

TITLE OF THE INVENTION

POLYMER DISSOLUTION AND BLEND FORMATION IN IONIC LIQUIDS

The present application is based on U.S. Provisional Application Serial No. 60/556,484, filed March 26, 2004, the entire contents of which are hereby incorporated by reference.

BACKGROUND OF THE INVENTIONField Of The Invention:

The present invention relates to processes utilizing ionic liquids for the dissolution of various polymers and/or copolymers, the formation of resins and blends, and the reconstitution of polymer and/or copolymer solutions, along with the dissolution and blending of "functional additives" and/or various polymers and/or copolymers to form advanced composite materials.

Background Of The Invention:

The use of ionic liquids as replacements for conventional organic solvents in chemical, biochemical and separation processes has been demonstrated. Graenacher, U.S. Patent 1,943,176, first suggested a process for the preparation of cellulose solutions by heating cellulose in a liquid N-alkylpyridinium or N-arylpyridinium chloride salt, especially in the presence of a nitrogen-containing base such as pyridine. However, that finding seems to have been treated as a novelty of little practical value because the molten salt system was, at the time, somewhat esoteric. This original work was undertaken at a time when ionic

liquids were essentially unknown and the application and value of ionic liquids as a class of solvents had not been realized.

Ionic liquids are now a well-established class of liquids containing solely ionized species, and having melting points largely below 150°C, or most preferably below 100°C. In most cases, ionic liquids (ILs) are organic salts containing one or more cations that are typically ammonium, imidazolium or pyridinium ions, although many other types are known. The range of ionic liquids that are applicable to the dissolution of cellulose are disclosed in U.S. Patent Application 2003/0 157351, herein incorporated in its entirety by reference, and in Swatloski et al., J. Am. Chem. Soc. 2002, 124:4974-4975.

Traditional cellulose dissolution processes, including the cuprammonium and xanthate processes, are often cumbersome or expensive, and require the use of unusual solvents, typically with a high ionic strength. These processes are also used under relatively harsh conditions (Kirk-Othmer "Encyclopedia of Chemical Technology", Fourth Edition 1993, volume 5, p. 476-563). Such solvents include carbon disulfide, *N*-methylmorpholine-*N*-oxide ((NMMO), mixtures of *N,N*-dimethylacetamide and lithium chloride (DMAC/LiCl), dimethylimidazolone/LiCl, concentrated aqueous inorganic salt solutions (ZnCl/H₂O, Ca(SCN)₂/H₂O), concentrated mineral acids (H₂SO₄/H₃PO₄) or molten salt hydrates (LiClO₄·3H₂O, NaSCN/KSCN/LiSCN/H₂O).

These traditional cellulose dissolution processes break the cellulose polymer backbone resulting in regenerated products that contain an average of about 500 to about 600 glucose units per molecule rather than the native larger number of about 1500 or more glucose units per molecule. In addition, processes such as that used in rayon formation, proceed via xanthate intermediates, and tend to leave some residual derivatized (substituent groups bonded to) glucose residues as in xanthate group-containing cellulose.

Other traditional processes that can provide a solubilized cellulose, do so by forming a substituent that is intended to remain bonded to the cellulose, such as where cellulose esters like the acetate and butyrate esters are prepared, or where a carboxymethyl, methyl, ethyl, 2-hydroxyalkyl (for example, hydroxyethyl or hydroxypropyl), or the like group, is added to the cellulose polymer. Such derivative (substituent) formation also usually leads to a lessening of the degree of cellulose polymerization so that the resulting product contains fewer cellobiose units per molecule than the cellulose from which it was prepared.

Physical and chemical processing methods for treating cellulosic resources are numerous. Chemical, enzymic, microbiological and macrobiological catalysts can be used to accelerate the process under conditions selected to be thermodynamically favorable to product formation.

Chemical processes include oxidation, reduction, pyrolysis, hydrolysis, isomerization, esterification, alkoxylation and copolymerization. Chemical and enzymatic hydrolysis of cellulose is discussed in The Encyclopedia of Polymer Science and Technology, 2nd Ed, J. I. Kroschwitz (Ed in Chief), Wiley (New York), 1985. Wood, paper, cotton, rayon, cellulose acetate, and other textiles are a few examples of the broad range of cellulosic materials.

With increasing industrial pollution and consequent governmental regulations, the need to implement "green" processes to prevent pollution and waste production and to utilize renewable resources is becoming increasingly prominent. The efficiency of existing methods for dissolving and derivatizing cellulose can be significantly improved by the availability of suitable solvents for refined and natural cellulose; an example is N-methylmorpholine-N-oxide (NMMO), used as a solvent for non-derivatizing dissolution of cellulose for the production of lyocell fibers. [<http://www.lenzing.com>.]

