525 Solutions, Inc. Publications Related to Cellulose

1. Recent advances in the electrospinning of biopolymers

By Shamshina, Julia L.; Rogers, Robin D.

Edited By:Horzum, Nesrin

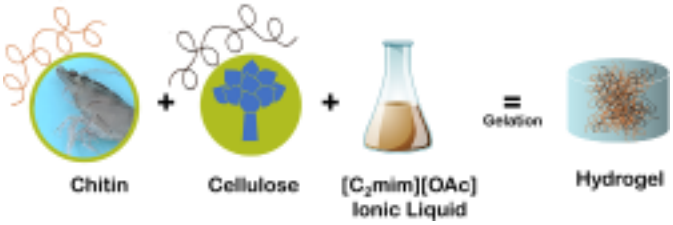
From Green Electrospinning (2019), 189-216. DOI:10.1515/9783110581393-008

Polymers constitute the largest group of chems. that are currently used for manufg. of nanofibers via electrospinning. Among those, use of synthetic polymers is nearly exclusive, mainly because of ease of their handling either through soln. or melt processing. In recent years, there has been a growing shift toward the use of biopolymers including cellulose, chitin, and chitosan, because of many attractive properties of biopolymers (e.g., tissue biocompatibility and biodegradability), which inspired multiple big industry players in using them for the development of materials of the future. Yet, traditional electrospinning methods from common solvents (such as volatile org. solvents) are not suitable for biopolymers due to their insoly. in those solvents. This chapter focuses on recent advances in the electrospinning of biopolymers, which led to the development of an enabling technol. based on a new class of materials known as ionic liqs. (literally liq. salts) that allow electrospinning of virtually any biopolymer directly from its natural source. This innovative process technol. leads to significant productivity enhancement, waste minimization, lower carbon footprint, and greener, more sustainable products and processes, as well as provides access to new greener products across a wide swath of industry.

2. 110th Anniversary: High-Molecular-Weight Chitin and Cellulose Hydrogels from Biomass in Ionic Liquids without Chemical Crosslinking

By Berton, Paula; Shen, Xiaoping; Rogers, Robin D.; Shamshina, Julia L.

From Industrial & Engineering Chemistry Research (2019), 58(43), 19862-19876. DOI:10.1021/acs.iecr.9b03078



Cellulose, chitin, and composite 3D hydrogels and membranes were fabricated without any chem. modification from high-mol.-wt. chitin and cellulose-rich material (CRM) extd. from shrimp shell or poplar wood, resp., using the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]). The hydrogels were prepd. by redissoln. of the extd. biopolymers in the same IL, or in a one-pot process directly from a soln. of the biomass after extn., followed by molding/gelation ("3D gels") or casting (membranes), and then washing. For comparison, the prepn. of gels was attempted using com. microcryst. cellulose or chitin. From all of the sources, the regenerated CRM or chitin required significantly lower load. Hydrogels were also converted to aerogels via transformation to alcogels and then Sc-CO_2 drying, giving materials of low d., high porosity, favorable compressibility, high water uptake, and moderate antioxidant activity. Air-dried membranes were dense, of high tensile strength, and exhibited high water-vapor transmission.

3. Biopolymeric microbeads as alternatives to synthetic plastics

By Shamshina, Julia L.; Zavgorodnya, Oleksandra; Rogers, Robin D.

From Household and Personal Care Today (2018), 13(4), 9-12. Language: English, Database: CAPLUS

Biopolymeric beads can be used as alternatives to synthetic microplastics that have recently been taken out of prodn. by many healthcare and cosmetic industry players as a result of governmental regulations. We have recently reported an innovative technique for biopolymeric beads prepn. from chitin and cellulose involving ionic liqs. (ILs) via initial dissoln. of the biopolymers in the IL followed by rapid stirring in a coagulation bath. Chitin beads possess a large sp. surface area of 24.93 m^2/g, suggesting their micro- and mesoporosity which could make them suitable delivery vehicles for a variety of uses as sustainable, biodegradable, non-toxic, and biocompatible materials. Recent establishment of Mari Signum Mid-Atlantic, LLC as an industrial-scale chitin processing facility and thus large-scale and stable, consistent supply of chitin translates into a very exciting opportunity for scaling up this technol. and aligns closely with the Societal need to remove plastics from the environment.

~1 Citing

4. Printing of biopolymers from ionic liquid

By Rogers, Robin D.; Zavgorodnya, Oleksandra; Shamshina, Julia L.; Gurau, Gabriela

From PCT Int. Appl. (2019), WO 2019173689 A1 20190912, Language: English, Database: CAPLUS

FIG. 1B

The invention relates to a method of printing a three-dimensional (3D) article, comprising: extruding a printing compn. from a deposition nozzle moving relative to a substrate, the printing compn. comprising a biopolymer dissolved in an ionic liq. solvent; depositing one or more layers comprising the printing compn. in a predetd. pattern on the substrate; and treating the one or more layers to form the 3D article. A 3D printed article derived from a method of the invention is also claimed. The invention also relates to a printing compn., consisting essentially of: a biopolymer present in an amt. of 0.1 - 50 wt%, preferably 0.1 - 25 wt%, based on the wt. of the printing compn.; a synthetic polymer, wherein the biopolymer and the synthetic polymer are in a wt. ratio of 1:0.1 - 1:20, preferably 1:1 - 1:20, more preferably 1:1 - 1:10; an ionic liq. solvent for dissolving the biopolymer and synthetic polymer; and a 3D printing additive, preferably selected from a biol. active compd., a plasticizer, a pigment, a fire retardant, a catalyst, a cross-linker, a heat or light stabilizer, an org. or inorg. filler such as a

nano-filler, a fiber reinforcement, or a combination thereof.

5. Enhanced heavy metal adsorption ability of lignocellulosic hydrogel adsorbents by the structural support effect of lignin

By Shen, Xiaoping; Xie, Yanjun; Wang, Qingwen; Yi, Xin; Shamshina, Julia L.; Rogers, Robin D.

From Cellulose (Dordrecht, Netherlands) (2019), 26(6), 4005-4019. DOI:10.1007/s10570-019-02328-w

Cellulose beads possess some adsorption capacities for heavy metal ions, but the effect of lignin remaining in the beads on the adsorption behavior is not clear yet. In this study, lignocellulosic and cellulosic hydrogel beads were prepd. by ionic liq. (IL) dissoln. and reconstitution in water and further functionalization through magnetization and carboxymethylation. Compared to pure cellulosic beads made from Kraft pulp and microcryst. cellulose, the presence of lignin in the lignocellulosic beads from IL-extd. cellulose-rich material (CRM) helped support the porous structure, leading to a higher hydroxyl no. and porosity, and thus higher efficacy in magnetization and carboxymethylation. CRM beads, therefore, exhibited greater Cu^{2+} and Pb^{2+} uptake than the cellulosic beads both before and after modification. However, excessive lignin in the beads prepd. directly from poplar wood powder caused neg. effects on the adsorption capacity due to agglomeration and occlusion of the adsorptive sites.

6. Scaling-up ionic liquid-based technologies: How much do we care about their toxicity? Prima Facie information on 1-ethyl-3-methylimidazolium acetate

By Ostadjoo, Shaghayegh; Berton, Paula; Shamshina, Julia L.; Rogers, Robin D.

From Toxicological Sciences (2018), 161(2), 249-265. DOI:10.1093/toxsci/kfx172

A review. The potential of the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) to dissolve a variety of biopolymers such as cellulose and chitin, makes it an attractive candidate for scaled-up industrial utilization. In fact, the first steps towards its use at industrial scale have been taken. This increases the urgency to fill the knowledge gaps in its toxicity and environmental impact in order to predict and control its environmental fate. In this mini-review, we discuss the available literature surrounding this key IL. The literature (through the anal. of toxicity of the anion and the cation sep.) suggests that [C_2mim][OAc] is a relatively safe choice for industrial applications. However, because the IL should be considered as a compd., with unique properties arising from the interactions between the ions, comprehensive toxicity information for this particular IL is still required. To decide, prima facie, if this IL is toxic or not, evaluation of its influence on human health and ecotoxicity is needed prior to its large scale utilization. We chose in this mini-review to focus on toxicity surrounding this IL and evaluate what is known and what is not. Here with all the information in hand, we hope that the urgent need for [C_2mim][OAc] toxicol. assessment before it can be used in numerous technologies is highlighted. In the near future, we expect that the assessment of toxicity and environmental fate and impact can be integrated directly into any research into the industrial utilization of this IL and any others contemplated for industrial application.

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7. Graphene-biopolymer composite materials and methods of making thereof

By Rogers, Robin D.; Zavgorodnya, Oleksandra; Shamshina, Julia L.; Gurau, Gabriela

From PCT Int. Appl. (2018), WO 2018176037 A1 20180927, Language: English, Database: CAPLUS

Methods for making graphene-biopolymer composite materials are described. The methods can comprise contacting an ionic liq. with a biopolymer and graphene, thereby forming a mixt.; contacting the mixt. with a non-solvent, thereby forming the graphene-biopolymer composite material in the non-solvent; and collecting the graphene-biopolymer composite material from the non-solvent.

8. In Search of Stronger/Cheaper Chitin Nanofibers through Electrospinning of Chitin-Cellulose Composites Using an Ionic Liquid Platform

By Shamshina, Julia L.; Zavgorodnya, Oleksandra; Choudhary, Hemant; Frye, Brandon; Newbury, Nathaniel; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2018), 6(11), 14713-14722. DOI:10.1021/acssuschemeng.8b03269

The ability of the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) to solubilize natural biopolymers (e.g., chitin and cellulose) without any chem. modification has been used to develop a one-pot process to prep. a spinning dope by extg. chitin from shrimp shell, codissolving microcryst. cellulose (MCC, DP = 270), and electrospinning nanomats from shrimp shell-ext./MCC solns. The resulting spinning dopes were prepd. with optimal viscosity of 380 to 900 cP, and cond. and surface tension of ~2.8 mS/cm and ~36 dyn/cm, resp.; however, nanofibers could only be prepd. when the chitin/MCC ratios in SS-ext./MCC soln. were between 9/1 and 6/4. Compared to nanomats electrospun from shrimp shell-ext. soln., 7/3 chitin/MCC composite nanomats demonstrated a 2-fold improvement in hardness and 3-fold improvement in elasticity, although further increase in MCC content resulted in lowering both parameters which nonetheless were higher than the pure chitin nanomats. This one pot process for prepg. spinning dopes directly from shrimp shell-ext. is a viable method to prep. chitin/MCC composites of improved strength/elasticity at lower costs.

9. Electrospinning of biopolymers and biopolymeric composites from ionic liquids

By Zavgorodnya, Oleksandra; Shamshina, Julia L.; Rogers, Robin D.

From Abstracts of Papers, 254th ACS National Meeting & Exposition, Washington, DC, USA, August 20-24, 2017 (2017), POLY-504. Language: English, Database: CAPLUS

Electrospining of biopolymers as an alternative to synthetic plastic has gained significant attention due to raised concerns for the environment. Among the biopolymers that can be used for electrospinning, native chitin, extd. from crustacean shells using the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) can be electrospun into interconnected fiber networks. Electrospinning of chitin results in high surface area nanofibrous mats which are unique due to the presence of N-acetyl group in chitin structure that can easily be converted into reactive amines and be used for tethering any functionality to the structure. Furthermore, chitin can be electrospun with variety of biopolymers including cellulose to yield composite nano- and microfibrous materials or can be used as a support for applications in catalysis. However, practical application of electrospun chitin and chitin composites requires scale-up. Here, we will present our efforts to develop large scale electrospinning and ultimate applications for the resulting products.

10. Coagulation of biopolymers from ionic liquid solutions using co2

By Rogers, Robin D.; Barber, Patrick S.; Griggs, Chris S.; Gurau, Gabriela; Lu, Xingmei; Zhang, Suojiang

From U.S. Pat. Appl. Publ. (2015), US 20150368371 A1 20151224, Language: English, Database: CAPLUS

Disclosed herein are processes for providing a biopolymer from a biomass or source of chitin using ionic liqs. The processes involve contacting a biomass or source of chitin with an ionic liq. to produce a biopolymer comprising soln. and pptg. the biopolymer from the soln. with supercrit. CO_2, gaseous CO_2, or combinations thereof.

11. Ionic liquid systems for the processing of biomass, their components and/or derivatives, and mixtures thereof

By Rahman, Mustafizur; Rodriguez, Hector; Sun, Ning; Swatloski, Richard P.; Daly, Daniel T.; Rogers, Robin D.

