525 Solutions, Inc. Publications Related to Chitin

1. Farmed Jumbo shrimp molts: an ionic liquid strategy to increase chitin yield per animal while controlling molecular weight

By Wineinger, Hannah B.; Kelly, Adrian; Shamshina, Julia L.; Rogers, Robin D.
From Green Chemistry (2020), 22(18), 6001-6007. DOI:10.1039/d0gc02216k

In pursuit of bioplastics which require a controlled biopolymer mol. wt., consistency, and supply, we have examd. the chitin in the molts of farm raised Hybrid (H1) Pacific whiteleg shrimp (Litopenaeus vannamei) by collecting the molts during the shrimp growth cycle, sorting by shrimp av. body wt. (ABW), and extg. the chitin from the molts using the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]). The amt. of available chitin in the molts increases with the age/size of the molting shrimp, 19% in juveniles to 22% in adults. As expected from the biol. of molting, the chitin in the final shell peeled from the adult shrimp contained the most chitin (29%). It is neither easier nor harder to ext. the chitin from molts or peels, and the extd. chitin was equiv. in purity and degree of acetylation with comparable extn. efficiency (67% for molts, 63% for peels). In addn., the wt. av. mol. wt. (MW) of the chitin has the potential to be controlled by shrimp age/size. The MWs of the chitin in the smaller animals (5-10 and 10-20 g ABW) were comparable at ~ 4-5 MDa, while the chitin obtained from the large adult molts (30-40+ g ABW) exhibited a significantly higher MW of 23 MDa. Thus, by collecting and using the shrimp molts, the industrial viability of chitin can be improved by providing both a larger amt. of chitin per shrimp (an ca. 8-fold increase) and by providing the opportunity to ext. chitin of a specific MW.

2. 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.

3. A method for determining the uniquely high molecular weight of chitin extracted from raw shrimp shells using ionic liquids

By Wineinger, Hannah B.; Shamshina, Julia L.; Kelly, Adrian; King, Catherine; Rogers, Robin D.
From Green Chemistry (2020), 22(12), 3734-3741. DOI:10.1039/d0gc00753f

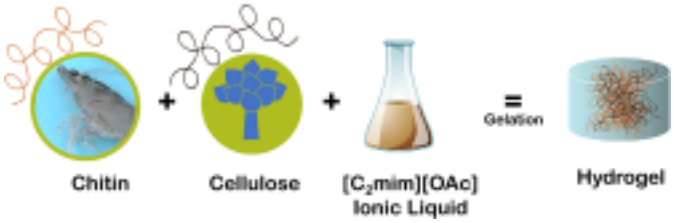
Because the very high mol. wt. of biopolymers extd. from biomass using ionic liqs. (ILs) cannot be accurately detd. using conventional methodologies (e.g., gel permeation chromatog., intrinsic viscosity

measurements, etc.) due to their insoly. in the solvents used for such measurements, we have developed a new method for Mw detn. based on static light scattering (SLS) in IL soln. The method, based on using SLS measurements to calc. wt. av. mol. wt. (Mw) via the Rayleigh equation, was validated by detg. the Mw for both com. available (practical grade, PG-) chitin and chitin extd. from raw shrimp shell using 1-ethyl-3-methylimidazolium acetate. We have shown that on av. the IL-extd. chitin has a high av. Mw value, almost two and a half times larger than that for PG-chitin, has a comparatively low polydispersity, and has a degree of acetylation nearly ideal (98(1)% vs. PG-chitin at 82(1)%), thus making the IL-extd. polymer preferable for utilization in materials prepn.

4. Advances in Processing Chitin as a Promising Biomaterial from Ionic Liquids
By Shamshina, Julia L.; Zavgorodnya, Oleksandra; Rogers, Robin D.
From Advances in Biochemical Engineering/Biotechnology (2019), 168(Application of Ionic Liquids in Biotechnology), 177-198. DOI:10.1007/10_2018_63

A review. Chitin isolated through microwave-assisted dissoln. using ionic liqs. is a high mol. wt. (MW) polymer that can be manufd. into materials of different architectures (e.g., fibers, films, microspheres, nanostructured materials) to be used as wound care dressings, drug delivery devices, scaffolds, etc. However, because of differences from traditional isolation methods and, thus, differences in polymer length and degree of deacetylation, it could exhibit bio-related properties that differ from those of traditionally 'pulped' chitin. Here we present the initial assessments of bio-related chitin properties in order to provide a useful scientific basis for clin. applications: biocompatibility, cytotoxicity (intracutaneous reactivity), wound healing efficacy, histol. evaluation of the wounds treated with chitin dressing, and antibacterial activity. We also provide the studies that outline potential applications of chitin as a raw polymer for prepn. of biomaterials.Graphical Abstr.

5. 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 ([C2mim][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-CO2 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.

6. 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.

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 m2/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.

7. Agricultural uses of chitin polymers
By Shamshina, Julia L.; Kelly, Adrian; Oldham, Tetyana; Rogers, Robin D.
From Environmental Chemistry Letters (2020), 18(1), 53-60. DOI:10.1007/s10311-019-00934-5

A review. Due to strict legislation which governs the use of pesticides, fertilizers and plant growth regulators, there is a demand for org. alternatives. Potential risks for people, possible long-term health effects, and pesticide environmental fate resulted in a widespread societal issue. Because sustainable agriculture interconnects the economically and socially, the use of environmentally sound compds. has become popular. Improving plant growth using natural compds. such as chitin, a carbohydrate chain polymer, and its derivs. is a promising sustainable agriculture strategy. Chitin and its derivs. exhibit a unique mode of action being at the same time safe and non-toxic by nature. They are recognized as promising soil amendments for improving soil quality, induce abiotic and biotic plant stress tolerance, boost defense mechanism of plants against invading microorganisms, elicit the prodn. of secondary metabolites, and protect the safety of edible products. Here, we review beneficial effects of chitin as a fertilizer, soil conditioning agent, plant disease control agent, antitranspirant, ripening retardant, and seed and fruit coating.