It has been reported that cellulose can be dissolved in solvents described as ionic liquids that are substantially free of water, nitrogen-containing bases and other solvents (U.S. Patent Application 2003/0157351). However, processes for producing cellulose blends and other polymeric blends with a wide range of possible polymeric components, and a wide range of properties, have yet to be fully developed.

SUMMARY OF THE INVENTION

Accordingly, one object of the invention is to provide a process for preparing a polymeric resin using an ionic liquid.

Another object of the invention is to provide a process for preparing a polymeric blend using an ionic liquid.

Another object of the invention is to provide a process for making a polymer resin or blend with targeted properties.

Another object of the invention is to provide a process for making a polymer resin or blend with targeted rheological properties.

Another object of the invention is to provide a polymer resin consisting of one or more polymers.

Another object of the invention is to provide a polymer blend consisting of two or more polymers.

Another object of the invention is to provide a polymer resin or blend with targeted properties.

Another object of the invention is to provide a polymer resin or blend with targeted rheological properties.

These and other objects of the present invention have been satisfied, either individually or in combinations thereof, by the discovery of a process for the making a

polymeric resin or blend comprising mixing one or more polymeric materials with at least one ionic liquid and separating the resin or blend from the ionic liquid; and the resins and blends prepared therefrom.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a Scanning Electron Micrograph (SEM) of PAN reconstituted from IL, and regeneration into water ($\times 500$).

Fig. 2 is a Thermogravimetric analysis (TGA) of (I) pure PAN and (II) regenerated PAN powder.

Figs. 3A-3F are Scanning Electron Micrographs (SEM) of various cellulose (wood pulp, DP=1056)/ polyacrylonitrile (PAN) blend, wherein (A) is regenerated cellulose; (B) is cellulose/PAN; 20/80 (weight ratio); (C) is cellulose/PAN 40/60; (D) is cellulose/PAN 60/40; (E) is Cellulose/PAN, 80/20; and (F) is Regeneration PAN ($\times 500$ and $\times 5000$).

Figs. 4A-4E are Scanning Electron Micrographs (SEM) of various cellulose/poly-2-hydroxymethylmethacrylate (PHEMA) blends wherein (A) is cellulose/PHEMA 20/80; (B) is cellulose/PHEMA 40/60; (C) is cellulose/PHEMA 60/40(1); (D) is cellulose/PHEMA 60/40(2); and (E) is cellulose/PHEMA 80/20 ($\times 500$ and $\times 5000$).

Figs. 5A-5D are Scanning Electron Micrographs (SEM) of Cellulose/PVA blends at different ratios, wherein (A) is cellulose/PVA 20/80; (B) is cellulose/PVA 40/60; (C) is cellulose/PVA 60/40; and (D) is cellulose/PVA ($\times 500$ and $\times 5000$). Equipment and procedure are similar to Fig. 1.

Figs. 6A-6D are Scanning Electron Micrographs (SEM) of cellulose/ polyaniline emeraldine base (PANI) blends at different ratios, wherein (A) is cellulose/ PANI 20/80;

(B) is cellulose/PHEMA 40/60; (C) is cellulose/PANI 60/40; and (D) is cellulose/PANI 80/20 ($\times 500$ and $\times 5000$).

Figs. 7A-7B are Scanning Electron Micrographs (SEM) of cellulose/Polyethylene glycol -2000 (PEG) blends at different ratios, wherein (A) is cellulose/PEG 40/60; and (B) is cellulose/PEG 60/40. The layer like structure is indicative of an immiscible blend ($\times 300$ and $\times 2000$).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term resin as used herein, includes one or more polymers, one or more copolymers and combinations thereof.

The term blend as used herein, includes two or more polymers, two or more copolymers and combinations thereof, immiscible or miscible at the molecular level or domain level. The term polymer includes a polymer prepared from one monomeric unit.

The term copolymer includes a polymer prepared from two or more monomeric units.

The term polymeric materials includes one or more polymers, copolymers and mixtures thereof.

The present invention provides a process utilizing ionic liquids for the dissolution of various polymers, the formation of polymer resins and blends, and reconstitution of said polymeric solutions. The unique solvation properties of ionic liquids allow for the dissolution of a wide range of polymers, which in turn, allows for the creation of new materials with adjustable properties. Ionic liquids provide a unique opportunity for multiple polymer dissolutions, which allow for the formation of blends comprising binary, ternary and multi-component systems. The reconstituted resins from non-solvents find application in engineering materials, extruded objects, fibers, beads, and membranes.