From U.S. (2014), US 8668807 B2 20140311, Language: English, Database: CAPLUS

Disclosed herein are compns. and methods that involve ionic liqs. and biomass. Multiphasic compns. involving ionic liqs. and a polymer and uses of such compns. for fractioning various components of biomass are disclosed. Methods of making and using

compns. comprising an ionic liq., biomass, and a catalyst are also disclosed.

12. Methods for dissolving polymers using mixtures of different ionic liquids and compositions comprising the mixtures

By Rogers, Robin D.; Daly, Daniel T.; Gurau, Gabriela

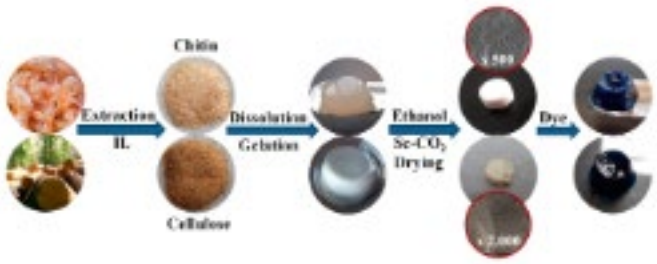
From U.S. Pat. Appl. Publ. (2012), US 20120216705 A1 20120830, Language: English, Database: CAPLUS

Disclosed are methods for dissolving biopolymers and synthetic polymers using mixts. of different ionic liqs. and compns. comprising the mixt. The methods involve contacting a polymer with a mixt. of ionic liqs. to provide a compn. of polymer and the mixt.; the mixt. of ionic liqs. is prepd. by either mixing ionic liqs. or by a process comprising reacting ionic liq. precursors in one-pot to form the ionic liqs.

13. Comparison of Hydrogels Prepared with Ionic-Liquid-Isolated vs Commercial Chitin and Cellulose

By Shen, Xiaoping; Shamshina, Julia L.; Berton, Paula; Bandomir, Jenny; Wang, Hui; Gurau, Gabriela; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2016), 4(2), 471-480. DOI:10.1021/acssuschemeng.5b01400



Phys. and/or covalently linked (chem.) hydrogels were prepd. from chitin and cellulose extd. with ionic liq. from shrimp shells and wood biomass, resp., and compared with hydrogels prepd. from com. available biopolymers, practical grade chitin, and microcryst. cellulose. The highly porous aerogels were formed by initial dissoln. of the biopolymers in NaOH/urea aq. systems using freeze/thaw cycles, followed by thermal treatment (with or without epichlorohydrin as a cross-linker) and supercrit. CO_2 drying. The ionic-liq.-extd. cellulose pulp and chitin, as well as practical grade chitin could form both stable phys. and chem. hydrogels, whereas biopolymers of lower apparent mol. wt. such as microcryst. cellulose required a covalent cross-linker for hydrogel formation and com. available pure chitin was not suitable for the prepn. of hydrogels of either type. Hydrogels prepd. from the ionic-liq.-extd. biopolymers exhibited properties substantially different from those made from the com. available biopolymers. Loading of an active ingredient into the hydrogel and its subsequent release was demonstrated using indigo carmine and revealed that the release rate was controlled mainly

by the biopolymer concn. of the gel network.

14. Hydrogels based on cellulose and chitin: fabrication, properties, and applications

By Shen, Xiaoping; Shamshina, Julia L.; Berton, Paula; Gurau, Gabriela; Rogers, Robin D.

From Green Chemistry (2016), 18(1), 53-75. DOI:10.1039/C5GC02396C

A review. This review is focused on the fabrication, properties, and applications of hydrogels prepd. from two of the most abundant biopolymers on earth, cellulose and chitin. The review emphasizes the latest developments in hydrogel prepn. (including solvent systems, crosslinker types, and prepn. methods, which det. the "greenness" of the process) using these biocompatible and biodegradable biopolymers. The prepn. of both phys. (without covalent crosslinks) and chem. (with covalent crosslinks) hydrogels via dissoln./gelation is discussed. Addnl., formation of injectable thermoset and/or pH sensitive hydrogels from aq. solns. of derivs. (chitosan, Me cellulose, and hydroxypropylmethyl cellulose) with or without a crosslinker are discussed. This review also compares the design parameters for different applications of various pure and composite hydrogels based on cellulose, chitin, or chitosan, including applications as controlled and targeted drug delivery systems, improved tissue engineering scaffolds, wound dressings, water purifn. sorbents, and others.

15. Dissolution of Biomass Using Ionic Liquids

By Wang, Hui; Gurau, Gabriela; Rogers, Robin D.

From Structure and Bonding (Berlin, Germany) (2014), 151(Structures and Interactions of Ionic Liquids), 79-105. DOI:10.1007/978-3-642-38619-0_3

Ionic liqs. (ILs) have been shown to be effective in dissolving cellulose and other biopolymers that are structurally quite different from each other. It would be quite interesting to figure out the common points of the dissoln. of structurally different biopolymers in various kinds of ILs. In this chapter, the IL dissoln. of pure biopolymers such as cellulose, lignin, hemicellulose, chitin, silk, wool, etc., is reviewed. By analyzing the structures of the biopolymers and those of the ILs, it is concluded that the dissoln. of most of these biopolymers (except lignin) in ILs is mainly due to the disruption of the intra- and intermol. hydrogen bonding in the polymers by the ILs. Both the cations and anions of the ILs influence the dissoln. process, although current work suggests the anions have a larger effect.

16. Homogeneous blending of chitin with biopolymers for advanced biodegradable sorbents for uranium extraction from

seawater

By Bandomir, Jenny; Kelley, Steven P.; Shamshina, Julia L.; Gurau, Gabriela; Rogers, Robin D.

From Abstracts of Papers, 249th ACS National Meeting & Exposition, Denver, CO, United States, March 22-26, 2015 (2015), I+EC-47. Language: English, Database: CAPLUS

Our group is investigating an ionic liq. based process for extg. and purifying chitin from biomass for use as a renewable and biodegradable sorbent backbone from the extn. of uranium from seawater. One advantage of this approach is that ionic liqs. such as 1-ethyl-3-methylimidazolium acetate can ext. biopolymers from other biomass sources as well, such as cellulose and lignin from wood pulp. This can allow us to prep. novel, entirely biorenewable composites directly from biomass by homogeneously combining biopolymer solns. and spinning from the resulting blend. We have selected cellulose and lignin as additives to improve the physicochem. properties of chitin sorbents due to their extreme abundance as renewable resources and advantageous properties. Cellulose chitin blends exhibit improved strength relative to the individual materials, and lignin is a crosslinking agent with anti-microbial properties which may help to control the rate of biodegrdn. Here we present the prepn. of composite materials from these three biopolymers and examine the effects of cellulose and lignin on sorbent strength, uranium uptake capacity, and biodegrdn. as a function of compn.

17. Catalytic conversion of biomass in ionic liquids

By Wang, Hui; Block, Leah E.; Rogers, Robin D.

From RSC Catalysis Series (2014), 15(Catalysis in Ionic Liquids), 1-29. Language: English, Database: CAPLUS

A review. This article describes the catalytic conversion of biomass in ionic liqs. In this article the catalytic dissoln. and degrdn. of pure cellulose, lignin (including lignin model compd.), hemicellulose and raw lignocellulosic biomass materials in the presence of ionic liq. were discussed.

18. Oxygen Enhances Polyoxometalate-based Catalytic Dissolution and Delignification of Woody Biomass in Ionic Liquids

By Cheng, Fangchao; Wang, Hui; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2014), 2(12), 2859-2865. DOI:10.1021/sc500614m

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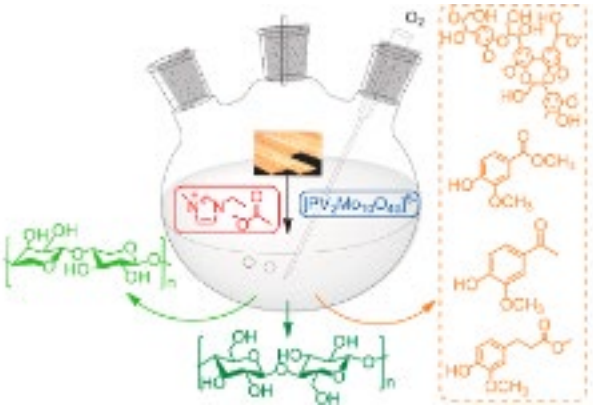
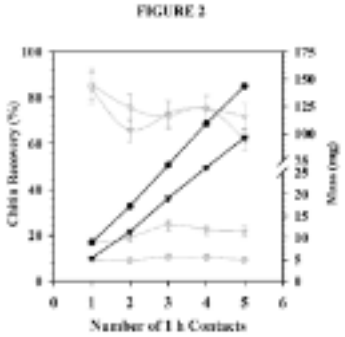


Complete dissoln. and over 90% delignification of Southern yellow pine (<0.125 mm) can be achieved in the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) at 110 °C for 6 h by the catalytic action of polyoxometalate in the presence of an appropriate O_2 feed. Cellulose-rich materials (CRMs), or pulps, and hemicellulose with a limited lignin content and free lignin were subsequently recovered by adding antisolvents to the IL soln., followed by filtration. Comparison of wood processing in [C_2mim][OAc]/POM with or without O_2 revealed that the presence of oxygen can greatly facilitate the dissoln., delignification, sepn. of hemicellulose, and oxidn. of lignin. The main products from lignin oxidn. were extd. from the IL using benzene and then THF, and were shown by gas chromatog.-mass spectrometry (GC-MS) to be Me vanillate, acetovanillone, vanillic acid, Me 3-(3-methoxy-4-hydroxyphenyl) propionate, and Me 4-hydroxybenzoate. This study suggests that treating wood with a [C_2mim][OAc]/POM/O_2 system could be a viable strategy to sep. wood components with high efficiency and obtain cellulose with high purity for materials or biorefinery applications, particularly those that desire smaller lignin oxidn. fragments for further processing.

19. Coagulation of biopolymers from ionic liquid solutions using CO2

By Rogers, Robin D.; Barber, Patrick S.; Griggs, Chris S.; Gurau, Gabriela; Lu, Xingmei; Zhang, Suojiang

From PCT Int. Appl. (2014), WO 2014125438 A1 20140821, Language: English, Database: CAPLUS



Disclosed herein are processes for providing a biopolymer from a biomass or source of chitin using ionic liqs. The processes involve contacting a biomass or source of chitin with an ionic liq. to produce a biopolymer comprising soln. and pptg. the biopolymer from the soln. with supercrit. CO_2, gaseous CO_2, or combinations thereof. An ionic liq. contg. 3-ethyl-1-methyl-1H-imidazol-3-ium acetate was used to prep. chitin with the help of a microwave oven.

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20. Facile pulping of lignocellulosic biomass using choline acetate

By Cheng, Fangchao; Wang, Hui; Chatel, Gregory; Gurau, Gabriela; Rogers, Robin D.

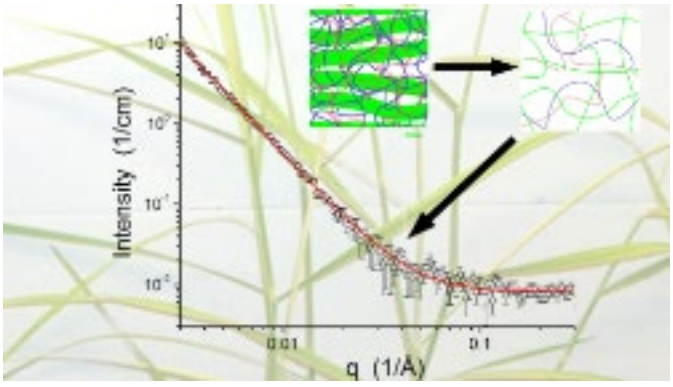
From Bioresource Technology (2014), 164, 394-401. DOI:10.1016/j.biortech.2014.05.016

Treating ground bagasse or Southern yellow pine in the biodegradable ionic liq. (IL), choline acetate ([Cho][OAc]), at 100 °C for 24 h led to dissoln. of hemicellulose and lignin, while leaving the cellulose pulp undissolved, with a 54.3% (bagasse) or 34.3% (pine) redn. in lignin content. The IL soln. of the dissolved biopolymers can be sepd. from the undissolved particles either by addn. of water (20 wt% of IL) followed by filtration or by centrifugation. Hemicellulose (19.0 wt% of original bagasse, 10.2 wt% of original pine, contg. 14-18 wt% lignin) and lignin (5.0 wt% of original bagasse, 6.0 wt% of original pine) could be subsequently pptd. The pulp obtained from [Cho][OAc] treatment can be rapidly dissolved in 1-ethyl-3-methylimidazolium acetate (e.g., 17 h for raw bagasse vs. 7 h for pulp), and pptd. as cellulose-rich material (CRM) with a lower lignin content (e.g., 23.6% for raw bagasse vs. 10.6% for CRM).