8. 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,

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.

9. Green chemistry as a business model: it is sustainable

By Rogers, Robin D.

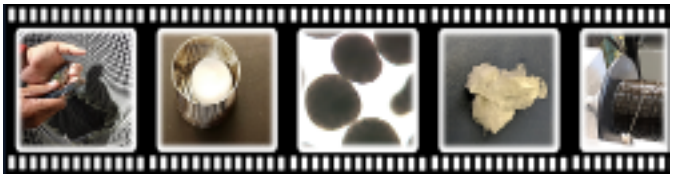
From Abstracts of Papers, 257th ACS National Meeting & Exposition, Orlando, FL, United States, Mar. 31-Apr. 4, 2019 (2019), SCHB-0023.

Academic institutions and small and large companies are now talking about building a more sustainable future, where technologies and products are created with consideration to the environmental and social impact they may have. Green Chem. provides such an opportunity to produce and support innovative and evolutionary, environmentally-aware research and development efforts, focused toward developing and sustaining future industrial processes and products based on pos. environmental and economic advances. The question remains whether one can actually make money and sustain a business with a green chem. business model. This presentation will discuss our efforts to transition from academic research, to university-incubated start-up, to full scale commercialization using the extn. and prodn. of chitin as example.

10. Advances in Functional Chitin Materials: A Review

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

From ACS Sustainable Chemistry & Engineering (2019), 7(7), 6444-6457.
DOI:10.1021/acssuschemeng.8b06372



A review. Chitin is a promising natural polymer to produce functional materials due to the attractive combination of abundance, price, favorable biol. properties, and biodegradability. However, multiple literature examples often confuse processing of chitosan, the deacetylated version of chitin, due to chitosan's much higher soly. in traditional solvents. Nonetheless, despite current challenges to solubilize natural chitin, there is still a large body of literature demonstrating multiple ways to manipulate this polymer into materials of desired forms and properties. Here we review one such area where chitin promises both technol. superiority and potential for com. success, the use of chitin in biomedical research. We discuss techniques which have been utilized to process chitin and to prep. chitin-based functional materials, particularly in the prodn. of fibers, films, beads, and hydrogels. Emphasis is given to the most recent methods and a compilation of a compelling collection of examples based on current research and existing products. These examples demonstrate the suitability of chitin for prodn. of surgical sutures, wound care materials, tissue engineering biomaterials, and other various biomedical applications.

11. 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 ([C2mim][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 [C2mim][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 [C2mim][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.

12. 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,

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.

13. Metal particle-chitin composite materials, methods of making thereof, and their use as catalysts for coupling reactions
By Rogers, Robin D.; Zavgorodnya, Oleksandra; Shamshina, Julia L.
From U.S. Pat. Appl. Publ. (2018), US 20180273710 A1 20180927,

The invention relates to a method of making a metal particle-chitin composite material, comprising: contacting an ionic liq. with chitin, thereby forming a mixt.; contacting the mixt. with a non-solvent, thereby forming a chitin substrate in the non-solvent; collecting the chitin substrate from the non-solvent; deacetylating the collected chitin substrate, thereby forming a deacetylated chitin substrate; contacting the deacetylated chitin substrate with a metal salt, thereby forming an impregnated precursor composite material; and contacting the impregnated precursor composite material with a reducing agent, thereby reducing the metal salt to form a plurality of metal particles dispersed on the chitin substrate and forming the metal particle-chitin composite material. An article of manuf. comprising the metal particle-chitin composite material made by the inventive method is also claimed. A catalyst comprising the metal particle-chitin composite material made by the inventive method is also disclosed. A method of use of the catalyst to catalyze a coupling reaction is also claimed.

14. 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 ([C2mim][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.

15. Enzymatic hydrolysis of ionic liquid-extracted chitin

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

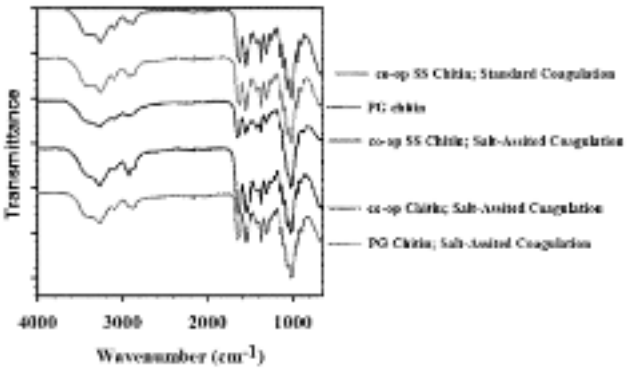
From Carbohydrate Polymers (2018), 199, 228-235. DOI:10.1016/j.carbpol.2018.07.014

Chitin, one of Nature's most abundant biopolymers, can be obtained by either traditional chem. pulping or by extn. using the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate. The IL extn. and coagulation process provides access to a unique chitin, with an open hydrated gel-like structure. Here, enzymic hydrolysis of this chitin hydrogel, dried shrimp shell, chitin extd. from shrimp shells using IL and then dried, and com. chitin was carried out using chitinase from Streptomyces griseus. The enzymic hydrolysis of shrimp shells resulted only in the monomer N-acetylglucosamine, while much higher amts. of the dimer (N,N'-diacetylchitobiose) compared to the monomer were detected when using all forms of 'pure' chitin. Interestingly, small amts. of the trimer (N,N',N''-triacetylchitotriose) were also detected when the IL-chitin hydrogel was used as substrate. Altogether, our findings indicate that the product distribution and yield are highly dependent on

the substrate selected for the reaction and its hydrated state.