The processes of the present invention use polymers that contain various repeating monomeric units. These monomer units may contain polar, non-ionic, and charged groups, including, but not limited to, -NH_2 -, -NHR -, -NR_2 -, $\text{-N}^+\text{R}_3\text{X}^-$ -, -O- -, -OH -, -COOH -, -COO^- M^+ -, -SH -, $\text{-SO}_3^-\text{M}^+$ -, $\text{-PO}_3^{2-}\text{M}^{2+}$ -, -PR_3 -, -NH-CO-NH_2 and -NHC(NH)NH_2 . These groups may be present in sufficient numbers along, or pendent to, the polymeric backbone, in polymers, such as, polyacrylamide, polyvinyl alcohol, polyvinyl acetate, poly(N-vinylpyrrolidinone) and poly(hydroxyethyl acrylate). These groups also impact the solubility of the respective polymer. The polymer can have a complex structure due to intramolecular hydrogen bonding, ionic interactions, intermolecular interactions, and chain-chain complexation. These interactions govern the solution properties and performance. Solvent properties such as polarity, charge, hydrogen bonding, interactions between the polymer and the solvent are also important in effective dissolution and blending.

The present invention provides a new process of dissolution and reconstitution of unique polymer resins and blends due to the enhanced solvation properties of ionic liquids. For example, three abundant polysaccharides, cellulose, starch, and chitin do not dissolve in most common solvents directly, due to their unique molecular and supermolecular structure. One way to enhance a polymer's dissolution is to chemically modify it, for example, by adding one or more hydroxyethyl, hydroxypropyl, methyl, carboxymethyl, sulfate, or phosphate groups to the polymer structure. These modifications alter the polymer's aforementioned interactions, thereby, increasing its solubility in common organic solvents and in many cases water. Instead of chemically altering the polymer, the present invention provides a method of processing the virgin polymer using ionic liquids as the solvent, thus lessening chemical usage and processing steps, and making the overall process more environmentally and economically sustainable.

Ionic liquids are a class of solvents composed of ionized species in contrast to traditional organic or aqueous solvents which are molecular nonionics. Ionic liquids are being implemented as potentially green solvents to replace common volatile organic compounds. Ionic liquids are typically comprised of an organic cation usually created by alkylation of a compound, including, but not limited to, imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines, and combinations thereof.

The anionic portion of the ionic liquid can be composed of an inorganic or organic moiety and typically comprises halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates, triflates and noncoordinating anions; and wherein R includes, but is not limited to, hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof. By altering the combination of cations and anions, one has the ability to fine-tune the ionic liquid with the desired solvent properties needed for a specific dissolution/blending.

Ionic Liquids ("ILs") have a more complex solvent behavior compared with traditional aqueous and organic solvent, because ILs are salts and not a molecular, nonionic solvent. Types of interactions between ILs with many solutes, include dispersion, π - π , n - π ,

hydrogen bonding, dipolar and ionic/ charge-charge. The Abraham solvation equation is an important method used to characterize ILs solvent property to understand the polymer dissolution behavior in ILs. Some typical C_4mim ILs interaction parameters are shown in Table 1 below. ILs that have strong dipolarity, hydrogen bond accepting (A) ability, and hydrogen bond donating (B) ability are compared with other solvents that are capable of dissolving cellulose (see table below). C_4mimCl , one of the most unique solvents, shows the largest A ($a = 4.860$) and a strong ability to interact with solute molecules via non-bonding or π -electron interaction ($r = 0.408$). The cation C_4mim , in combination with the anion Cl^- , exhibits significant ability to interact with π - systems of solute molecules (*Anderson, J.L. et. al*). The smaller Gibbs free energies of hydration of Cl^- ($\Delta G_{hyd} = -347$ kJ/mol) shows a larger HBA 4.860, compared to that of 1.660 of $[BF_4]^-$ ($\Delta G_{hyd} = -200$ kJ/mol).