21. Physical Insight into Switchgrass Dissolution in Ionic Liquid 1-Ethyl-3-methylimidazolium Acetate

By Wang, Hui; Gurau, Gabriela; Pingali, Sai Venkatesh; O'Neill, Hugh M.; Evans, Barbara R.; Urban, Volker S.; Heller, William T.; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2014), 2(5), 1264-1269. DOI:10.1021/sc500088w

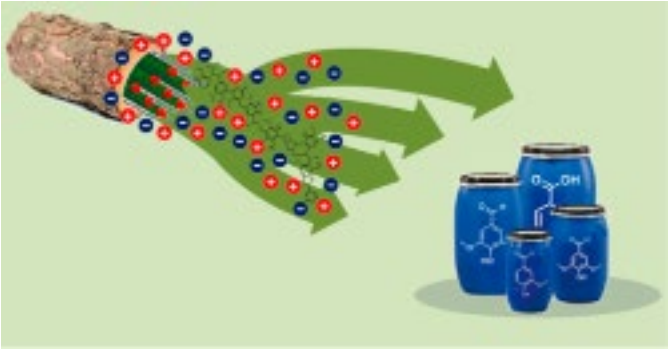


Small-angle neutron scattering was used to characterize solns. of switchgrass and the constituent biopolymers cellulose, hemicellulose, and lignin, as well as a phys. mixt. of them mimicking the compn. of switchgrass, dissolved in the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate. The results demonstrate that the IL dissolves the cellulose fibrils of switchgrass, although a supramol. biopolymer network remains that is not present in solns. of the individual biopolymers and that does not self-assemble in a soln. contg. the phys. mixt. of the individual biopolymers. The persistence of a network-like structure indicates that dissolving switchgrass in the IL does not disrupt all of the phys. entanglements and covalent linkages between the biopolymers created during plant growth. Reconstitution of the IL-dissolved switchgrass yields carbohydrate-rich material contg. cellulose with a low degree of crystallinity, as detd. by powder x-ray diffraction, which would impact potential downstream uses of the biopolymers produced by the process.

22. Review: Oxidation of Lignin Using Ionic Liquids-An Innovative Strategy To Produce Renewable Chemicals

By Chatel, Gregory; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2014), 2(3), 322-339. DOI:10.1021/sc4004086



A review. Lignin, one of the three subcomponents of lignocellulosic biomass (along with cellulose and hemicellulose), represents more than 20% of the total mass of the Earth's biosphere. However, essentially due to its complex structure, this renewable polymer derived from biomass is mainly burned as a source of energy in the pulp and paper industry. Today, the valorization of lignin into the prodn. of chem. feedstocks represents a real challenge in terms of both sustainability and environmental protection. This review first briefly outlines the main points of this challenge and compares the different methods investigated by chemists over the past several decades, pointing out the major difficulties met. Next, the review highlights the recent use of ionic liqs. (ILs) as solvents that have provided some new opportunities to efficiently convert lignin and lignin model compds. into value-added arom. chems. Particular focus is given to these new strategies in terms of selectivity, sepn. and the unique compds. obtained for the oxidn. of lignin using ILs. Finally, an assessment of the challenges that must be resolved in order for ILs to become an eco-friendly way of producing chems. from biomass, including lignin, is proposed.

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23. Coagulation of Chitin and Cellulose from 1-Ethyl-3-methylimidazolium Acetate Ionic-Liquid Solutions Using Carbon Dioxide

By Barber, Patrick S.; Griggs, Chris S.; Gurau, Gabriela; Liu, Zhen; Li, Shan; Li, Zengxi; Lu, Xingmei; Zhang, Suojiang; Rogers, Robin D.

From Angewandte Chemie, International Edition (2013), 52(47), 12350-12353. DOI:10.1002/anie.201304604

The authors demonstrated that the chemisorption of CO_2 is a viable mechanism for coagulation of chitin and cellulose dissolved in [C_2mim][OAc] using supercrit. carbon dioxide and carbon dioxide through the zwitterionic imidazolium carboxylate that sequesters the acetate anions from the system thus pptg. the biopolymer. The use of carbon dioxide chemisorption as an alternative coagulating process has the potential to provide an economical and energy-efficient method for recycling the IL by eliminating the need to distill higher boiling coagulation solvents from the IL, or at least reducing the amt. of antisolvent which

must be removed.

24. Microwave-assisted dissolution and delignification of wood in 1-ethyl-3-methylimidazolium acetate

By Wang, Hui; Maxim, Mirela L.; Gurau, Gabriela; Rogers, Robin D.

From Bioresource Technology (2013), 136, 739-742. DOI:10.1016/j.biortech.2013.03.064

Microwave irradn. can facilitate the dissoln. and delignification of lignocelluloses in ionic liqs. compared to simple oil bath heating as demonstrated here where 92.5% of 0.5 g ground southern yellow pine was dissolved in 10 g 1-ethyl-3-methylimidazolium acetate using microwave irradn. in only 4 min. Cellulose-rich material (pulp) regenerated from the wood/ionic liq. soln. had a lignin content of ∼10%; significantly lower than the lignin content of the original wood (31.9%) or that of pulp obtained from the same expt. but using 16 h of oil bath heating (16-24%). The 10% lignin content obtained with the microwave method was close to that of pulp obtained from the oil bath heating method when polyoxometalate catalysts were used (5-9%).

25. Advanced biopolymer composite materials from ionic liquid solutions

By Maxim, Mirela L.; White, Jacqueline F.; Block, Leah E.; Gurau, Gabriela; Rogers, Robin D.

From ACS Symposium Series (2012), 1117(Ionic Liquids), 167-187. DOI:10.1021/bk-2012-1117.ch007

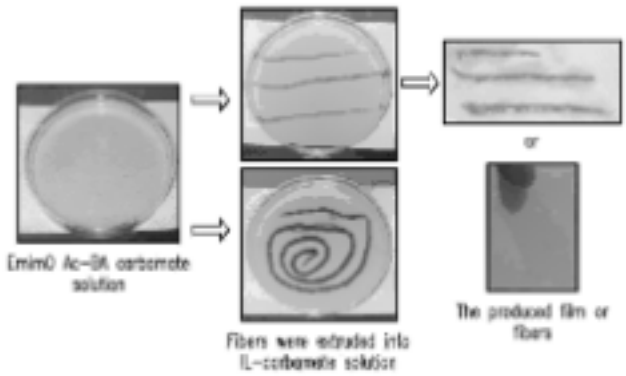
Advanced biocomposite materials from microcryst. cellulose (MCC) and alginic acid (AA) were produced using 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) as the biopolymers' solvent. The effect of factors such as the mass ratio of cellulose and alginic acid in the materials as well as the soaking agent used for the removal of residual ionic liq. (IL) from them were evaluated. While the phys. properties of the biopolymer blends (surface morphol., thermal properties, absorption capacity) were not affected by the increase in the AA content, the materials exhibited significant changes when aq. 4.8 wt% $CaCl_2$ soln. was used as soaking agent. Firstly, the surface morphol. imaged by SEM showed increased porosity. The materials showed better thermal stability mainly due to the presence of Ca^{2+} ions in the blend. The mech. properties of the composite fibers extruded by the dry-jet wet spinning process showed an increase in strain, but exhibited a significant decrease in strength. The soaking agent affected also the absorption capacity of the materials. The hydrophilic nature of the Ca^{2+} ions improved the absorption capacity significantly.

26. Compositions containing recyclable ionic liquids for use in biomass processing

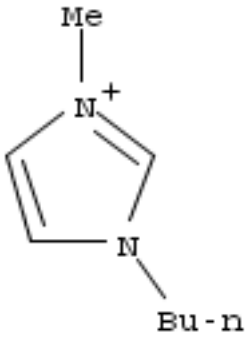
525 Solutions, Inc. Publications Related to Cellulose

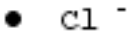
By Daly, Daniel T.; Rogers, Robin D.; Qin, Ying

From U.S. Pat. Appl. Publ. (2012), US 20120245336 A1 20120927, Language: English, Database: CAPLUS



Compns. contg. biomass, an ionic liq., and an amide are described herein. Methods of their prepn. and use in extg. and processing biomass are also described herein. Further described herein are films and fibers prepd. from the compns. Methods of recovering the ionic liqs. used to process the biomass are also provided. Thus, stirring 0.2 g microcryst. cellulose with 5 g 1-butyl-3-methylimidazolium chloride at 100° gave a 4% cellulose soln. which was combined with triethanolamine and stirred for 2 min at room temp. to give a gel. Heating a the gel at 90° for 3 h liquefied the gel. Bubbling the soln. above with CO_2 at a flow rate of 70 cm^3/min at 40° for up to 24 h gave ppt. which could be isolated.





~1 Citing

27. Reinforced magnetic cellulose fiber from ionic liquid solution

By Maxim, Mirela L.; Sun, Ning; Wang, Hui; Sterner, Joseph R.; Haque, Anwarul; Rogers, Robin D.

From Nanomaterials and Energy (2012), 1(4), 225-236. DOI:10.1680/nme.12.00010

Composite fibers were prepd. by homogeneous dispersion of nanomagnetite (NM) in the ionic liq. 1-ethyl-3-methylimidazolium acetate ([C_2mim]OAc) using ultrasonication followed by dissoln. of microcryst. cellulose at 90°C and dry-jet wet spinning into a water coagulation bath. The processing method with specific successive steps regarding the addn. of the components has a large influence on the quality of dispersion and thus the mech. properties of the fibers. A nanomagnetite load of up to 0.75% (mass ratio expressed in percent of nanomagnetite to cellulose) in the cellulose matrix results in significantly improved mech. properties of the fibers, while at loads higher than 1% NM, the ultimate stress and modulus of the fibers are lower because of the formation

of large agglomerates that create defects within the fibers. Fibers with uniform diam. and better reproducibility of mech. properties can be produced utilizing high-performance equipment for fiber processing.

28. Extraction of uranium with regenerated chitin from the dissolution of shrimp shells in ionic liquid

By Rogers, Robin D.; Barber, Patrick S.; Griggs, Chris S.; Kelley, Stephen P.; Gurau, Gabriela

From Abstracts of Papers, 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19-23, 2012 (2012), I+EC-106. Language: English, Database: CAPLUS

Ionic liqs. (ILs) have the ability to dissolve large polysaccharides such as cellulose and chitin under mild conditions giving unprecedented access to high mol. wt. biopolymers directly from biomass. We are interested in using this ability to dissolve chitin directly from shrimp shell waste and generate chitin-based resins for the extn. of uranium from seawater. In addn. to being a strong, environmentally friendly, and renewable material, the easily accessible deacetylated deriv. chitosan provides a useful tether for attaching any no. of functional groups. While chitin and chitosan have been used to ext. heavy metals from waste water streams, chitin processed by ILs has not been studied. We will present our efforts towards the "green" processing of shrimp shell waste to manuf. a uniquely high purity/high surface area absorbent chitin material for the extn. of uranium from seawater.

29. Chlorine-free alternatives to the synthesis of ionic liquids for biomass processing

By Gurau, Gabriela; Wang, Hui; Qiao, Yun; Lu, Xingmei; Zhang, Suojiang; Rogers, Robin D.

From Pure and Applied Chemistry (2012), 84(3), 745-754. DOI:10.1351/PAC-CON-11-11-10

Ionic liqs. (ILs) are desirable for use in a large no. of applications because of their unique properties; however, compns. comprising only a single IL are expensive to synthesize and difficult to purify, and the widely used chloride-based ILs can be toxic and corrosive. Therefore, there is a need for new IL compns. that minimize common disadvantages encountered with single IL compn. and synthetic methods which avoid halide intermediates. In this study, IL mixts., which are chloride-free, were synthesized by a one-pot process, and the mixts. were used to dissolve biopolymers. The synthesized IL mixts. show high capability to dissolve the two exemplary biopolymers, cellulose and chitin.

30. Cellulosic biocomposites as molecular scaffolds for nano-architectures

By Daly, Daniel T.; Spear, Scott K.; Turner, Megan B.; Hough, Whitney Lauren; Rogers, Robin D.