16. Coagulation of chitin from ionic liquid solutions using kosmotropic salts

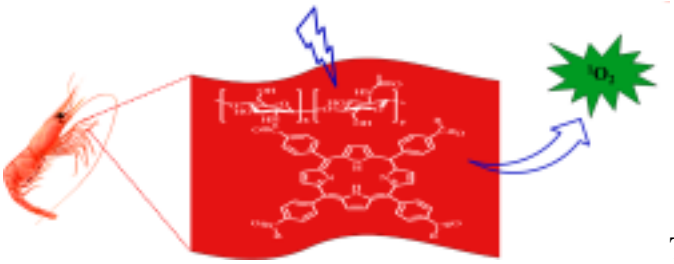
By Rogers, Robin D.; Galpothdeniya, Waduge Indika S.; Shamshina, Julia L.; Zavgorodnya, Oleksandra
From U.S. Pat. Appl. Publ. (2018), US 20180194864 A1 20180712,



The invention relates to a A method for sepg. chitin from a chitinous biomass, comprising: contacting the mixt. with an aq. soln. of a kosmotropic salt, thereby coagulating the chitin, and forming a biphasic system comprising an ionic liq.-chitin phase, and an aq. kosmotropic salt phase; sepg. the ionic liq.-chitin phase from the aq. kosmotropic salt phase; and collecting the chitin from the sepd. ionic liq.-chitin phase, thereby forming a recycled ionic liq.

17. Singlet Oxygen Production and Tunable Optical Properties of Deacetylated Chitin-Porphyrin Crosslinked Films

By Li Kai; Berton Paula; Kelley Steven P; Rogers Robin D; Li Kai; Rogers Robin D; Rogers Robin D
From Biomacromolecules (2018), 19(8), 3291-3300.

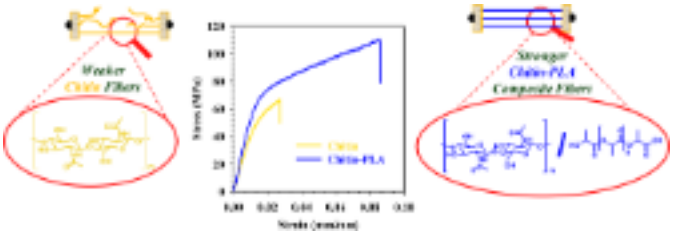


The increasing need for biocompatible materials as supports to immobilize photosensitizer molecules for photodynamic therapy (PDT), led us to investigate the use of chitin as a support for 4,4',4",4"'-(porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid) (mTCPP) for singlet oxygen production. Chitin was first extracted from shrimp shells using the ionic liquid 1-ethyl-3-methyl-imidazolium acetate ([C2mim][OAc]), coagulated as a floc into water, and then deacetylated to varying degrees of deacetylation using 4 M NaOH. The deacetylated chitin (DA-chitin) was dissolved in [C2mim][OAc] and mTCPP was covalently attached by reaction between the amino groups of DA-chitin and the carboxyl groups of mTCPP using N-(3-(dimethylamino)propyl)- N'-ethylcarbodiimide hydrochloride (EDC) and N-hydroxysuccinimide (NHS) as activators. The resulting composite polymers were cast as a film and coagulated with water to remove IL and excess reagents, resulting in homogeneous DA-chitin/mTCPP films. Attempts to prepare films by coagulation from a solution containing chitin and mTCPP to physically entrap the porphyrin, resulted in aggregation of mTCPP in the film. The DA-chitin/mTCPP films had strong optical absorbance and their absorbance intensity could be tuned by changing the mTCPP content and degrees of deacetylation of DA-chitin in a predictive manner. In addition, metal ions (Cu(2+), Zn(2+), Gd(3+), and Fe(3+)) could be easily chelated into the DA-chitin/mTCPP films through mixing metal salt solutions with the films and heating. After chelating metal ions, optical properties, such as absorption region and intensities, of the films changed, suggesting chelating metal ions could tune their optical properties. Moreover, the DA-chitin/mTCPP films could generate singlet oxygen under light irradiation and, hence, might serve as a photosensitizer in PDT. The methodology used in this study is also applicable for developing other functional biomaterial devices.

18. Ionic Liquid Platform for Spinning Composite Chitin-Poly(lactic acid) Fibers

By Shamshina, Julia L.; Zavgorodnya, Oleksandra; Berton, Paula; Chhotaray, Pratap K.; Choudhary, Hemant; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2018), 6(8), 10241-10251.
DOI:10.1021/acssuschemeng.8b01554



In the design of stronger chitin fibers reinforced with poly(lactic acid) (PLA), an ionic-liq.-based (IL-based) approach was developed in which both polymers were codissolved in an 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) and wet-jet spun into composite fibers. Chitin, directly extd. from shrimp shell, had a soly. in the IL of 2.75 wt %, while PLA of MW 700,000 g/mol had a soly. of 49 wt %. Keeping the IL satd. in chitin, homogeneous solns. of chitin and PLA could be obtained up to 27 wt % (relative to the IL) PLA. Spinning dopes were prepd. by maintaining the chitin concn. relative to the IL at 1.75 wt % and adding PLA in chitin to PLA wt. ratios of 1:0.1 through 1:1 (PLA concns. of 0.175-1.75 wt % relative to the IL). Homogeneous chitin/PLA fibers could be spun when the chitin to PLA ratio was between 1:0.1 and 1:0.3. The tensile strength and plasticity of the fibers depended on the chitin to PLA ratio with the highest plasticity (8.8% vs 3.0% for pure chitin fibers), strength (112 vs 71 MPa), and stiffness (5.9 vs 4.2 GPa) obsd. for fibers with a chitin to PLA ratio of 1:0.3. Studies of the fracturing surface of the fibers indicated that fracturing occurred through an initial disruption of the interactions between polymer chains, followed by complete fiber breakage. The work not only demonstrates that homogeneous composite fibers can be spun using a biopolymer and PLA additive, but also suggests a versatile platform for prepn. of multiple biopolymer-PLA materials using soln. processing methods.