Table 1					
Ionic liquid	R	S	A	B	1
$C_4mim Cl$	0.408	1.826	4.860	-0.121	0.392
$C_4mim BF_4$	-0.141	1.365	1.660	-0.283	0.473
$C_4mim PF_6$	0	1.540	1.369	0	0.439
Dimethylacetamide	.36	1.33	0	.78	.787
Dimethylformamide	.37	1.31	0	.74	.6468
Dimethylsulfoxide	.52	1.74	0	.88	.776

• R is the excess molecular refraction,

- 1 is the molecular volume
 - A is the hydrogen bond acidity parameter
 - B is the hydrogen bond basicity parameter
- S is the polarity/polarisability parameter

Advanced materials prepared using the processes and resins and blends of the invention can be used in an array of technologies. Examples include self-forming nanodevices, intelligent textiles, and new materials for drug delivery, advanced sensors, and separations.

The resins and blends of the present invention are useful as molded or extruded plastic objects, fibers, beads, or films. Moreover, various additives can be added to enhance properties. Regenerated cellulose can be used to encapsulate one or more substances as reported in U.S. 2004/0038031, which is herein incorporated in its entirety by reference.

The present invention provides a process for preparing polymeric resins and blends using one or more ionic liquids. The present invention also provides a separation step wherein the ionic liquid(s) is removed from the polymeric resin or blend. The ionic liquid may be removed by use of a liquid substance that will dissolve the ionic liquid, but not the resin or blend (i.e., a suitable liquid substance that will act as a solvent to the ionic liquid and as a non-solvent to the resin or blend, hereinafter denoted as a "non-solvent"). Suitable non-solvents include, but are not limited to, polar liquid systems, such as water, alcohols and other hydric liquids. In a preferred embodiment, the ionic liquid is removed by the addition of water.

In one embodiment of the invention, the ionic liquid may be a liquid salt complex that exists in the liquid phase between about -70 to about 300°C .

In another embodiment of the invention, the polymeric resin or blend is prepared from two or more polymers or copolymers. In a preferred embodiment, a mixture of at least two polymeric materials are provided in a ratio to yield a resin or blend with predicted

properties, including, but not limited to, chemical, thermal and mechanical properties. Specific properties include, but are not limited to, viscosity, melting point, melt index, surface properties, oxidation resistance and solubilities. In another embodiment, a mixture of at least two polymeric materials are provided in a ratio to yield a polymer blend with predicted domain sizes.

The present invention also provides the mixing of one or more polymers and/or copolymers with one or more ionic liquids. Mixing can be accomplished by any conventional procedure in the art, including, but not limited to, various stirring mechanisms, agitation mechanisms, sonication and vortexing. In a preferred embodiment, the mixture is heated to about 100°C. The addition of heat may be supplied by any conventional and non-conventional heat source, including, but not limited to, a microwave source. It has been found that microwave radiation not only provides heat, but also facilitates the dissolution of polymeric materials in the ionic solvent. It is speculated that the facilitated dissolution may be due to the absorption and resulting increase molecular motions of solute and solvent.

Ionic liquids allow for the dissolution of cellulose without derivatization, in high concentration. Such a solution may be heated to about 100 °C, or to about 80 °C, in an ultrasonic bath. This heating can be effectively accomplished by using microwave radiation supplied by a domestic microwave oven. In one embodiment of the invention, an admixture of hydrophilic ionic liquid and cellulose is heated to a temperature of about 100 to about 150 °C, using microwave radiation.

Polymers and Copolymers

Suitable polymers and copolymers for use in the process of the present invention include, but are not limited to, polymers and copolymers formed by step, chain, ionic, ring-opening and catalyzed polymerizations.

Suitable polymers and copolymers can be derived from natural and synthetic sources, including, but are not limited to, polysaccharides, polyester, polyamide, polyurethane, polysiloxane, phenol polymers, polysulfide, polyacetal, polyolefins, acrylates, methacrylates and dienes. In particular, preferred polymers include, but are not limited to, cellulose, hemicellulose, starch, chitin, silk, wool, poly-2-hydroxymethylmethacrylate, poly-2-hydroxyethylmethacrylate, polyamides, polyesters, polyimideamides, polybenzimidazole, aramides, polyimides, polyvinyl alcohol, polyaniline, polyethylene glycol, polyacrylonitrile, polystyrene, polyethylene oxide with terminal amine groups, linear polyethyleneimine, and branched polyethyleneimine.

Monomers include, but are not limited to, α -olefins, 2-hydroxyalkylmethacrylate, aniline, acrylonitrile, ethylene, isobutylene, styrene, vinyl chloride, vinyl acetate, vinyl alcohol, methyl methacrylate, ethylene glycol, cellobiose, vinylidene chloride, tetrafluoroethylene, formaldehyde, acetaldehyde, vinylpyrrolidinone, butadiene and isoprene.