From U.S. Pat. Appl. Publ. (2012), US 20120122691 A1 20120517, Language: English, Database: CAPLUS

Disclosed are composites that comprise regenerated cellulose, a first active substance, a second active substance, and a linker. Methods for prepg. the composites that involve the use of ionic liqs. are also disclosed. Articles prepd. from the disclosed composites and methods of using them are further disclosed. For example, regenerated cellulose film was obtained by treating original cellulose with 1-butyl-3-methylimidazolium chloride, and the regenerated cellulose film was treated with poly-lysine hydrobromide to give a functionalized cellulose film. The film was further reacted with glutaraldehyde and laccase to give to give a functionalized composite film, which was used for transestification of Et butyrate to Bu butyrate.

31. Ionic liquids and shrimp shell waste - emerging technologies for the manufacture of nanochitin materials

By Gurau, Gabriela; Rogers, Robin D.

From Abstracts of Papers, 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012 (2012), IEC-117. Language: English, Database: CAPLUS

Chitin, the second most plentiful biopolymer on earth after cellulose, is the most abundant polymer in the marine environment. Crustacean shells are currently the major source of chitin available for industrial processing. The bioactivity, biocompatibility, and low toxicity of chitin make it suitable for com. use, and contribute to the diversity of over 300 end-use applications, including water treatment, cosmetics and toiletries, food and beverages, agrochems., medical/healthcare, and cell culture. Taking advantage of the ability of Ionic Liqs. (ILs, salts with m.ps. below 100 °C) to dissolve almost any type of biomass, we have developed an IL manufg. process which allows for the extn. of chitin under relatively mild conditions, and enables the prodn. of high purity/high mol. wt. chitin nano-fibers that were previously not feasible, because the harsh conditions currently required to dissolve chitin-contg. shells degrades the chitin.

32. Physicochemical properties of maize cob cellulose powders reconstituted from ionic liquid solution

By Azubuike, Chukwuemeka P.; Rodriguez, Hector; Okhamafe, Augustine O.; Rogers, Robin D.

From Cellulose (Dordrecht, Netherlands) (2012), 19(2), 425-433. DOI:10.1007/s10570-011-9631-y

Suitable α-cellulose and cellulose II powders for use in the pharmaceutical industry can be derived from maize cob. α-Cellulose was extd. from an agricultural residue (maize cobs) using a non-dissolving method based on inorg. substances. Modification of this α-cellulose was carried out by its dissoln. in the ionic liq. 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl), and subsequent regeneration by addn. of either water or acetone at room temp., or of boiling water. X-ray diffraction and IR spectroscopy results showed that the regenerated celluloses had lower crystallinity, and proved that the treatment with [C_4mim]Cl led to the conversion of the cryst. structure of α-cellulose from cellulose I to cellulose II. Thermogravimetric anal. and differential scanning calorimetry data showed quite similar thermal behavior for all cellulose samples, although with somewhat lower stability for the regenerated celluloses, as expected. The comparison of physicochem. properties of the regenerated celluloses and the native

cellulose mainly suggests that the regenerated ones might have better flow properties. For some of the characterizations carried out, it was generally obsd. that the sample regenerated with boiling water had more similar characteristics to the α-cellulose sample, evidencing an influence of the regeneration strategy on the resulting powder after the ionic liq. treatment.

33. Ionic liquid processing of cellulose

By Wang, Hui; Gurau, Gabriela; Rogers, Robin D.

From Chemical Society Reviews (2012), 41(4), 1519-1537. DOI:10.1039/c2cs15311d

A review. Utilization of natural polymers has attracted increasing attention because of the consumption and over-exploitation of non-renewable resources, such as coal and oil. The development of green processing of cellulose, the most abundant biorenewable material on Earth, is urgent from the viewpoints of both sustainability and environmental protection. The discovery of the dissoln. of cellulose in ionic liqs. (ILs, salts which melt below 100 °C) provides new opportunities for the processing of this biopolymer, however, many fundamental and practical questions need to be answered in order to det. if this will ultimately be a green or sustainable strategy. In this crit. review, the open fundamental questions regarding the interactions of cellulose with both the IL cations and anions in the dissoln. process are discussed. Investigations have shown that the interactions between the anion and cellulose play an important role in the solvation of cellulose, however, opinions on the role of the cation are conflicting. Some researchers have concluded that the cations are hydrogen bonding to this biopolymer, while others suggest they are not. Our review of the available data has led us to urge the use of more chem. units of soly., such as "g cellulose per mol of IL" or "mol IL per mol hydroxyl in cellulose" to provide more consistency in data reporting and more insight into the dissoln. mechanism. This review will also assess the greenness and sustainability of IL processing of biomass, where it would seem that the choices of cation and anion are crit. not only to the science of the dissoln., but to the ultimate greenness' of any process.

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34. Disruptive technology for biomass processing using ionic liquids

By Daly, Daniel T.; Rogers, Robin D.; Gurau, Gabriela

From Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, August 28-September 1, 2011 (2011), BMGT-15. Language: English, Database: CAPLUS

The inevitable depletion of petroleum-based resources and increasing worldwide interest in finding alternative renewable resources combined with the potential to produce multiple products from lignocellulosic biomass offers unique business opportunities if a disruptive technol. which reduces the burden of high transportation cost can be developed. This development will then allow low-vol., but high-value chems. to provide added value to the low-value, but high-vol. liq. transportation fuels being developed. Current biol. and chem. approaches being taken to utilize biomass are limited by the difficulty in processing (particularly pre-treating) lignocellulosic materials and the energy needed for sepn. of the components. Clean sepn. of the three major components of biomass (cellulose, lignin, and hemicellulose,) is the most important challenge for producing reproducible feedstocks for further processing. Ionic liqs. (ILs), defined as salts which melt below 100 °C, have opened a door to effectively

explore the carbohydrate economy by direct dissoln. of lignocellulosic biomass and partial sepn. of the major biopolymer constituents (by reconstitution of the dissolved wood using selected solvents), which facilitates enzymic hydrolysis.

35. Rapid dissolution of lignocellulosic biomass in ionic liquids using temperatures above the glass transition of lignin
By Li, Weiying; Sun, Ning; Stoner, Breena; Jiang, Xinyu; Lu, Xingmei; Rogers, Robin D.
From Green Chemistry (2011), 13(8), 2038-2047. DOI:10.1039/c1gc15522a

Rapid dissoln. of bagasse and southern yellow pine has been achieved in the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C_2mim]OAc) by using a dissoln. temp. above the glass transition of lignin (ca. 150°). When 0.5 g of bagasse or pine is added to 10 g of [C_2mim]OAc, complete dissoln. can be obtained in 5-15 min for bagasse at a temp. of 175-195°, compared to 15-16 h at 110°, and over 90% of added pine can be dissolved with heating at 175° for 30 min. Upon regeneration in acetone/water, lignin and carbohydrate can be partially sepd. as lignin and a cellulose-rich material (CRM, pulp). Compared to published methods with lower temps. and longer times (e.g., 110°, 16 h), processing bagasse in [C_2mim]OAc at 185° for 10 min results in higher yields of both recovered lignin (31% vs. 26% of the available lignin) and carbohydrate (carbohydrate yield = 66% vs. 63% of the available carbohydrate). In addn., the CRM pulp recovered using the higher temp. method has much lower residual lignin content (6% vs. 20%). Similar results were obtained for pine (lignin content in CRM with higher vs. lower temp. method = 16.1% vs. 23.5%). The IL was recycled and reused although the efficiency decreased and ca. 15% of the IL had degraded after the higher temp. process. These latter results suggest further optimization of the choice of IL and heating conditions might be needed to develop an energy and chem. efficient process.

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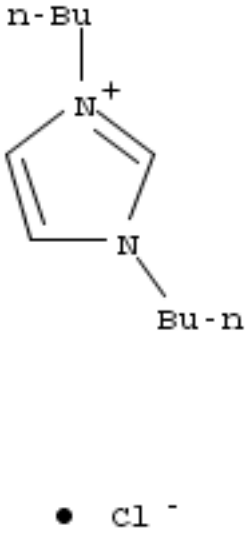
36. Methods for dissolving polymers using mixtures of different ionic liquids and compositions comprising the mixtures
By Rogers, Robin D.; Daly, Daniel T.; Gurau, Gabriela
From PCT Int. Appl. (2011), WO 2011056924 A2 20110512, Language: English, Database: CAPLUS

Disclosed are methods for dissolving biopolymers and synthetic polymers using mixts. of different ionic liqs. and compns. comprising the mixt. The methods involve contacting a polymer with a mixt. of ionic liqs. to provide a compn. of polymer and the mixt.; the mixt. of ionic liqs. is prepd. by either mixing ionic liqs. or by a process comprising reacting ionic liq. precursors in one-pot to form the ionic liqs. Thus, a 2:1:1 statistical mixt. of 1-butyl-3-methylimidazolium acetate, 1,3-dibutylimidazolium acetate, and 1,3-dimethylimidazolium acetate was synthesized from formaldehyde (37 %)(25 mL, 0.3 mol), butylamine (99.5 %) (33.2 mL, 0.3 mol), methylamine (40 %) (28 mL, 0.3 mol), glacial acetic acid (99-100%) (19.1 mL, 0.3 mol) and glyoxal (40%) (38.0 mL, 0.3 mol), purified and then freeze-dried. Room temp. (25°) cond. (2.70 mS/cm) and viscosity (97.5 cP) of neat soln. of the above ionic liq. were measured (water content 2365 ppm). Microcryst. cellulose (0.01 g) was placed in 1.5 g 2:1:1 statistical ionic liq. mixt. of 1-butyl-3-methylimidazolium, 1,3-dibutylimidazolium, and 1,3-dimethylimidazolium chloride in a glass vial and the resulting mixt. was stirred at room temp. until complete dissoln. was obsd. Solns. can be prepd. in this manner with varying concn. of up to about 5 wt.% of cellulose. The viscous soln. was heated (by means of an oil bath) at 100 °, when became

clear. The soln. was increasingly viscous with cellulose concn. At 25 wt.% of cellulose a viscous gel was formed. The soly. of cellulose and the rate of dissoln. can be accelerated by microwave pulses.



37. Composite fibers spun directly from solutions of raw lignocellulosic biomass dissolved in ionic liquids

By Sun, Ning; Li, Weiying; Stoner, Breena; Jiang, Xinyu; Lu, Xingmei; Rogers, Robin D.

From Green Chemistry (2011), 13(5), 1158-1161. DOI:10.1039/c1gc15033b

Lignocellulosic biomass composite fibers (southern yellow pine and bagasse) were successfully prepd. directly from the ionic liq., 1-ethyl-3-methylimidazolium acetate ([C_2mim]OAc) with a dry-jet wet spinning process using short dissoln. times (10-30 min) and temps. above the glass transition temp. of lignin. Fibers could not be spun at all from solns. of pine dissolved using previously reported dissoln. methods (110 °C, 16 h), while bagasse fibers spun using the higher temp./shorter time method were stronger than those obtained using the lower temp./longer time method.

38. Conductive composites prepared using ionic liquids

By Spear, Scott K.; Daly, Daniel T.; Frazier, Rachel M.; Rogers, Robin D.; Haque, Anwarul

From PCT Int. Appl. (2011), WO 2011011322 A1 20110127, Language: English, Database: CAPLUS

Disclosed are conductive composites prepd. from ionic liqs., compns. for prepg. the composites, and methods of making and using the composites.

39. Where are ionic liquid strategies most suited in the pursuit of chemicals and energy from lignocellulosic biomass?
By Sun, Ning; Rodriguez, Hector; Rahman, Mustafizur; Rogers, Robin D.
From Chemical Communications (Cambridge, United Kingdom) (2011), 47(5), 1405-1421. DOI:10.1039/C0CC03990J

A review. Certain ionic liqs. dissolve cellulose, other biopolymers, and even raw biomass under relatively mild conditions. This particular ability of some ionic liqs., accompanied by concurrent advantages, enables the development of improved processing strategies for the manufg. of a plethora of biopolymer-based advanced materials. The more recent discoveries of dissoln. of lignocellulosic materials (e.g., wood) in ionic liqs., with at least partial sepn. of the major constituent biopolymers, suggest further paths towards the achievement of a truly sustainable chem. and energy economy based on the concept of a biorefinery which provides chems., materials, and energy. Nonetheless, questions remain about the use of ionic liqs. and the advisability of introducing any new process which uses bulk synthetic chems. which have to be made, disposed of, and prevented from entering the environment. The authors discuss their own journey from the discovery of the dissoln. of cellulose in ionic liqs. to the cusp of an enabling technol. for a true biorefinery and some of the key questions which remain are discussed.