19. Chitin for the replacement of fluoropolymers in the assembly of electrochemical devices

By King, Catherine; Easton, Max E.; Rogers, Robin D.

From ChemRxiv (2018), 1-10.

Chitin and graphene/chitin composite films were prepd. using ionic liq. processing and tested as separators and electrodes, resp., in a supercapacitor to demonstrate the construction and function of an energy storage device which is constructed solely from bio-based polymer materials. The dry films possessed high thermal (Td = 265 and 246°) and mech. (tensile strength = 5(1) and 1.7(2) MPa) stabilities. Once soaked in an aq.

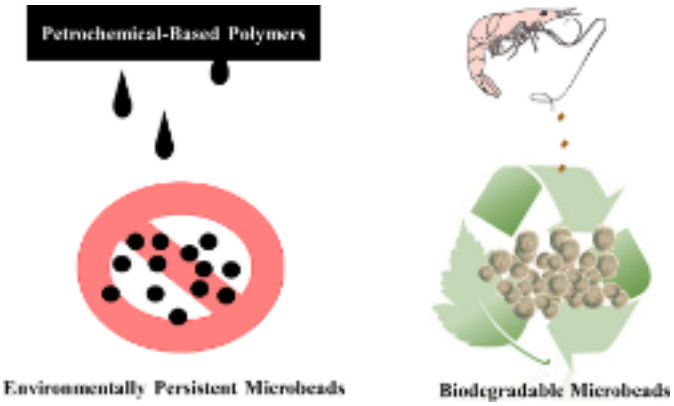
electrolyte (2 M (NH4)2SO4) for use in a supercapacitor test cell, the device reached a peak capacitance value of 2.4 F/g. This work demonstrates a first step towards a scalable method for the prepn. and assembly of biorenewable electrochem. devices, which avoid the use of unsustainable fluoropolymers and solvents, and is poised to be an important part of environmentally-sustainable economies.

20. Porous Chitin Microbeads for More Sustainable Cosmetics

By King, Catherine A.; Shamshina, Julia L.; Zavgorodnya, Oleksandra; Cutfield, Tatum; Block, Leah E.; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2017), 5(12), 11660-11667.

DOI:10.1021/acssuschemeng.7b03053



The microbead form is a material architecture that is promising for use in biomedical and cosmetic applications; however, the use of petroleum-based microbeads (i.e., plastics) has raised significant environmental concerns in recent years. Microbeads prepd. from renewable polymers could represent a sustainable alternative to these synthetic microbeads. This work explores the use of chitin in prepg. biodegradable, biocompatible microbeads of low toxicity. Chitin microbeads were synthesized using the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]); the IL was used to both ext. chitin directly from waste shrimp shell and to prep. the porous microbeads by coagulation in polypropylene glycol (PPG). The effects of biopolymer source and bead-prepn. parameters on the formation of beads were investigated, as well as the effects of the drying conditions on the dry bead structure. It was found that IL-extd. chitin could be used to prep. beads of homogeneous size distribution (with 60% of beads 125-250 μm) and shape, while com. available practical grade chitin could not, suggesting that high mol. wt. chitin is required for bead-material formation. Supercrit. CO2 drying and lyophilization of the wet beads led to dry chitin beads with an opaque appearance, porous interiors, and uniform shape. Loading and release studies of representative active compds. (indigo dye and sodium salicylate) into the chitin beads indicated that the dry beads could be easily loaded from an aq. soln. of active compd. and could release 90% of the active compd. within 7 h in deionized (DI) water at room temp.

21. Can ionic liquids be disruptive enough to save the world?
By Rogers, Robin D.
From Abstracts, 52nd Midwest Regional Meeting of the American Chemical Society, Lawrence, KS, United States, October 18-20 (2017), MWRM-244.

Our role as scientists is vital in the development of green transformational technologies and achieving Society's goal of a sustainable world. Given the early promises of the Ionic Liq. (IL) field to tackle major sustainability issues, perhaps it's time to ask, is the field all talk and no action. This presentation will provide an overview of a personal journey from a pure academic to a business person using the combined motivations of what the IL field has demonstrated it can do and what industry has steadfastly said it cannot do. Given the ability of ILs to dissolve renewable biomass, the technol. gives the perfect platform for commercialization. In 2010, we demonstrated the dissoln. and extn. of chitin directly from shrimp shells at 100 mL scale, with the resultant chitin polymer maintaining a high-mol. wt., providing a material with high strength and unprecedented control of the final form. In 2012, we, together with 525 Solns., Inc., built a 3 L Lab. Demonstration Pilot Unit further scaled-up to a 20 L mini pilot in 2014-2015. Currently, 525 Solns., Inc. has formed a joint venture with a zero-waste sustainable shrimp farm to build a three 500 L line chitin extn. plant to be sited worldwide with each new shrimp farm established. The first plant will be built this year. Sometimes, we as academics will have to stop just trying to convince others to do what we tell them is good for them, and instead just do it ourselves.