Ionic Liquids

The ionic liquids comprise one or more cations and one or more anions. In a preferred embodiment of the invention, a mixture of cations and anions is selected and optimized for the dissolution of a particular polymeric blend.

In one embodiment, the cation is preferably derived from an organic compound, including, but not limited to, the following heterocyclics: imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrrolidines, annulenes,

phthalazines, quinazolines and quinoxalines, quinolines, pyrrolidines, isoquinolines, and combinations thereof.

The anionic portion of the ionic liquid preferably comprises at least one of the following groups: halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates, triflates and noncoordinating anions; and wherein R is at least one member selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

In a preferred embodiment, cations that contain a single five-membered ring free of fusion to other ring structures, such as an imidazolium cation are particularly preferred, and the anion of the ionic liquid is preferably a halogen or pseudohalogen. For example, a 1,3-di-(C_1 - C_6 alkyl or C_1 - C_6 alkoxyalkyl)-substituted-imidazolium ion is a particularly preferred cation. The corresponding anion can preferably be a halogen or pseudohalogen. In addition, a 1-(C_1 - C_6 alkyl)-3-(methyl)-imidazolium [C_n mim, where $n=1-6$] cation is also preferred, and a halogen is a preferred anion.

A contemplated ionic liquid is liquid at or below a temperature of about 200 °C, and preferably below a temperature of about 150° C, and above a temperature of about -100°C. For example, N-alkylisoquinolinium and N-alkylquinolinium halide salts have melting points of less than about 200°C. The melting point of N-methylisoquinolinium chloride is about 183 °C, and N-ethylquinolinium iodide has a melting point of about 158 °C. More preferably, a contemplated ionic liquid is liquid (molten) at or below a temperature of about

120 °C, and above a temperature of minus 44 °C (-44 °C). Most preferably, a contemplated ionic liquid is liquid (molten) at a temperature of about -10 to about 100 °C.

Further examples of ionic liquids include, but are not limited to, [C₂mim]Cl, [C₃mim]Cl, [C₄mim]Cl, [C₆mim]Cl, [C₈mim]Cl, [C₂mim]I, [C₄mim]I, [C₄mim][PF₆], [C₂mim][PF₆], [C₃mim][PF₆], [iC₃mim][PF₆], [C₆mim][PF₆], [C₄mim][BF₄], [C₂mim][BF₄], [C₂mim][C₂H₃O₂] and [C₂mim][C₂F₃O₂].

Illustrative 1-alkyl-3-methyl-imidazolium ionic liquids, [C_nmim]X [n=4 and 6, X=Cl⁻, Br⁻, SCN⁻, (PF₆)⁻, (BF₄)⁻] and [C₈mim]Cl have been prepared. The dissolution of cellulose (fibrous cellulose, from Aldrich Chemical Co.) in those illustrative ionic liquids under ambient conditions with heating to 100 °C, with sonication and with microwave heating, has been examined. Dissolution is enhanced by the use of microwave heating. Cellulose solutions can be prepared very quickly, which is energy efficient and provides associated economic benefits.

A contemplated ionic liquid and a solution prepared from such a liquid is substantially free of water or a nitrogen-containing base. As such, such a liquid or solution contains about one percent or less water or a nitrogen-containing base. Thus, when a solution is prepared, it is prepared by admixing the ionic liquid and cellulose in the absence of water or a nitrogen-containing base to form an admixture.

A range of different cations can be employed of those screened from the common sets used to prepare ionic liquids; imidazolium salts appear to be most effective, with the smallest imidazolium cation exhibiting the easiest dissolution. Alkyl-pyridinium salts free of organic base were less effective. Smaller phosphonium and ammonium quaternary salts containing shorter chain alkyl substituents are known, but have higher melting points and are often not liquid within the acceptable range for definition as ionic liquids.

The use of an imidazolium chloride ionic liquid as solvent for cellulose provides a significant improvement over the previously-reported solubility of cellulose in the organic salt/base N-benzylpyridinium chloride/pyridine as discussed in U.S. Patent 1,943,176, and in which the maximum solubility was 5 weight percent. Indeed, additional nitrogen-containing bases as were used in that patent are not required to obtain good solubility of cellulose in the ionic liquids.

Other ionic liquids include, but are not limited to, those ionic liquids disclosed in U.S. Application 2003/0157351 and U.S. Application 2004/0038031, the contents of each being hereby incorporated by reference.