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40. Use of Polyoxometalate Catalysts in Ionic Liquids to Enhance the Dissolution and Delignification of Woody Biomass
By Sun, Ning; Jiang, Xinyu; Maxim, Mirela L.; Metlen, Andreas; Rogers, Robin D.
From ChemSusChem (2011), 4(1), 65-73. DOI:10.1002/cssc.201000272

A well-known polyoxometalate, $[PV_2Mo_{10}O_{40}]^{5-}$, in both acidic (acidic POM, $H_5[PV_2Mo_{10}O_{40}]$) and ionic liq.-compatible form ($[C_2mim]$POM, [1-ethyl-3-methylimidazolium]$_4H[PV_2Mo_{10}O_{40}]$), has been studied as a catalyst for the dissoln. and delignification of wood in the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ($[C_2mim]$OAc). Differences were obsd. with variables such as the form of POM, POM loading, and reaction conditions. Generally, the addn. of POM leads to a faster dissoln., a lower lignin content in the recovered cellulose-rich materials (isolated pulp), and a lower isolated yield of lignin due to its oxidn. Acidic POM decreases the lignin content of the pulp without compromising the yield of the pulp. $[C_2mim]$POM in the IL facilitates greater delignification (lower lignin content in pulp) than the IL with acidic POM; however, the overall pulp yield is also lower indicating some degrdn. of the carbohydrates. The POM can be recovered with $[C_2mim]$OAc after evapn. of the reconstitution solvent (e.g., acetone/water) and can be reused, albeit with some loss of POM and loss of POM activity under the current conditions.

41. Process for forming films, fibers, and beads from chitinous biomass
By Qin, Ying; Rogers, Robin D.; Daly, Daniel T.
From PCT Int. Appl. (2010), WO 2010141470 A2 20101209, Language: English, Database: CAPLUS

Disclosed is a process for forming films, fibers, and beads comprising a chitinous mass, for example, chitin, chitosan obtained from one or more biomasses. The disclosed process can be used to prep. films, fibers, and beads comprising only polymers, i.e., chitin, obtained from a suitable biomass, or the films, fibers, and beads can comprise a mixt. of polymers obtained from a suitable biomass and a naturally occurring and/or synthetic polymer. Disclosed herein are the films, fibers, and beads obtained from the disclosed process. This Abstr. is presented solely to aid in searching the subject matter disclosed herein and is not intended to define, limit, or otherwise provide the full scope of the disclosed subject matter.

42. Properties of cellulose/TiO2 fibers processed from ionic liquids

By Maxim, Mirela L.; Sun, Ning; Swatloski, Richard P.; Rahman, Mustafizur; Harland, Adam G.; Haque, Anwarul; Spear, Scott K.; Daly, Daniel T.; Rogers, Robin D.

From ACS Symposium Series (2010), 1033(Cellulose Solvents), 261-274. DOI:10.1021/bk-2010-1033.ch014

Continuous composite fibers of cellulose with dispersed TiO_2 particles were pulled by a dry-jet wet spinning process from 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl) ionic liq. solns. The effects of various factors such as cellulose source, d.p., and concn., along with the concn. of the additive were evaluated. The surface texture of the fibers depends greatly on the concn. of TiO_2 used, as the particles have the tendency to outcrop the surface. Five wt.% TiO_2 was found to be the optimal concn. that didn't cause significant changes in the mech. properties of the fibers.

43. Ionic liquid systems for the processing of biomass, their components and/or derivatives, and mixtures thereof

By Rahman, Mustafizur; Qin, Ying; Maxim, Mirela L.; Rogers, Robin D.

From PCT Int. Appl. (2010), WO 2010056790 A1 20100520, Language: English, Database: CAPLUS

Disclosed herein are compns. and methods that involve ionic liqs. and biomass. In one aspect, the disclosure relates to ionic liq. systems for the processing of biomass, their components and/or derivs., and mixts. thereof.

44. Wood delignification using polyoxometalates in ionic liquid

By Sun, Ning; Jiang, Xinyu; Maxim, Mirela L.; Rogers, Robin D.

From Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010 (2010), FUEL-14.

Language: English, Database: CAPLUS

We have recently been exploring the feasibility of using ionic liqs. (ILs) to dissolve, sep., and recover cellulose, hemicellulose, and lignin from lignocellulosic biomass such as wood. We have previously demonstrated total dissoln. and partial sepn. of the biopolymers. Our results suggest that this process could be enhanced with the use of a catalyst or reagent that could selectively cleave lignin-carbohydrate bonds. We have recently begun the exploration of polyoxometalates (POMs) to enhance biomass dissoln. and increase delignification without sacrificing the pulp or holocellulose yield indicating the high selectivity of POM in IL systems. This presentation will overview our current progress in wood delignification with POMs in IL media and suggest how ILs may provide unique routes to new materials and processes which utilize renewable resources.

45. Dissolution and regeneration of wood in [C2mim]OAc and formation of wood composite fibers

By Stoner, Breena; Sun, Ning; Rogers, Robin D.

From Abstracts of Papers, 239th ACS National Meeting, San Francisco, CA, United States, March 21-25, 2010 (2010), CHED-725. Language: English, Database: CAPLUS

Currently there is increasing interest in the use of renewable resources such as biomass todecrease society's reliance on fossil fuels. Previous research has shown that bothhardwoods and softwoods can be effectively dissolved by the ionic liq. [C2mim]OAc. However, current dissoln. techniques require 16 h of const. heat and stirring. It is desirable to det. more efficient heating parameters to allow max. dissoln. and regeneration of cellulose materials in min. time. Different temps. and dissoln. times have been attempted for traditional oil bath heating, and microwave heating for different times has also been compared. Mass balance and the ligninholocellulose sepn. efficiency has been evaluated. Wood composite fibers can be prepd. directly from the wood/IL soln. By altering initial treatment of the wood,fiber compn. may be varied, allowing the formation of fibers with differing properties. The biodegradable wood composite fibers are then characterized, and the variation of fiber properties with lignin content and different heating conditions is discussed.

46. Biphasic liquid mixtures of ionic liquids and polyethylene glycols

By Rodriguez, Hector; Francisco, Maria; Rahman, Mustafizur; Sun, Ning; Rogers, Robin D.

From Physical Chemistry Chemical Physics (2009), 11(46), 10916-10922. DOI:10.1039/b916990c

We have found that 1-alkyl-3-methylimidazolium chloride ionic liqs. (ILs) can form immiscible liq. mixts. with some polyethylene glycols (PEGs). Binary mixts. of 1-ethyl-3-methylimidazolium chloride with PEG of mol. wt. 1500, 2000, or 3400 g mol^{-1}, or of 1-butyl-3-methylimidazolium chloride with PEG of mol. wt. 2000 or 3400 g mol^{-1}, have been found to give rise to entirely liq., stable biphasic systems over a significant temp. range (from 333.15 K to 413.15 K), while mixts. of 1-ethyl-3-methylimidazolium chloride with PEG-1000 and 1-butyl-3-methylimidazolium chloride with PEG-1000 and PEG-1500 are miscible. The mutual immiscibility of the IL and the PEG increases as the temp. increases. The evolution of the compn. of

the phases in equil. with the mol. wt. of the PEG, or with the variation of the length of the alkyl substituent chain of the imidazolium cation of the IL, has been explored. The trends obsd. are explained through the complexity of interactions present within the binary system. A thermodn. anal. of the liq.-liq. equil. data indicates neg. values for the change of enthalpy and entropy of mixing. The potential application of these biphasic, entirely liq. systems, with low volatility and good solvation properties, for the dissoln. and sepn. of cellulose and lignin at elevated temp. has been preliminarily explored, although only modest results have been achieved to date.

47. Substrates for delivery of physiologically active agents by using regenerated cellulose

By Daly, Daniel T.; Spear, Scott K.; Frazier, Rachel M.; Hough-Troutman, Whitney Lauren; Rogers, Robin D.

From PCT Int. Appl. (2009), WO 2009131692 A1 20091029, Language: English, Database: CAPLUS

Disclosed are substrates that can deliver one or more physiol. active agents. The substrates can be combined with regenerated cellulose to form cellulose composites that serve as a method for delivering the physiol. active agents in vivo, in vitro, and ex vivo.

48. Ionic liquid systems for fractionation of biomass, their components and/or derivatives, and mixtures thereof

By Rahman, Mustafizur; Rodriguez, Hector; Sun, Ning; Swatloski, Richard P.; Daly, Daniel T.; Rogers, Robin D.

From PCT Int. Appl. (2009), WO 2009105236 A1 20090827, Language: English, Database: CAPLUS

Disclosed herein are compns. and methods that involve ionic liqs. and biomass. Multiphasic compns. involving ionic liqs. and a polymer and uses of such compns. for fractioning various components of biomass are disclosed. Methods of making and using compns. comprising an ionic liq., biomass, and a catalyst are also disclosed.

49. Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate

By Sun, Ning; Rahman, Mustafizur; Qin, Ying; Maxim, Mirela L.; Rodriguez, Hector; Rogers, Robin D.

From Green Chemistry (2009), 11(5), 646-655. DOI:10.1039/b822702k

Both softwood (southern yellow pine) and hardwood (red oak) can be completely dissolved in the ionic liq. 1-ethyl-3-methylimidazolium acetate ([C_2mim]OAc) after mild grinding. Complete dissoln. was achieved by heating the sample in an oil bath, although wood dissoln. can be accelerated by microwave pulses or ultrasound irradn. It has been shown that

[C_2mim]OAc is a better solvent for wood than 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) and that variables such as type of wood, initial wood load, particle size, etc. affect dissoln. and dissoln. rates; for example, red oak dissolves better and faster than southern yellow pine. Carbohydrate-free lignin and cellulose-rich materials can be obtained by using the proper reconstitution solvents (e.g., acetone/water 1 : 1 vol./vol.) and approx. 26.1% and 34.9% redns. of lignin content in the reconstituted cellulose-rich materials (from pine and oak, resp.) have been achieved in one dissoln./reconstitution cycle. The regenerated cellulose-rich materials and lignin fractions were characterized and compared with the original wood samples and biopolymer stds. For pine, 59% of the holocellulose (i.e., the sum of cellulose and hemicellulose) in the original wood can be recovered in the cellulose-rich reconstituted material; whereas 31% and 38% of the original lignin is recovered, resp., as carbohydrate-free lignin and as carbohydrate-bonded lignin in the cellulose-rich material.

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50. Dissolution and Separation of Biomass Utilizing Ionic Liquids

By Sun, Ning; Rahaman, Mustafizur; Qin, Ying; Maxim, Mirela; Rogers, Robin D.

From Abstracts, 60th Southeast Regional Meeting of the American Chemical Society, Nashville, TN, United States, November 12-15 (2008), SERM-250. Language: English, Database: CAPLUS

With the inevitable depletion of petroleum materials, there has been an increasing interest in finding alternative sources. Wood is a common biomass resource with applications in biofuels, papermaking, and construction. The major components of wood are cellulose, hemicellulose, and lignin. Currently only cellulose and hemicellulose have been utilized in producing paper, fibers, and membranes, while lignin is only burned for energy. The reason of their underutilization comes from the difficulty of dissoln. and the energy needed for sepn. of the different components from wood. The current pulping process involves caustic chems. and generates a large amt. of pollutants. The recent discovery of wood dissoln. in ionic liqs. (ILs) has opened a door to utilize and sep. biomass components more efficiently. In this presentation, we will discuss how ILs can be designed to dissolve and process biomass and how to manipulate soln. properties to process and regenerate biopolymers into a desirable form for specialized applications.

51. Calix[4]arenes immobilized in a cellulose-based platform for entrapment and detection of NOx gases

By Hines, Jane H.; Wanigasekara, Eranda; Rudkevich, Dmitry M.; Rogers, Robin D.

From Journal of Materials Chemistry (2008), 18(34), 4050-4055. DOI:10.1039/b803289k

The ability of some ionic liqs. to co-dissolve cellulose and other polymers, as well as very hydrophobic mols., such as gas-sensing calix[4]arenes, allows for the ready construction of nitrogen oxide (NO_x) sensors and storage devices. The authors report here the use of a cellulose-based platform for the immobilization of calix[4]arenes and the subsequent use of these materials for the reversible colorimetric detection of NO_x. These sensors may be exposed directly to NO_x gas for quick colorimetric calixarene-NO^+ complexation, which can be rapidly or slowly reversed with humidity, depending on the desired application (e.g., sensing vs. storage).