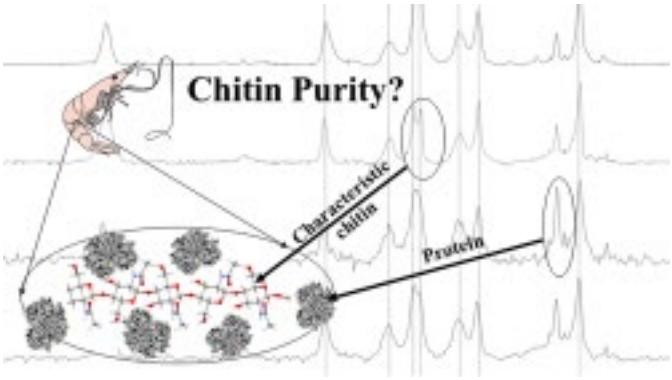
22. Electrospinning of biopolymers and biopolymeric composites from ionic liquids
By Zavgorodnya, Oleksandra; Shamshina, Julia L.; Rogers, Robin D.
From Abstracts of Papers, 254th ACS National Meeting & Exposition, Washington, DC, USA, August 20-24, 2017 (2017), POLY-504.

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 ([C2mim][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.

23. Measuring the Purity of Chitin with a Clean, Quantitative Solid-State NMR Method

By King, Catherine; Stein, Robin S.; Shamshina, Julia L.; Rogers, Robin D.

From ACS Sustainable Chemistry & Engineering (2017), 5(9), 8011-8016.
DOI:10.1021/acssuschemeng.7b01589



Chitin is a versatile biopolymer which can be extd. directly from biomass and used for the prepn. of high value materials, but such materials often require high-purity chitin. However, complete removal of proteinaceous material from chitin, which was obtained from biomass sources, can be difficult to det. Here the authors report a quick, nondestructive method to measure chitin content using solid-state multiCP 13C NMR, which requires only 105 min and allows for recovery of the sample. A calibration curve was constructed from spectra of mass-based mixts. of com. chitin and bovine serum albumin protein. This allowed for the quantification of chitin content (and therefore purity) in both chitinous biomass and extd. chitin samples in a quick, clean, nondestructive manner that agreed with measurements made by the method of Black and Schwartz, within the error of each of the methods.

24. Electrospinning Biopolymers from Ionic Liquids Requires Control of Different Solution Properties than Volatile Organic Solvents

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

From ACS Sustainable Chemistry & Engineering (2017), 5(6), 5512-5519.
DOI:10.1021/acssuschemeng.7b00863

We report the correlation between key soln. properties and spinability of chitin from the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) and the similarities and differences to electrospinning solns. of nonionic polymers in volatile org. compds. (VOCs). We found that when electrospinning is conducted from ILs, cond. and surface tension are not the key parameters regulating spinability, while soln. viscosity and polymer concn. are. Contrarily, for electrospinning of polymers from VOCs, soln. cond. and viscosity have been reported to be among some of the most important factors controlling fiber formation. For chitin electrospun from [C2mim][OAc], we found both a crit. chitin concn. required for continuous fiber formation (>0.20 wt %) and a required viscosity for

the spinning soln. (between ca. 450-1500 cP). The high viscosities of the biopolymer-IL solns. made it possible to electrospin solns. with low, less than 1 wt %, polymer concn. and produce thin fibers without the need to adjust the electrospinning parameters. These results suggest new prospects for the control of fiber architecture in nonwoven mats, which is crucial for materials performance.

25. 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,

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. CO2, gaseous CO2, or combinations thereof.

26. "Practical" Electrospinning of Biopolymers in Ionic Liquids
By Shamshina, Julia L.; Zavgorodnya, Oleksandra; Bonner, Jonathan R.; Gurau, Gabriela; Di Nardo, Thomas; Rogers, Robin D.
From ChemSusChem (2017), 10(1), 106-111. DOI:10.1002/cssc.201601372

To address the need to scale up technologies for electrospinning of biopolymers from ionic liqs. to practical vols., a setup for the multi-needle electrospinning of chitin using the ionic liq. 1-ethyl-3-methylimidazolium acetate, [C2mim]-[OAc], was designed, built, and demonstrated. Materials with controllable and high surface area were prepd. at the nanoscale using ionic-liq. solns. of high-mol.-wt. chitin extd. with the same ionic liq. directly from shrimp shells.

27. 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,

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.

28. Chitin and alginate composite fibers
By Rogers, Robin D.; Gurau, Gabriella; Shamshina, Julia L.; Daly, Daniel T.
From U.S. Pat. Appl. Publ. (2016), US 20160082141 A1 20160324,

Disclosed herein are composite fibers that comprises chitin and alginate. The formation of the chitinous-alginate composite fiber involves the use of ionic liqs. and high mol. wt. pure chitin obtained directly from chitin biomass. Optional additive such as vitamin E is successfully incorporated in to the composite fiber.

The chitinous alginate fiber formed has a continuous and homogenous morphol., even with the addn. of additive. Methods of making and using the chitinous-alginate composite fiber as wound dressing is also disclosed.

29. Diversifying the chitin economy: Different sources of biomass for chitin extraction and biomaterial formation

By Achinivu, Ezinne C.; Shamshina, Julia L.; Rogers, Robin D.

From Abstracts, 68th Southeastern Regional Meeting of the American Chemical Society, Columbia, SC, United States, October 23-26 (2016), SERMACS-1095.

Chitin is a biocompatible, antimicrobial, and biodegradable polymer, which has been utilized for the prodn. of a range of low- and high-value materials, for a variety of applications. Most often, chitin is obtained from crustacean shells, where it exists in a matrix consisting primarily of CaCO3, proteins, and pigments. Chitin extd. from shrimp shell biomass, using the ionic liq. (IL) 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]), has been shown to possess high mol. wt., high purity, and a high degree of acetylation,1-2 thus receiving significant attention as a potential bioresource for the prodn. of high value biomaterials. Due to the region-specific nature of shrimp shell biomass availability, it is important to expand on the various biomass feedstocks available for chitin prodn. The work presented here describes a study of several different biomass sources suitable for chitin extn. with the same extn. technique. Using shrimp shell biomass as a benchmark, the various biomass sources have been systematically examd. for their exact compn. (protein, minerals and ash), chitin isolation yield and the biomaterials prepd. This study presents a step toward broadening the biomass choices for chitin isolation-a necessary step for the commercialization of biomaterials and bioproducts from chitin.