Additives

Any conventional additive used in polymeric formulations can be incorporated into the resins and blends of the present invention. If these additives are incorporated during the dissolution stage of resin or blend, it is important that such additives do not interfere with the solute-solvent and solvent-solvent interactions. Examples of conventional additives include, but are not limited, plasticizers, fillers, colorants, UV-screening agents and antioxidants. Other additives include, but are not limited to those additives disclosed in U.S. Application 2004/0038031.

The inventive process is further illustrated, using the following examples, but there is no intention that the invention be restricted thereto.

EXAMPLES

Example 1 Polyacrylonitrile dissolution in [C₄mim]Cl and reconstitution

Polyacrylonitrile (PAN) is typically processed in polar aprotic solvents such as dimethylformamide, dimethyl-sulfoxide (DMSO), and γ -butyrolactone, as well as a few molten salts such as M^+SCN^- (M: Li, Na, K). Due to the fact that PAN and cellulose are

readily dissolved by the aforementioned solvents, blends of cellulose/PAN are well studied and characterized.

Up to 10 wt% of PAN has been successfully dissolved in the ionic liquid [C₄mim]Cl at room temperature. The solutions of PAN/IL can be reconstituted in a similar fashion to cellulose-in-IL reconstitution. Using water as a coagulating solvent, flocks, fibers, films and molded forms can be generated, depending on the method of regeneration. For example, pouring IL/PAN solutions in the rapidly stirring water will result in a powdery floc, whereas extruding solutions through a syringe into water allows for the formation of fibers/rods. Finally films can be produced using coating rods to form a uniform layer of IL/PAN on a glass plate. Once the films are produced the IL is gently removed using water.

After washing the films with copious amounts of water, they were allowed to dry in an oven at 104 °C. As the water was evaporated the films began to shrink to form hard, porous films with pore sizes ranging from 10-20 µm in diameter, as shown in Fig. 1. Fig. 2 shows TGA curves for pure PAN and reconstituted PAN from [C₄mim]Cl. For the pure PAN the onset of decomposition is approximately 290°C, while the regenerated PAN, exhibits a lower onset temperature for decomposition, but a higher char yield until 800°C. TGA of regenerated PAN indicated a small amount of [C₄mim]Cl might be trapped or encapsulated within the PAN matrix during the regeneration process.

Example 2 Cellulose/ Polyacrylonitrile (PAN) blend in [C₄mim]Cl

A 5% cellulose (DP=1056) and a 2 % PAN (M_w=86,000) solution were each prepared in [C₄mim]Cl. Dissolution was achieved with mixing at 104°C over 48 h time period. The two solutions were then mixed at 104°C in varying proportions; yielding relative composition ranges of the two polymers from 20/80 to 80/20, as a ratio of weight percent of cellulose to PAN. Next the blended solutions were allowed to cool, and then

coagulated as membranes using water. The films were then placed in a water bath and allowed to soak for 24 h, in order to allow the maximum amount of IL to diffuse from the blended composite. Finally the composites were washed several times with water. The resulting soft, flexible cellulose/PAN membranes were dried in the oven for 24 h. The resulting films were then analyzed using SEM and DSC. Figure 3 shows a series of SEM pictures for cellulose/PAN blends. On examination of the photographs, it appears that the surface is homogenous-indicating a miscible blend at all ratios from Fig. 3B to Fig. 3E. The blended materials all have different textures than that of the pure cellulose (A) or the pure PAN (F).

Example 3 Cellulose/ PHEMA blend in [C₄mim]Cl

Blends of cellulose and PHEMA were prepared as above, and displayed similar characteristics to the blends of cellulose/PAN. The cellulose/PHEMA blends formed using [C₄mim]Cl appear to form miscible blends from SEM in Figure 4.

Example 4 Cellulose/ Polyvinyl alcohol (PVA) blend in [C₄mim]Cl

Cellulose/PVA blends were prepared as in the previous examples, and are another example of miscible blends. The cellulose/PVA membranes were colorless with good flexibility. Figure 5 indicates that the cellulose/PVA blends were quite smooth and homogenous.

Example 5 Cellulose with polyaniline base blend. (im miscible example)

Polyaniline base (PANI) is a blue polymer. Compositions of cellulose and PANI are examples of immiscible blends. The preparation of these materials was the same as the

miscible blends. The SEM analysis shown in Figure 6 indicates that the typical phase separation has taken place, especially for the low cellulose percentages. Unlike the previous miscible examples which appeared to be homogeneous, cellulose/PANI blends were not miscible. PANI is a non-conductive polymer, but its polyaniline emerald line base is a conductive polymer; therefore, it should be useful in conductive membranes at specific pH.