525 Solutions, Inc. Publications Related to Cellulose

52. Cellulose composite fibers prepared from ionic liquid-based solution

By Sun, Ning; Swatloski, Richard P.; Maxim, Mirela L.; Rahman, Mustafizur; Harland, Adam G.; Haque, Anwarul; Spear, Scott K.; Daly, Dan T.; Rogers, Robin D.

From Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6-10, 2008 (2008), CELL-285.

Language: English, Database: CAPLUS

Cellulose composite fibers have been prepd. by a dry-jet wet spinning process from the ionic liq. (IL) 1-ethyl-3-methylimidazolium chloride. After dissoln. of the cellulose in the IL, an active ingredient (e.g., TiO2 or Fe3O4) was dispersed homogeneously in the soln., and the composite fibers were extruded into a water coagulation bath. The properties of composite fibers prepd. with different concns. of dispersed ingredients and different concns. and d.p. of cellulose under the same extrusion conditions were analyzed. It was found that an increase in d.p. and/or cellulose concn. resulted in stronger fibers, and conversely the addn. of active substances weakened overall mech. properties, in most cases. This presentation will overview current progress in fiber spinning, our overall biomass program in general, and suggest where ILs may provide unique routes to new materials and processes which utilize renewable resources.

53. Dissolution and processing of cellulosic and related biomass with ionic liquids: Fundamentals and applications

By Rogers, Robin D.; Rahman, Mustafizur; Qin, Ying; Sun, Ning; Maxim, Mirela L.

From Abstracts of Papers, 235th ACS National Meeting, New Orleans, LA, United States, April 6-10, 2008 (2008), CELL-164.

Language: English, Database: CAPLUS

The dissoln. of biomass in ionic liqs. (ILs) has enabled us to utilize these valuable bioresources in novel ways to produce new and old materials. For example, cellulose can be extd., functionalized, and processed easily using a variety of ILs, to prep. a) advanced textile fibers (e.g., fibers with magnetic, antimicrobial properties, etc.), b) polymer blends (using both synthetic and biopolymers) with improved mech. properties, c) chem. and bio-responsive cellulose membranes contg. immobilized enzymes, or other task-specific additives, to name a few. In this presentation, we will discuss how the components of biomass interact with ILs and how these interactions can be used to manipulate soln.-properties to process and regenerate biopolymers into a desirable form for specialized applications. It is clear, that the unique properties of ILs can be used to explore the world of biorenewable resources and yield endless possibilities for forming environmentally-friendly new and enhanced materials.

525 Solutions, Inc. Publications Related to Cellulose

54. Magnetite-embedded cellulose fibers prepared from ionic liquid

By Sun, Ning; Swatloski, Richard P.; Maxim, Mirela L.; Rahman, Mustafizur; Harland, Adam G.; Haque, Anwarul; Spear, Scott K.; Daly, Daniel T.; Rogers, Robin D.

From Journal of Materials Chemistry (2008), 18(3), 283-290. DOI:10.1039/B713194A

A dry-jet wet spinning process was developed for manuf. of magnetic cellulose fibers using the ionic liq. (IL) 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl) as solvent. Cellulose from different sources with various d.p. was dissolved in the IL, then magnetite particles were dispersed in the soln., and fibers were coagulated in a water bath under appropriate spinning conditions. The mech. properties, thermal stability, microstructure, and magnetic properties of the fibers were correlated to cellulose source and concn. of magnetite. The fiber texture was dependent on overall magnetite concn., and cellulose concn. and mol. wt. in the spinning soln. Increasing d.p. and/or cellulose concn. resulted in more robust fibers, and conversely the addn. of magnetite particles weakened the overall mech. properties of the fibers.

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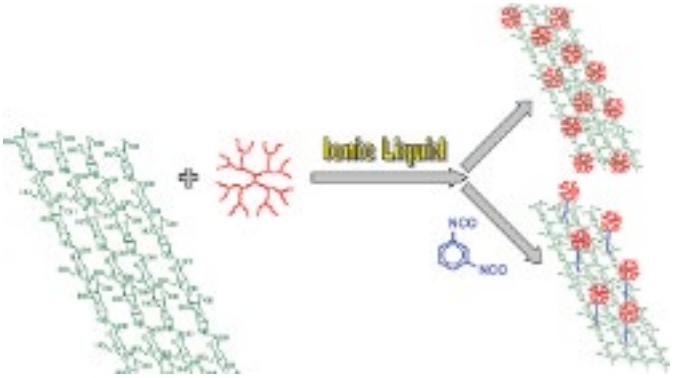
55. Ionic Liquid-Based Preparation of Cellulose-Dendrimer Films as Solid Supports for Enzyme Immobilization

By Bagheri, Mozhgan; Rodriguez, Hector; Swatloski, Richard P.; Spear, Scott K.; Daly, Daniel T.; Rogers, Robin D.

From Biomacromolecules (2008), 9(1), 381-387. DOI:10.1021/bm701023w



Surface-active cellulose films for covalent attachment of bioactive moieties were achieved by codissoln. of cellulose with polyamidoamine (PAMAM) dendrimers in an ionic liq. followed by regeneration of the composite as a film. Different generations of PAMAM were used for the formation of cellulose-dendrimer composites, as well as films with the dendrimer covalently bonded to the cellulose by means of the linker 1,3-phenylene diisocyanate. Surface characterization, thermal stability, and utility for immobilization of laccase were detd. The presence of the dendrimer amino groups was confirmed by detailed characterization of the films' surfaces. These modified films exhibit acceptable thermal stability, comparable to that of other regenerated cellulose films, but the no. of active functional groups on the surface is much smaller than the theor. amt. expected. Films made with 1,3-phenylene diisocyanate as linker for covalently bound cellulose and dendrimers exhibit a better performance for immobilization of laccase than those prepd. by simple mixing of the cellulose and dendrimer. In general, a linear correspondence between the dendrimer generation within the films and the specific activity of immobilized laccase in such films was not obsd.

56. Sensor technologies based on a cellulose supported platform

By Poplin, Jane Holly; Swatloski, Richard P.; Holbrey, John D.; Spear, Scott K.; Metlen, Andreas; Gratzel, Michael; Nazeeruddin, Mohammad K.; Rogers, Robin D.

From Chemical Communications (Cambridge, United Kingdom) (2007), (20), 2025-2027. DOI:10.1039/B704651K

A simple approach to sensor development based on encapsulating a probe mol. in a cellulose support followed by regeneration from an ionic liq. soln. is demonstrated here by the codissoln. of cellulose and 1-(2-pyridylazo)-2-naphthol in 1-butyl-3-methylimidazolium chloride followed by regeneration with water to form strips which exhibit a proportionate (1: 1) response to Hg(II) in aq. soln.

57. Ionic liquid reconstituted cellulose composites as solid support matrices with good transparency for biocatalytic reaction

By Rogers, Robin D.; Daly, Daniel T.; Turner, Megan B.; Spear, Scott K.; Holbrey, John D.

From PCT Int. Appl. (2007), WO 2007005388 A2 20070111, Language: English, Database: CAPLUS

Disclosed are composites comprising regenerated cellulose, a first active substance, a second active substance, and a linker. Thus, microcryst. cellulose was dissolved in 1-butyl-3-methylimidazolium chloride using microwave pulse heating at 120-150°, cooled to 60° to form a super-cooled liq., 20% (based on cellulose) poly(L-lysine hydrobromide) was added therein, homogenized, cast onto a glass plate, the resulting film soaked in water for at least 24 h to leach residual from the film to give a reconstituted cellulose film, showing good transparency.

58. Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride

By Fort, Diego A.; Remsing, Richard C.; Swatloski, Richard P.; Moyna, Patrick; Moyna, Guillermo; Rogers, Robin D.

From Green Chemistry (2007), 9(1), 63-69. DOI:10.1039/B607614A

The bulk of the cellulose currently employed by industry is isolated from wood through Kraft pulping, a process which traditionally involves a barrage of environmentally detrimental chems. and is undeniably 'non-green.'. In this report the authors present a simple and novel alternative approach for the processing of lignocellulosic materials that relies on their soly. in solvent systems based on the ionic liq. (IL) 1-n-butyl-3-methylimidazolium chloride ([C_4mim]Cl). Dissoln. profiles for woods of

different hardness are presented, making emphasis on the direct anal. of the cellulosic material and lignin content in the resulting liquors by means of conventional ^{13}C NMR techniques. The authors also show that cellulose can be readily reconstituted from the IL-based wood liquors in fair yields by the addn. of a variety of pptg. solvents. Spectroscopic and thermogravimetric studies indicate that the polysaccharide obtained in this manner is virtually free of lignin and hemicellulose and has characteristics that are comparable to those of pure cellulose samples subjected to similar processing conditions.

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59. Preparation of magnetic cellulose composites using ionic liquids

By Swatloski, Richard P.; Holbrey, John D.; Weston, James L.; Rogers, Robin D.

From Chimica Oggi (2006), 24(2), 31-32, 34-35. Language: English, Database: CAPLUS

Cellulose-magnetite composites have been prepd. by suspension and dispersion of magnetite particles in a homogeneous ionic liq. soln. of cellulose, followed by regeneration into water, enabling the prepn. of magnetically responsive films, floes, fibers, or beads. The materials prepd. were ferromagnetic, with a small superparamagnetic response, characteristic of the initial magnetite added. X-ray diffraction data indicated that the magnetite particles were chem. unaltered after encapsulation with an av. particle size of approx. 25 nm.

60. Keynote address: new solvent for cellulose extrusion

By Broughton, Roy; Wang, Weijun; Shen, Guanglin; Farag, Ramsis; Swatloski, Richard P.; Rogers, Robin D.

From Proceedings - Beltwide Cotton Conferences (2005), 3291/1-3291/5. Language: English, Database: CAPLUS

A variety of celluloses have been dissolved in the ionic liq. 1-butyl-3-methylimidazolium chloride. The solns. were extruded in a dry-jet, wet-spinning process using water as a coagulation bath to produce a fiber having a tenacity of 2.0-4.4 g/denier (1.8-4.0 cN/dtex) and a breaking elongation of 4-20% depending on the extrusion conditions. This ionic liq. appears to be versatile as a cellulose extrusion solvent with minimal polymer degrdn. As none of the extrusion, coagulation, and drawing conditions have been optimized, the authors conclude that this new solvent has significant potential for the manuf. of regenerated cellulose fibers.

61. How understanding the ionic liquid/cellulose dissolution mechanism can guide the generation of advanced cellulose-based materials

By Swatloski, Richard P.; Broughton, Roy M.; Moyna, Guillermo; Daly, Dan T.; Spear, Scott K.; Rogers, Robin D.

From Abstracts of Papers, 231st ACS National Meeting, Atlanta, GA, United States, March 26-30, 2006 (2006), IEC-204.

525 Solutions, Inc. Publications Related to Cellulose

Language: English, Database: CAPLUS

Abstr. not provided.

62. Use of ionic liquids for the processing and analysis of lignocellulosic materials

By Remsing, Richard C.; Fort, Diego A.; Swatloski, Richard P.; Moyna, Patrick; Rogers, Robin D.; Moyna, Guillermo

From Abstracts of Papers, 231st ACS National Meeting, Atlanta, GA, United States, March 26-30, 2006 (2006), IEC-151.

Language: English, Database: CAPLUS

Cellulose is the most abundant renewable biopolymer on Earth. While its most notable uses are related to the paper and textile industries, it also finds application in the prodn. of synthetic polymers, membranes, and paint additives. Cellulosic materials are extd. from wood using variations of the Kraft pulping process using a barrage of environmentally detrimental chems. We describe a simple and novel method to ext. cellulose from wood using "green" solvent systems based on the ionic liq. (IL) 1-n-butly-3-methylimidazolium chloride ([C_4mim]Cl). Extn. profiles for different woods are presented, making particular emphasis on the anal. of cellulose content in the IL-based wood liquors by means of ^{13}C NMR techniques. In addn., we show that cellulose virtually free of lignin can be easily reconstituted from the IL liquors. Modifications to the methodol., including the use of pulping and bleaching additives and the in situ derivatization of wood components, are discussed as well.