30. A platform for more sustainable chitin films from an ionic liquid process

By King, Catherine; Shamshina, Julia L.; Gurau, Gabriela; Berton, Paula; Khan, Nur Farahnadiah Abdul Faruk; Rogers, Robin D.

From Green Chemistry (2017), 19(1), 117-126. DOI:10.1039/C6GC02201D

A versatile platform for the prepn. of chitin films with tunable strength, morphol., and efficacy of application has been designed from an ionic liq. process for the prodn. of more sustainable high value materials. Films were prepd. by a simple casting method from a soln. of chitin in the ionic liq. 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]). The chitin source, the loading in ionic liq., and the drying methods defined film properties such as strength, porosity, and water absorbency. Only chitin directly extd. from shrimp shells using the ionic liq. (rather than com. available chitin) could be used to cast films strong enough to be handled and dried. The optimal loading of chitin in the ionic liq. was detd. to be 2.5 wt% and different drying methods led to different film properties (e.g., hard and rigid vs. soft and porous). As an exemplary application, loading and release of a model drug (caffeine) was investigated. Interestingly, a burst release of the majority of the caffeine was obsd. in the first 20 min, followed by slow release of the remainder. Although more investigations are needed, the chitin film platform can be thought of as an attr(M. Rinaudo, Prog. Polym. Sci., 2006, 31, 603-632) made from one of Nature's most abundant polymers.active new tool in the development of packaging materials, biomedical devices, and absorbent materials (M. Rinaudo, Prog. Polym. Sci., 2006, 31, 603-632) made from one of Nature's most abundant polymers.

31. Chitin-based sorbents for mining metals from oceans: A sustainable alternative to terrestrial mining

By Rogers, Robin D.; Berton, Paula

From Abstracts, 44th Middle Atlantic Regional Meeting of the American Chemical Society, Riverdale, NY, United States, June 9-12 (2016), MARM-174.

The increased pressure from society for more sustainable practices is leading to the promotion of less material- and energy-intensive activities, together with the diminishing or even elimination of waste generated during the processes. In particular, it has been proposed that mining the oceans has lower environmental impacts than terrestrial mining and represents an alternative to reduce the generation of waste during the extn. processes. Among the possible materials that can be used for ocean mining, chitin-based sorbents have been developed by our group as biodegradable extractants for harvesting metals from seawater. Native chitin (poly(N-acetylglucosamine)) can be extd. from biomass by dissoln. in ionic liqs. (IL) such as 1-ethyl-3-methylimidazolium acetate and shaped into usable materials such as fibers or nanomats. The final sorbents are insol. in most other solvents and can be exposed to solns. of reactive chems. to selectively functionalize only the exposed surfaces. The surface-specific functionalization of chitin results in a measurable change in metal affinity without compromising bulk phys. properties such as strength. Addnl., the nucleophilic amine in chitin can be easily tied to almost any functional group with almost any linker, giving chitin-based materials potential for fine tuning. Here we present the prepn. and characterization of these materials, together with examples of their affinity for specific metal ions.

32. Chemical pulping of chitinous biomass for chitin and treatment of biomass composition

By Barber, Patrick S.; Griggs, Chris S.; Rogers, Robin D.; Gurau, Gabriela; Shamshina, Julia L.

From U.S. Pat. Appl. Publ. (2016), US 20160060363 A1 20160303,

Methods of sepg. chitin from a chitinous biomass that contains chitin and nonchitin material by a chem. pulping process that uses a protic ionic liq. or a compn. comprising acid and base precursor mols. are described. Also methods for purifying chem. pulped chitin resulting in a pure chitin material with a high mol. wt. and a higher degree of acetylation, compared to traditional pulping and ionic liq. extn. based methods are described.

33. 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. CO2 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.

34. 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.

35. 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.

36. Uranium-from-seawater sorbents from fishing industry waste - cost reduction through solvent recycle

By Shamshina, Julia L.; Gurau, Gabriela; Kelley, Steven P.; Rogers, Robin D.
From Abstracts of Papers, 249th ACS National Meeting & Exposition, Denver, CO, United States, March 22-26, 2015 (2015), I+EC-50.

The sorbent for recovery of uranium from seawater is currently too expensive and environmentally damaging to allow uranium from seawater mining to be economically viable. For very large scale deployment there is a need for cheap and biodegradable sorbent materials. The ability of ionic liqs. (ILs) to ext. and dissolve high mol. wt. chitin directly from crustacean shells allows nanostructured sorbent materials to be electrospun. We have proven the general feasibility of the concept; and a typical process involves chitin dissoln. in the ionic liq. followed by its electrospinning into water. This process is currently costly not only because it requires large vols. of (currently) expensive ionic liqs. but also because of inefficient solvent recovery. A traditional method to remove water traces is prolonged heating of ILs under vacuum for 48 h. This is not suitable for the hydrophilic types of ILs which form strong hydrogen bonds between themselves and water. The process is also energy consuming. Therefore, in order to utilize the breakthrough sorbent-prodn. technol., the recovery and recycle of ionic liqs. is essential. The presentation will discuss methods that allow for the recovery and recycle of ionic liqs., and their effect on the process economics.

37. Dual functional chitin based sorbents for coextraction of aqueous copper and uranium

By 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-48.

