the electrospinning of synthetic polymers (and some biopolymers) from organic solvents for enzyme immobilization, and of the application of these fibers in fuel cells, biosensing, and catalysis.[83] However, the intractability of cellulose has thus far prevented the use of this biopolymer in the fabrication of such promising composite membranes. The incorporation of enzymes into cellulose/RTIL mixtures and their deposition to form composite films (non-fibrous) has already been reported. Holbrey *et al.*[74] demonstrated that laccase enzymes immobilized within cellulose films that were coated from RTILs could retain their activity and be used to catalyze oxidation reactions. The same authors demonstrated the RTIL-casting of magnetite/cellulose composite films with ferromagnetic properties. RTIL-electrospinning could allow the fabrication of highly functional nanofibrous membranes with much higher specific surface areas and porosities from these same types of cellulose composites.

Finally, biopolymer/nanoparticle fiber mats could also be of interest in the fabrication of biocompatible and flexible energy devices. Following the rationale employed in the fabrication of energy storage devices based on nanocomposite paper,[36] cellulose/CNT fibers electrospun as dispersions or in a coaxial fashion from an RTIL could form the basis for electrochemical devices in which the CNTs act as the electrode, cellulose as the separator, and the retained ionic liquid as the electrolyte. These integrated, biocompatible, flexible membranes would boast high surface areas and adjustable porosities. In addition, the active use of the RTIL as an electrolyte would allow the replacement of aqueous electrolyte solutions that are prone to evaporation and variable performance.[28] It is important to note that successful devices of this type are likely to be obtained only from highly oriented CNTs at high loadings where percolation allows an uninterrupted path for electrical conduction as is possible using electrospinning.

The relative simplicity and versatility of the electrospinning process, coupled with the unique dissolution capabilities of RTILs, show great promise in promoting the fabrication of

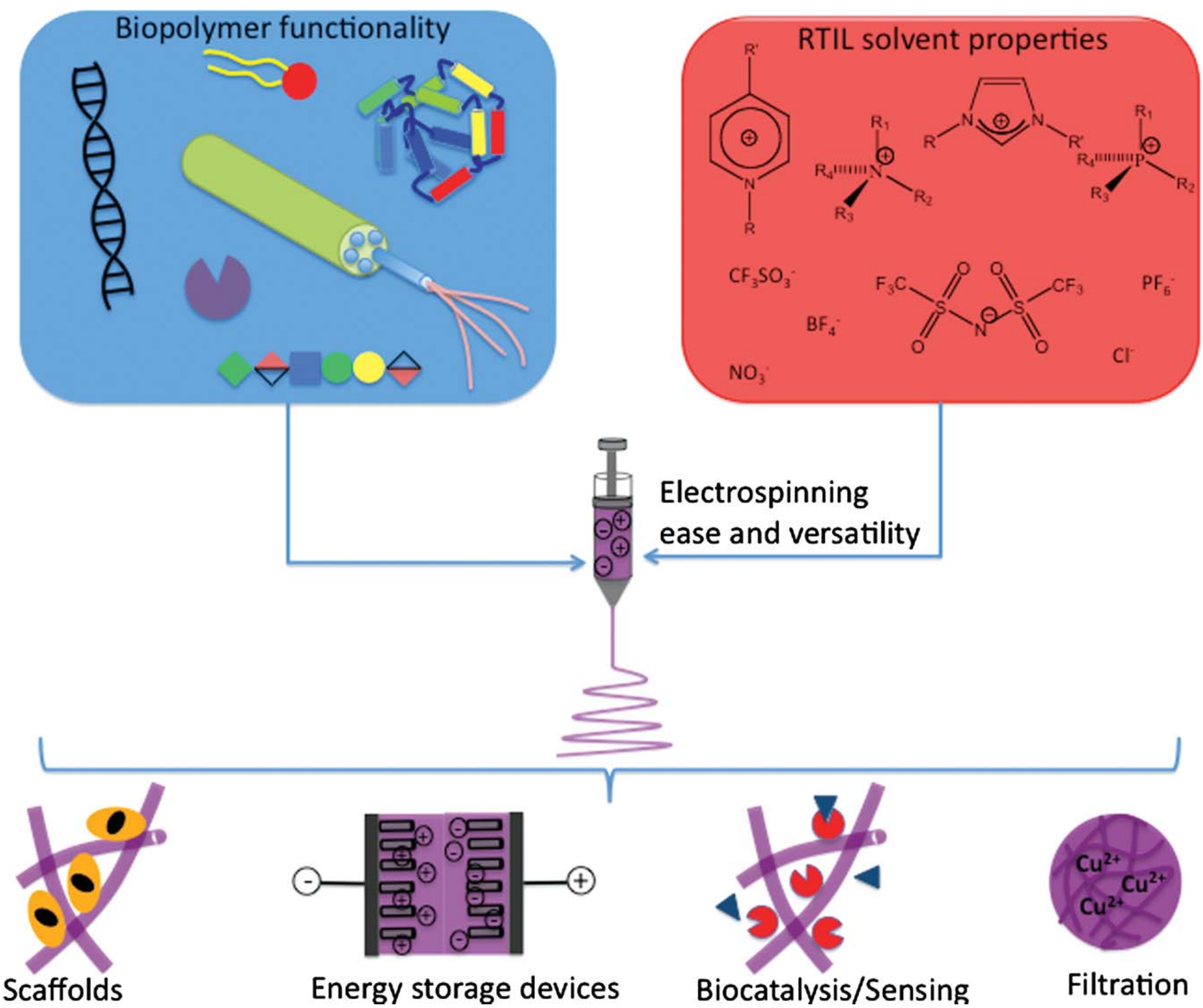

Fig. 3 Schematic diagram of potential functional, biopolymer-based fibrous materials and composites fabricated by electrospinning from RTILs for advanced applications.

a wide array of biopolymer-based fibrous materials and composites with enhanced functionality for a variety of advanced applications (Fig. 3).

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