63. Mechanism of cellulose dissolution in the ionic liquid 1-n-butyl-3-methylimidazolium chloride: a 13C and 35/37Cl NMR relaxation study on model systems

By Remsing, Richard C.; Swatloski, Richard P.; Rogers, Robin D.; Moyna, Guillermo

From Chemical Communications (Cambridge, United Kingdom) (2006), (12), 1271-1273. DOI:10.1039/b600586c

^{13}C and $^{35/37}$Cl NMR relaxation measurements on several model systems demonstrate that the solvation of cellulose by the ionic liq. (IL) 1-n-butyl-3-methylimidazolium chloride ([C_4mim]Cl) involves hydrogen bonding between the carbohydrate hydroxyl protons and the IL chloride ions in a 1:1 stoichiometry.

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64. Polymer dissolution and blend formation in ionic liquids

By Holbrey, John D.; Swatloski, Richard P.; Chen, Ji; Daly, Dan; Rogers, Robin D.

From PCT Int. Appl. (2005), WO 2005098546 A2 20051020, Language: English, Database: CAPLUS

The ionic liqs. are for the dissoln. of various polymers and/or copolymers, the formation of resins and blends, and the reconstitution of polymer and/or copolymer solns., and the dissoln. and blending of functional additives and/or various polymers and/or copolymers. Thus, ≥1 ionic liq., which is a liq. salt complex that exists in the liq. phase between about -70 to 300°, is mixed with ≥2 differing polymeric materials to form a mixt., and adding a nonsolvent to the mixt. to remove the ionic liq. from the resin or blend.

65. Applying ionic liquids for controlled processing of polymer materials

By Holbrey, John D.; Chen, Ji; Turner, Megan B.; Swatloski, Richard P.; Spear, Scott K.; Rogers, Robin D.

From ACS Symposium Series (2005), 913(Ionic Liquids in Polymer Systems), 71-87. DOI:10.1021/bk-2005-0913.ch005

A review. This perspective examines the potential, highlighting some examples from the on-going research program, to evaluate and apply ionic liqs. as advanced functional solvents for dissolving and processing polymers to prep. active materials and composites for sensor and smart materials applications integrating complexes or colorimetric and biol. receptors into biorenewable, biocompatible substrate matrixes.

66. Ionic liquid-reconstituted cellulose composites as solid support matrices for biocatalyst immobilization

By Turner, Megan B.; Spear, Scott K.; Holbrey, John D.; Daly, Daniel T.; Rogers, Robin D.

From Biomacromolecules (2005), 6(5), 2497-2502. DOI:10.1021/bm050199d

Prepn. of cellulose-polyamine composite films and beads, which provide high loading of primary amines on the surface allowing direct 1-step bioconjugation of active species, is reported using an ionic liq. dissoln. and regeneration process. Films and bead architectures were prepd. and used as immobilization supports for laccase as a model system demonstrating the applicability of this approach. Performance of these materials, compared to com. available products, was assessed using millimeter-sized beads of the composites and the lipase-catalyzed transesterification of Et butyrate.

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67. High-resolution 13C NMR studies of cellulose and cellulose oligomers in ionic liquid solutions

By Moulthrop, Jason S.; Swatloski, Richard P.; Moyna, Guillermo; Rogers, Robin D.

From Chemical Communications (Cambridge, United Kingdom) (2005), (12), 1557-1559. DOI:10.1039/b417745b

High-resoln. ^{13}C NMR studies of cellulose and cellulose oligomers dissolved in the ionic liq. (IL) 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) show that the β-(1→4)-linked glucose oligomers are disordered in this medium and have a conformational behavior which parallels the one obsd. in water, and thus, reveal that the polymer is disordered in IL soln. as well.

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68. High-resolution 13C NMR studies of amylose and cellulose oligomers in 1-butyl-3-methylimidazolium chloride solutions

By Moulthrop, Jason S.; Swatloski, Richard P.; Rogers, Robin D.; Moyna, Guillermo

From Abstracts of Papers, 228th ACS National Meeting, Philadelphia, PA, United States, August 22-26, 2004 (2004), CARB-063. Language: English, Database: CAPLUS

A high-resoln. ^{13}C NMR (NMR) spectroscopy study of amylose and cellulose oligomers dissolved in the ionic liq. (IL) 1-butyl-3-methylimidazolium chloride ([C4mim]Cl) is presented. Results for all the oligosaccharides studied, which included linear (1←4)-linked glucose dimers, tetramers, and hexamers in both α and β configurations as well as cyclic α-, β-, and γ-cyclodextrins, are comparable to those obtained in aq. soln. In particular, anal. of the anomeric carbon chem. shifts, which are known to have a periodic dependence with the glycosidic bond Φ and Ψ dihedral angles, indicates that the conformational preferences of these oligosaccharides in [C4mim]Cl and aq. solns. are similar. Preliminary results obtained for cellulose show that its conformational behavior in [C4mim]Cl soln. parallels the one obsd. for the smaller β-(1←4) glucose oligomers, and that the polysaccharide is disordered in the IL soln. The impact that these findings may have on green cellulose processing methods with potential industrial application is discussed.

69. Production of Bioactive Cellulose Films Reconstituted from Ionic Liquids

By Turner, Megan B.; Spear, Scott K.; Holbrey, John D.; Rogers, Robin D.

From Biomacromolecules (2004), 5(4), 1379-1384. DOI:10.1021/bm049748q

A new method for introducing enzymes into cellulosic matrixes which can be formed into membranes, films, or beads has been developed using a cellulose-in-ionic-liq. dissoln. and regeneration process. Initial results on the formation of thin cellulose films incorporating dispersed laccase indicate that active enzyme-encapsulated films can be prepd. using this methodol. and that precoating the enzyme with a second, hydrophobic ionic liq. prior to dispersion in the cellulose/ionic liq. soln. can provide an increase in enzyme activity relative to that of untreated films, presumably by providing a stabilizing microenvironment for the enzyme.

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525 Solutions, Inc. Publications Related to Cellulose

70. Applying ionic liquid solvent characteristics for controlled processing of polymer materials
By Holbrey, John D.; Chen, Ji; Turner, Megan B.; Swatloski, Richard P.; Spear, Scott K.; Rogers, Robin D.
From Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) (2004), 45(1), 297-298. Language: English, Database: CAPLUS

The unique, and controllable soly. parameters exhibited by Ionic Liqs. (ILs) as a general class of fluids, and by individual IL examples, can be applied to polymer dissoln. and processing, and can provide some potentially unique and exciting opportunities to enable formation of new polymer forms and composite materials. Examples of the use of ILs as solvents for the prepn., dissoln. and processing of polymer materials will be discussed, primarily concd. on using ILs as non-volatile solvents that allow prepn. of advanced cellulosic composites for sensor and smart materials applications, in which complexants, colorimetric, or biol. receptors into biorenewable, or biocompatible substrates.

~1 Citing

71. Ionic liquids as green solvents: Engineering bioactive cellulose materials
By Rogers, Robin D.; Holbrey, John D.; Spear, Scott K.; Turner, Megan B.
From Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004 (2004), CELL-198. Language: English, Database: CAPLUS

Bioactive membranes contg. enzymes phys. encapsulated within cellulose films have been prepd. using ionic liqs. as novel, non-derivitizing solvents to initially dissolve cellulose powder, allowing enzymes to be homogeneously dispersed prior to film prepn. The use of the resultant enzyme-in-cellulose films as sensors and supported biocatalysts, and approaches for enhancing enzyme stability, have been investigated and will be reported.

72. Cellulose-supported colorimetric sensors for mercury ion detection
By Poplin, Jane Holly; Swatloski, Richard P.; Holbrey, John D.; Spear, Scott K.; Rogers, Robin D.
From Abstracts of Papers, 227th ACS National Meeting, Anaheim, CA, United States, March 28-April 1, 2004 (2004), CELL-024. Language: English, Database: CAPLUS

Cellulose membranes are extremely porous and highly wetable which has advantages over hydrophobic, poorly wetting supports such as PVC or polyethylene for sensing in aq. systems by providing fast transport of water-sol. ions to the active sensing sites. Responsive, colorimetric cellulose materials can be prepd. by introducing a sensing moiety into cellulose-in-ionic liq. solns., providing a flexible route for forming indicating films by casting from water. PAN,1-(2-pyridylazo)-2-naphthol, a colorimetric complexant for transition metals can be readily incorporated into cellulose films, and is extremely responsive to metal-ions in soln., tuning from orange to a deep-red in the presence of mercury ions. Because the IL is capable of dissolving many org.

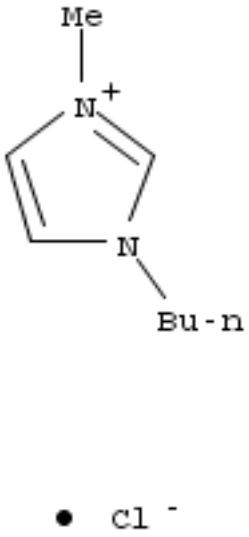
extractants, that are water insol., it is possible to introduce high loadings of the sensor complexant into the film.

73. Regenerated cellulose matrix-encapsulated active substances and method therefor

By Holbrey, John David; Spear, Scott K.; Turner, Megan B.; Swatloski, Richard Patrick; Rogers, Robin Don

From U.S. Pat. Appl. Publ. (2004), US 20040038031 A1 20040226, Language: English, Database: CAPLUS

The process involves encapsulation or immobilization of the active solid substance in a cellulose framework by regenerating cellulose dissolved in an ionic liq. solvent in a regenerating soln. The active substance can be initially present in the ionic liq. or in the regenerating solvent either as a soln. or dispersion. The invention is applicable to mol. encapsulation and to entrapping of larger particles including enzymes, nanoparticles and macroscopic components, and to the formation of bulk materials with a wide range of morphol. forms. Thus, carbamoylmethylphosphine oxide (I) encapsulated in a cellulose matrix was realized by adding I to a 10% soln. of cellulose in 1-butyl-3-methylimidazolium chloride (ionic liq.) under vigorous stirring and then removing the ionic liq. with water.



74. Ionic liquids for the dissolution and regeneration of cellulose

By Swatloski, Richard P.; Holbrey, John D.; Spear, Scott K.; Rogers, Robin D.

From Proceedings - Electrochemical Society (2002), 2002-19(Molten Salts XIII), 155-164. DOI:10.1149/200219.0155pv

There is an increasing willingness to develop new cellulose-based materials, particularly from homogeneous soln., due to the fact that cellulose is the earth's most abundant biorenewable resource. The opportunity to use ionic liqs. as solvents for clean extn. and processing of cellulose was investigated. Cellulose can be dissolved in a no. of ionic liqs. and easily regenerated by

contacting with water. This allows a simple, benign system for the processing of cellulose into fibers, monoliths, and films by forming into an aq. phase. This has potential environmental and cost advantages over current processing methodologies which make use of volatile or hazardous solvents.

75. Application of ionic liquid technologies to nuclear separations

By Rogers, Robin D.; Holbrey, John D.; Spear, Scott K.; Gutowski, Keith E.; Bridges, Nicholas J.; Cocalia, Violina A.; Swatloski, Richard P.

From Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003 (2003), NUCL-092. Language: English, Database: CAPLUS

Room temp. Ionic Liqs. (ILs), org. salts that are liq. at, or close to room temp. have great potential application for uses in liq.-liq. sepns. processes. As a class of liqs., ILs typically have wide liq. ranges, are non-volatile, and have solvent characteristics (hydro- and lipophilicity, hydrogen-bond donor and acceptor ability etc) that can be controlled and modified by suitable changes to either the cation or anionic components of the IL. We have begun the exploration of actinide sepns. using a variety of technologies based upon the use of ILs including, liq./liq. extn. using traditional extractants; incorporating an extractant functionality into an IL; immobilizing IL extractant phases on solid supports; and utilization of the solubilizing power of ILs to prep. cellulose-based materials for f-element sepns. ILs can thus be considered as a new class of materials for nuclear sepns., distinct from mol. solvents and from high temp. molten salts, with adjustable solvent characteristics, unique properties, and the potential for enhancing the principles of "green" chem. in various chem. processes.

76. Cellulose films regenerated from ILs and their role as scaffolding for enzyme attachment via glutaraldehyde

By Turner, Megan B.; Spear, Scott K.; Swatloski, Richard P.; Holbrey, John D.; Rogers, Robin D.

From Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003 (2003), IEC-190. Language: English, Database: CAPLUS

Immobilization of enzymes in a wide range of matrixes has been widely studied. Immobilization can increase enzyme stability and thus activity, and also enable simple recovery and recycling of catalysts. Here we describe the investigation of cellulose films contg. encapsulated laccase, from Rhus vernificera, prepd. by dissoln. and casting from 1-butyl-3-methylimidazole chloride ionic liq. soln. Laccase can be successfully immobilized in cellulose films prepd. in this way, while maintaining enzymic activity, and the activity can be controlled by pretreatment and processing methodologies. A comparison between the methods of film prepn., as well as their resp. activies will be presented.