Chitin-based sorbents have been developed by our group as biodegradable extractants for harvesting uranium from seawater. However, for these materials to be usable, a balance must be obtained between their shorter lifetime in the marine environment and the performance needs for their application. We are investigating the use coextn. of biocidal copper(II) ions naturally present in seawater along with uranium as one possible route to slowing down the biodegrdn. of the sorbent. Native chitin (poly(N-acetylglucosamine)) can be extd. from biomass by dissoln. in ionic liqs. such as 1-ethyl-3-methylimidazolium acetate and formed into usable materials such as fibers and films. Once pptd. from the IL, these materials are insol. in most other solvents and can be exposed to solns. of reactive chems. to selectively functionalize only the exposed surface mols. Deacetylation of chitin by sodium hydroxide gives glucosamine, which has a basic amino group which should show high affinity for early transition metals such as copper. The amino group can also be used as a nucleophile to tether a uranium selective functional group, such as amidoxime, to the chitin backbone. The functional groups can be segregated by joining two sep. functionalized resins or dispersed randomly amongst each other by varying the exposure time of the deacetylated chitin to further treatment. Here we present the prepn. and characterization of these materials, soln. studies on their affinity for copper(II) and uranyl ions, and the characterization of metals bound to the sorbent surface.

38. 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.

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.

39. Uranium-from-seawater sorbents from fishing industry waste - from batch to continuous production

By Gurau, Gabriela; Shamshina, Julia L.; Kelley, Steven P.; Rogers, Robin D.
From Abstracts of Papers, 249th ACS National Meeting & Exposition, Denver, CO, United States, March 22-26, 2015 (2015), I+EC-30.

A sustainable and viable sorbent technol. for extn. of uranium from seawater is far from being commercialized. While efforts are underway and some already proven (e.g., the braided plastic adsorbent developed by the Japanese in 2003), the costs and the environmental burdens make these efforts unattractive to investors. For very large scale (needed to ext. useful amts. of uranium from seawater), there is a need for cheap and biodegradable sorbent materials. Under a Department of Energy Small Business Innovation Research Phase I award, nanofibrous sorbents were made from waste shrimp shells by electrospinning and subsequently surface-modified with the amidoxime extractant as a benchmark. The detailed study conducted to find the optimal chitin source, conditions for electrospinning, and surface modification chem., revealed the general feasibility of the concept although, from an economic standpoint, an initial anal. showed that cost-redn. strategies are still needed to be developed to make this process sustainable at a continuous manufg. scale. This presentation will discuss the scale-up of the technol. proven in Phase I to a 20L prototype pilot scale, the chem. and engineering challenges, and the data needed for the full-scale operating plant design.

40. Nanofiber chitin mats for coextraction of value added metals from seawater: Improving the economics of uranium recovery

By Rogers, Robin D.; Kelley, Steven P.; Gurau, Gabriela; Shamshina, Julia L.
From Abstracts of Papers, 249th ACS National Meeting & Exposition, Denver, CO, United States, March 22-26, 2015 (2015), I+EC-15.

Chitin has a no. of phys. and chem. properties that make it advantageous as a sorbent backbone for the extn. of uranium from seawater. One which makes chitin particularly unique when compared to most other functional polymers is the presence of an N-acetyl group which can be easily converted to a reactive amine. We have shown that materials prepd. by extg. chitin from biomass using the ionic liq. 1-ethyl-3-methylimidazolium acetate, in which chitin is unusually sol., can be functionalized on the surface by exposure to treatment baths in which the bulk material is insol. While functionalization of synthetic polymers by methods such as copolymn. or synthetic modification of the monomer effectively results in a completely different polymer, the surface-specific functionalization of chitin results in a measurable change in metal affinity with no measurable changes to bulk phys. properties such as compn. and strength. Furthermore, the nucleophilic amine in chitin can be easily tethered to almost any functional group with almost any linker, giving chitin-based materials extreme potential for variability. We are currently researching new surface treatments to improve the economics and performance of chitin-based sorbents for uranium from seawater. By varying the extractant functional group, new metals can be targeted for addnl. value or added functionality to the polymer. The linker group which tethers the extractant can also be modified to improve performance. Examples of the synthesis, characterization, and testing of such functional materials will be presented here.

41. Chitin and alginate composite fibers for wound dressings
By Rogers, Robin D.; Gurau, Gabriella; Shamshina, Julia L.; Daly, Daniel T.
From PCT Int. Appl. (2014), WO 2014172703 A1 20141023,

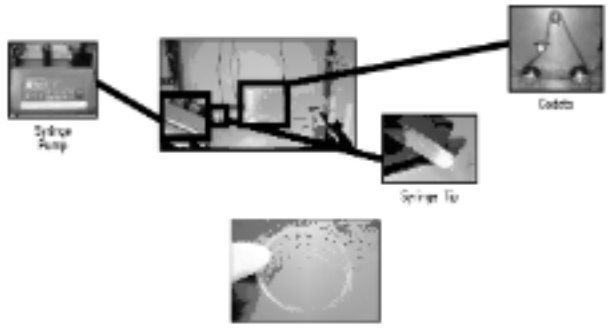
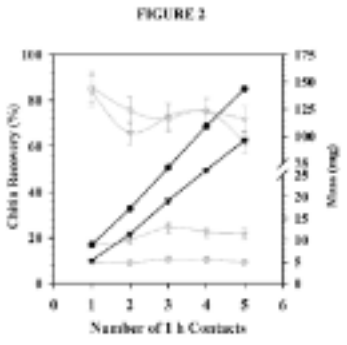


FIG. 1

Disclosed herein are composite fibers that comprises chitin and alginate. The formation of the chitinous-alginate composite fiber involves the use of ionic liqs. and high mol. wt. pure chitin obtained directly from chitin biomass. Optional additive such as vitamin E is successfully incorporated in to the composite fiber. The chitinous alginate fiber formed has a continuous and homogeneous morphol., even with the addn. of additive. Methods of making and using the chitinous-alginate composite fiber as wound dressing is also disclosed.

42. 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,



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. CO2, gaseous CO2, 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.