Example 6 Cellulose/ Polyethylene glycol -2000 (PEG) blend (immiscible blend)

PEG-2000 showed good dissolution in [C₄mim]Cl at temperature above the melting point of PEG (60 °C). At temperatures below 60°C it would precipitate from solution. Figure 7 shows the apparent phase separation between cellulose and PEG after blending and reconstitution.

Claims:

Claim 1: A process for forming a resin or blend, comprising:

mixing at least one ionic liquid, which is a liquid salt complex that exists in the liquid phase between about -70 to about 300°C , with at least two differing polymeric materials to form a mixture, and adding a non-solvent to the mixture to remove the ionic liquid from the resin or blend.

Claim 2: The process of Claim 1, wherein the mixture is heated to about 100°C .

Claim 3: The process of Claim 1, wherein the number of polymeric materials is two.

Claim 4: The process of Claim 1, wherein the number of polymeric materials is three.

Claim 5: The process of Claim 1, wherein the number of polymeric materials is four.

Claim 6: The process of Claim 1, wherein at least one of the polymeric materials is a member selected from the group consisting of cellulose, hemicellulose, starch, poly-2-hydroxymethylmethacrylate, polyamides, polyesters, polyimideamides, polybenzimidazole, aramides, polyimides, polyvinyl alcohol, polyaniline, polyethylene glycol, polyacrylonitrile, polyethylene oxide with terminal amine groups, linear polyethyleneimine, and branched polyethyleneimine.

Claim 7: The process of Claim 1, wherein the mixture is heated by a microwave.

Claim 8: The process of Claim 1, wherein the at least one ionic liquid comprises at least one organic cation wherein the organic portion is a member selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines,

piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines, and combinations thereof; and at least one anionic group selected from the group consisting of halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates, triflates and noncoordinating anions; and wherein R is a member selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

Claim 9: The process of Claim 1, wherein the non-solvent is water.

Claim 10: A process for forming a polymeric resin or blend comprising mixing a blend of cations and anions of one or more ionic liquids, wherein the blend is selected to optimize solubility of the polymeric resin or blend, with at least two differing polymeric materials, and adding a non-solvent to the mixture to remove the ionic liquid(s) from the resin or blend.

Claim 11: The process of Claim 10, wherein the mixture is heated to about 100°C.

Claim 12: The process of Claim 10, wherein the number of polymeric materials is two.

Claim 13: The process of Claim 10, wherein the number of polymeric materials is three.

Claim 14: The process of Claim 10, wherein the number of polymeric materials is four.

Claim 15: The process of Claim 10, wherein at least one of the polymeric materials is a member selected from the group consisting of cellulose, hemicellulose, starch, poly-2-hydroxymethylmethacrylate, polyamides, polyesters, polyimideamides, polybenzimidazole,

aramides, polyimides, polyvinyl alcohol, polyaniline, polyethylene glycol, polyacrylonitrile, polyethylene oxide with terminal amine groups, linear polyethyleneimine, and branched polyethyleneimine.

Claim 16: The process of Claim 10, wherein the mixture is heated by a microwave.

Claim 17: The process of Claim 10, wherein the one or more ionic liquids comprise at least one organic cation wherein the organic portion is a member selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines, and combinations thereof; and at least one anionic group selected from the group consisting of halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates, triflates and noncoordinating anions; and wherein R is a member selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

Claim 18: The process of Claim 10, wherein the non-solvent is water.

Claim 19: A process for forming a resin or polymer blend with targeted rheological properties, comprising mixing at least one ionic liquid, which is a liquid salt complex that exists in the liquid phase between about -70 to about 300°C , with at least two differing polymeric materials, in a ratio to give a polymer blend with predicted properties, to form a

mixture, and adding a non-solvent to the mixture to remove the ionic liquid from the resin or blend.

Claim 20: The process of Claim 19, wherein the mixture is heated to about 100°C.

Claim 21: The process of Claim 19, wherein the number of polymeric materials is two.

Claim 22: The process of Claim 19, wherein the number of polymeric materials is three.

Claim 23: The process of Claim 19, wherein the number of polymeric materials is four.

Claim 24: The process of Claim 19, wherein at least one of the polymeric materials is a member selected from the group consisting of cellulose, hemicellulose, starch, poly-2-hydroxymethylmethacrylate, polyamides, polyesters, polyimideamides, polybenzimidazole, aramides, polyimides, polyvinyl alcohol, polyaniline, polyethylene glycol, polyacrylonitrile, polyethylene oxide with terminal amine groups, linear polyethyleneimine, and branched polyethyleneimine.