77. Ionic liquids as green solvents: Engineering new bio-based materials

By Swatloski, Richard P.; Holbrey, John D.; Spear, Scott K.; Rogers, Robin D.

From Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003 (2003), IEC-090.

Language: English, Database: CAPLUS

The ideas and concepts of green chem. were established in order to facilitate the development and implementation of innovative sustainable non-polluting chem. technologies in an economically feasible manor. Not only is it important to lower process emissions, it is also imperative that a shift be made to the development of sustainable resources to complement, or replace diminishing petroleum-based feed-stocks. We have recently utilized 1-butyl-3-methylimidazolium chloride for the dissoln. of nature's most abundant renewable resources--cellulose. Because ionic liqs. can dissolve a wide range of materials, it can be anticipated that they will offer a route for incorporation of many functional mols. for sensing, recognition, or mol. binding into modified cellulose materials that have not been accessible in other traditional cellulose solvent systems. In this presentation we will examine the phys. properties of these new materials, as well as their possible application.

78. CMPO-impregnated cellulosic materials from ionic liquids for f-element separations

By Rogers, Robin D.; Holbrey, John D.; Spear, Scott K.; Gutowski, Keith E.; Swatloski, Richard P.

From Abstracts of Papers, 226th ACS National Meeting, New York, NY, United States, September 7-11, 2003 (2003), IEC-045.

Language: English, Database: CAPLUS

By taking advantage of the soly. of both cellulose and CMPO (octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide) in the ionic liq. 1-butyl-3-methylimidazolium chloride, we have prepd. CMPO-impregnated cellulosic materials as flocs, beads, rods, and membranes. Americium-241, plutonium-239, and uranium-233 all exhibit significant partitioning from aq. solns. to the cellulose impregnated materials with increasing concns. of nitric acid. In this presentation we will examine the phys. properties of these new materials, as well as their possible application in the sepns. of americium, plutonium, and uranium from acidic aq. solns.

79. Ionic liquid salt-induced inactivation and unfolding of cellulase from Trichoderma reesei

By Turner, Megan B.; Spear, Scott K.; Huddleston, Jonathan G.; Holbrey, John D.; Rogers, Robin D.

From Green Chemistry (2003), 5(4), 443-447. DOI:10.1039/b302570e

The potential for performing cellulase-catalyzed reactions on cellulose dissolved in 1-butyl-3-methylimidazolium chloride ([bmim]Cl) was investigated. Herem, the authors carried out a systematic study on the irreversible solvent and ionic strength-induced inactivation and unfolding of cellulase (EC 3.2.1.4) from T. reesei. Expts., varying both cellulase and ionic liq.

(IL) solvent concns., indicated that [bmim]Cl, and several other ILs, as well as dimethylacetamide-LiCl (a well-known solvent system for cellulose), inactivated cellulase under these conditions. Despite cellulase inactivity, the results obtained from this study led to valuable insights into the requirements necessary for enzyme activity in IL systems. Enzyme stability was detd. during urea, NaCl, and [bmim]Cl-induced denaturation obsd. through fluorescence spectroscopy. The protein stability of a PEG-supported cellulase in [bmim]Cl soln. was investigated and increased stability/activity of the PEG-supported cellulase in both the [bmim]Cl and citrate buffer solns. were detected.

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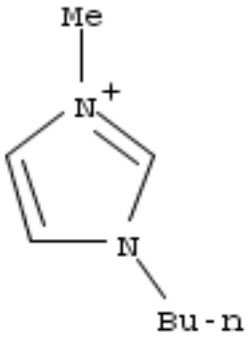
80. Dissolution and processing of cellulose using ionic liquids, cellulose solution, and regenerating cellulose

By Swatloski, Richard Patrick; Rogers, Robin Don; Holbrey, John David

From PCT Int. Appl. (2003), WO 2003029329 A2 20030410, Language: English, Database: CAPLUS

Cellulose is dissolved in an ionic liq. without derivatization, and is regenerated in a range of structural forms without requiring the use of harmful or volatile org. solvents. Cellulose soly. and the soln. properties can be controlled by the selection of the ionic liq. constituents, with small cations and halide or pseudohalide anions favoring soln.; dissoln. can be aided by irradn. An ionic liq., [C$_4$mim]Cl, proved to be the best for dissolving cellulose.



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81. Properties of regenerated cellulose from ionic liquids

By Swatloski, Richard P.; Holbrey, John D.; Spear, Scott K.; Rogers, Robin D.

From Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003 (2003), IEC-167.

Language: English, Database: CAPLUS

525 Solutions, Inc. Publications Related to Cellulose

Cellulose is the earth's most abundant biorenewable material. It has important com. applications across a wide variety of technologies. A hindrance in this field is due to the limited no. of solvents capable of completely dissolving cellulose. In our labs., we have utilized ionic liqs. (ILs) to successfully dissolve up to 30% wt/wt of cellulose without pretreatment or derivitization. Cellulose can easily be regenerated from the IL soln. simply by contacting the cellulosic soln. with water. We will describe methods for regeneration-capable of forming thin films, filaments, and membranes. Results from regenerated cellulose, as well as important phys. properties of the regenerated cellulose will be discussed. This research is sponsored by The PG Research Foundation, Inc.

82. Ionic liquids as green solvents for the dissolution and regeneration of cellulose

By Swatloski, Richard P.; Spear, Scott K.; Holbrey, John D.; Rogers, Robin D.

From Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003 (2003), CELL-131.

Language: English, Database: CAPLUS

With increasing governmental regulations restricting the use of current cellulose solvents, the need to replace them is becoming more important. Ionic Liqs. (ILs) have gained considerable attention for their potential use as green solvents, and the use of ILs as -green' replacements for the traditional org. solvents has been studied in recent literature. In our labs., we have utilized ILs as solvents, for the dissoln. of cellulose. We have successfully dissolved, without pretreatment or derivitization, up to 30% wt/wt of cellulose in ILs, which enables the use of ILs as a feasible and effective non-volatile alternatives to some of the environmentally undesirable solvent systems currently in use. The cellulose can be regenerated from the ionic liq. by simply contacting them with water. This allows a simple, benign system for the processing of cellulose into fibers, monoliths and films by forming into an aq. phase. Results from regenerated cellulose, as well as important intermol. forces responsible for the dissoln. of cellulose will be presented. This research is sponsored by The PG Research Foundation, Inc.

83. Ionic liquids: New solvents for nonderivitized cellulose dissolution

By Swatloski, Richard P.; Spear, Scott K.; Holbrey, John D.; Rogers, Robin D.

From Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002 (2002), IEC-076.

Language: English, Database: CAPLUS

There are only a limited no. of solvents that can effectively dissolve cellulose without derivitization; all have environmental downsides, and in some cases are even poor systems for the dissoln. Though it was first suggested in 1934 by Graenacher that molten N-ethylpyridinium chloride could be used to dissolve cellulose, at the time this seemed very impractical and of little value since the molten salt was, at the time, esoteric and a relatively high m.p. of 118 °C. Here we examine the history of cellulose solvents, the soly. of cellulose in ionic liqs. without activation or pretreatment, and the regeneration of cellulose from simple, nonvolatile ILs.

84. Cellulase activity in an ionic liquid

By Turner, Megan B.; Spear, Scott K.; Huddleston, Jonathan G.; Rogers, Robin D.

From Abstracts of Papers, 224th ACS National Meeting, Boston, MA, United States, August 18-22, 2002 (2002), IEC-023.

Language: English, Database: CAPLUS

The ionic liq., 1-butyl-3-methylimidazolium chloride will dissolve cellulose and we have begun to investigate the possibility of performing enzyme catalyzed reactions on the cellulose in this solvent. Expts. with both varied cellulase and [C4mim][Cl] concns. have indicated that [C4mim][Cl] inactivates cellulase under numerous exptl. conditions. Our results investigating the effects of alkali metal chloride salts and other agents to det. the nature of the obsd. inactivation will be presented.

85. Dissolution of cellulose with ionic liquids

By Swatloski, Richard P.; Spear, Scott K.; Holbrey, John D.; Rogers, Robin D.

From Journal of the American Chemical Society (2002), 124(18), 4974-4975. DOI:10.1021/ja025790m

Initial results that demonstrate that cellulose can be dissolved without activation or pretreatment in, and regenerated from, 1-butyl-3-methylimidazolium chloride and other hydrophilic ionic liqs. are reported. This may enable the application of ionic liqs. as alternatives to environmentally undesirable solvents currently used for dissoln. of this important bio-resource.

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86. Derivatization of chitin in room temperature ionic liquids

By Reichert, W. Matthew; Visser, Ann E.; Swatloski, Richard P.; Spear, Scott K.; Rogers, Robin D.

From Abstracts of Papers, 222nd ACS National Meeting, Chicago, IL, United States, August 26-30, 2001 (2001), IEC-025.

Language: English, Database: CAPLUS

Biorenewables are gaining attention as replacements for petroleum-based products, due to their favorable properties and natural abundance. Efficient processing and sepns. are usually the key steps preventing economic processing of biomass. Chitin is the world's second most abundant biopolymer, behind cellulose, and in this presentation, we will demonstrate the use of room temp. ionic liqs. as solvents in the chem. modification of chitin. In addn., the use of ionic liqs. for value added processing (e.g., decolorization of chitin) will be discussed.

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87. Temperature effects on polymer-based aqueous biphasic extraction technology in the paper pulping process

By Li, Mian; Willauer, Heather D.; Huddleston, Jonathan G.; Rogers, Robin D.

From Separation Science and Technology (2001), 36(5 & 6), 835-847. DOI:10.1081/SS-100103623

In order to apply a polymer-based aq. biphasic system (ABS) extn. to the paper pulping process, the partitioning behavior of 6 model lignin (I) species, i.e., Indulin AT (II), Indulin C (III), Reax 85A (IV), Reax 825E (V), Polyfon T (VI), and alkali lignin, were studied in PEG-2000/NaOH ABS prepd. from stock solns. of 40 wt.% PEG-2000 and increasing concns. of NaOH. In a given salt concn., the distribution ratios increased in the order VI < V < IV < III < alkali lignin < II because of the degree of sulfonation. In both chem. and organosolv pulping, temps. >120° are needed to solubilize I from the cellulose, but the availability of data on all relevant ABS system parameters, esp. phase diagrams under process conditions, is limited. Phase diagrams of PEG-2000/$(NH_4)_2SO_4$ at higher process temps. were thus measured. The partitioning of phthalic acid was studied in order to understand temp. effects, not only on system compn., but also on phase partitioning.

88. Investigation of aqueous biphasic systems for the separation of lignins from cellulose in the paper pulping process

By Willauer, Heather D.; Huddleston, Jonathan G.; Li, Mian; Rogers, Robin D.

From Journal of Chromatography B: Biomedical Sciences and Applications (2000), 743(1 + 2), 127-135.
DOI:10.1016/S0378-4347(00)00222-X

In efforts to apply a polymer-based aq. biphasic system (ABS) extn. to the pulping process, the study of the distribution of various lignin (I) and cellulose (II) fractions in ABS and the effects of temp. on system compn. and solute partitioning were investigated. The partitioning of 3 I species, i.e., Indulin AT, Indulin C, and Reax 85A, were studied in ABS prepd. from stock solns. of 40 wt.% polyethylene glycol (III) and increasing concns. of K_2CO_3, $(NH_4)_2SO_4$, and NaOH. The partitioning of these I samples is affected by the free energy of hydration of the salt forming the ABS, the tie line length, and the dissocn. of the sulfonic acid and OH groups of the distributed solutes. The partitioning of fibrous II and DEAE-II were studied in 40 wt.% III-$(NH_4)_2SO_4$ ABS. The hydrophilic nature of these species is important in terms of their phase preference when designing a polymer-based aq. biphasic extn. process for use in a pulping process. Both II samples do not dissolve, but rather report to the salt-rich phase of an ABS. In both chem. and organosolv pulping, temps. >120° are needed to solubilize I from the II fraction of wood. To study the effects of temp. on the phase diagram and solute partitioning, phthalic acid and NH_4 $^{99}TcO_4$ (as system probes) were partitioned in 40 wt.% III-$(NH_4)_2SO_4$ ABS at known tie line lengths as a function of temp. Temp. did not appear to affect the partitioning results beyond the expected increase in phase divergence as temp. was increased. The III polymer itself was stable to chem. pulping conditions.