Claim 25: The process of Claim 19, wherein the mixture is heated by a microwave.

Claim 26: The process of Claim 19, wherein the at least one ionic liquid comprises at least one organic cation wherein the organic portion is a member selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines, and combinations thereof; and at least one anionic group selected from the group consisting

of halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates, triflates and noncoordinating anions; and wherein R is a member selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

Claim 27: The process of Claim 19, wherein the non-solvent is water.

Claim 28: A resin or blend, comprising at least two differing polymeric materials isolated from one or more ionic liquids.

Claim 29: The process of Claim 28, wherein the mixture is heated to about 100°C.

Claim 30: The process of Claim 28, wherein the number of polymeric materials is two.

Claim 31: The process of Claim 28, wherein the number of polymeric materials is three.

Claim 32: The process of Claim 28, wherein the number of polymeric materials is four.

Claim 33: The process of Claim 28, wherein at least one of the polymeric materials is a member selected from the group consisting of cellulose, hemicellulose, starch, poly-2-hydroxymethylmethacrylate, polyamides, polyesters, polyimides, polybenzimidazoles, polybenzoximide, aramides, polyimides, polyvinyl alcohol, polyaniline, polyethylene glycol, polyacrylonitrile, polyethylene oxide with terminal amine groups, linear polyethyleneimine, and branched polyethyleneimine.

Claim 34: The process of Claim 28, wherein the mixture is heated by a microwave.

Claim 35: The process of Claim 28, wherein the at least one ionic liquid comprises at least one organic cation wherein the organic group is a member selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiozoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiozoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines, and combinations thereof; and at least one anionic group selected from the group consisting of halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates, triflates and noncoordinating anions; and wherein R is a member selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl, substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.

Claim 36: The process of Claim 28, wherein the amounts of the at least two differing polymeric materials are adjusted to produce a targeted property.

Claim 37: The process of Claim 28, wherein the amounts of the at least two differing polymeric materials are adjusted to produce a targeted rheological property.

Claim 38: A mixture comprising at least two differing polymeric materials and one or more ionic liquids.

Claim 39: The process of Claim 38, wherein the mixture is heated to about 100°C.

Claim 40: The process of Claim 38, wherein the number of polymeric materials is two.

Claim 41: The process of Claim 38, wherein the number of polymeric materials is three.

Claim 42: The process of Claim 38, wherein the number of polymeric materials is four.

Claim 43: The process of Claim 38, wherein at least one of the polymeric materials is a member selected from the group consisting of cellulose, hemicellulose, starch, poly-2-hydroxymethylmethacrylate, polyamides, polyesters, polyimideamides, polybenzoinide, aramides, polyimides, polyvinyl alcohol, polyaniline, polyethylene glycol, polyacrylonitrile, polyethylene oxide with terminal amine groups, linear polyethyleneimine, and branched polyethyleneimine.

Claim 44: The process of Claim 38, wherein the mixture is heated by a microwave.

Claim 45: The process of Claim 38, wherein the at least one ionic liquid comprises at least one organic cation wherein the organic group is a member selected from the group consisting of imidazoles, pyrazoles, thiazoles, isothiazoles, azathiazoles, oxothiazoles, oxazines, oxazolines, oxazaboroles, dithiazoles, triazoles, selenozoles, oxaphospholes, pyrroles, boroles, furans, thiophenes, phospholes, pentazoles, indoles, indolines, oxazoles, isoxazoles, isotriazoles, tetrazoles, benzofurans, dibenzofurans, benzothiophenes, dibenzothiophenes, thiadiazoles, pyridines, pyrimidines, pyrazines, pyridazines, piperazines, piperidines, morpholones, pyrans, annolines, phthalazines, quinazolines and quinoxalines, and combinations thereof; and at least one anionic group selected from the group consisting of halogens, BX_4^- , PF_6^- , AsF_6^- , SbF_6^- , NO_2^- , NO_3^- , SO_4^{2-} , BR_4^- , substituted or unsubstituted carboranes, substituted or unsubstituted metallocarboranes, phosphates, phosphites, polyoxometallates, substituted or unsubstituted carboxylates, triflates and noncoordinating anions; and wherein R is a member selected from the group consisting of hydrogen, alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heteroalkyl, heterocycloalkyl,

substituted heterocycloalkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, alkoxy, aryloxy, acyl, silyl, boryl, phosphino, amino, thio, seleno, and combinations thereof.