43. Surface modification of ionic liquid-spun chitin fibers for the extraction of uranium from seawater: seeking the strength of chitin and the chemical functionality of chitosan
By Barber, Patrick S.; Kelley, Steven P.; Griggs, Chris S.; Wallace, Sergei; Rogers, Robin D.
From Green Chemistry (2014), 16(4), 1828-1836. DOI:10.1039/C4GC00092G

Chitin fibers, prepd. by extg. chitin directly from shrimp shell waste and dry-jet wet spinning from the resulting ionic liq. (1-ethyl-3-methylimidazolium acetate) soln. in a one-pot process, were surface modified by taking advantage of the insoly. of chitin in common solvents (e.g., water, orgs.). In this proof of concept example, the chitin fiber surfaces were first deacetylated using aq. NaOH to make available the primary amine (the functional group of chitosan) on the surface. Further treatment of the fibers allowed for the task-specific tailoring of the functionality (here we appended amidoxime for the extn. of aq. uranyl ions from seawater). Compositional anal. and phys. property measurements (e.g., tensile strength and thermal decompn.) of the fibers before and after surface modification indicated minimal change to the bulk material; however, spectroscopy and sorption studies of uranyl ions from aq. soln. demonstrated surface modification. The lower cost, one-pot process used in this study resulted in weak and brittle fibers, suggesting that addnl. purifn. of the chitin before pulling fibers will greatly improve the strength and utility of the resulting material. Overall, a platform has been developed for the surface modification of chitin fibers that provides both the phys. properties of chitin and the functional properties of chitosan, resulting in an advanced material from a biorenewable resource with reduced chem. input.

44. Process for electrospinning chitin fibers from chitinous biomass solution and fibers and articles produced thereby
By Swatloski, Richard P.; Barber, Patrick S.; Opichka, Terrance; Bonner, Jonathan R.; Gurau, Gabriela; Griggs, Christopher Scott; Rogers, Robin D.
From PCT Int. Appl. (2014), WO 2014018586 A1 20140130,

Disclosed are methods for electrospinning chitinous biomass soln. to form chitin fibers, using ionic liqs. or other ion-contg. liqs. as solvent. Chitin fibers produced thereby and articles contg. such chitin fibers are also disclosed. The chitin fiber thus obtained has very high surface area and improved strength over currently com. available chitin materials.

45. 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 CO2 is a viable mechanism for coagulation of chitin and cellulose dissolved in [C2mim][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.

46. Novel chitin fibers for wound care
By Rogers, Robin D.; Gurau, Gabrielle
From Abstracts of Papers, 246th ACS National Meeting & Exposition, Indianapolis, IN, United States, September 8-12, 2013 (2013), SCHB-19.

525 Solns., Inc., a faculty start-up incubated at The University of Alabama with a mission to transfer fundamental research into new business enterprises while providing opportunities for students and staff to become entrepreneurs, proposes to use the newly discovered property of ionic liqs. (ILs; salts which melt below 100°C) to dissolve high mol. wt. chitin directly from biomass to design novel composite fibers of natural polymers with embedded additives to improve the immune system and facilitate wound healing. 525 Solns., Inc., will use the proprietary process to directly dissolve biopolymers (e.g., chitin, alginate, etc.) with or without functional additives into homogeneous solns. which will allow for the direct dry-jet wet spinning of composite materials.

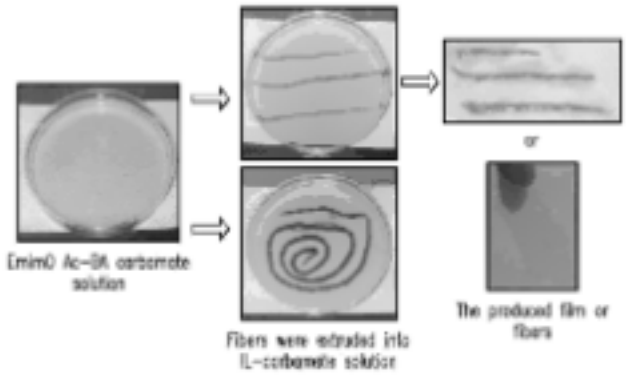
47. A "green" industrial revolution: using chitin towards transformative technologies
By Barber, Patrick S.; Shamshina, Julia L.; Rogers, Robin D.
From Pure and Applied Chemistry (2013), 85(8), 1693-1701. DOI:10.1351/PAC-CON-12-10-14

A review. Even with the high costs of environmental exposure controls, as well as the chance of control failures, options for industries wanting to implement sustainability through frameworks such as green chem. are not yet cost-effective. We foresee a "green" industrial revolution through the use of transformative technologies that provide cost-effective and sustainable products which could lead to new business opportunities. Through example, we promote the use of natural and abundant biopolymers such as chitin, combined with the solvating power of ionic liqs. (ILs), as a transformative technol. to develop industries that are overall better and more cost-effective than current practices. The use of shellfish waste as a source of chitin for a variety of applications, including high-value medical applications, represents a total byproduct utilization concept with realistic implications in crustacean processing industries.

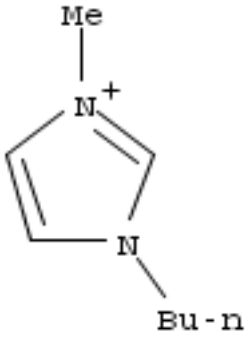
48. Electrospinning of chitin nanofibers directly from an ionic liquid extract of shrimp shells
By Barber, Patrick S.; Griggs, Chris S.; Bonner, Jonathan R.; Rogers, Robin D.
From Green Chemistry (2013), 15(3), 601-607. DOI:10.1039/c2gc36582k

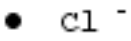
High mol. wt. chitin fibers were electrospun in a one-pot process directly from a 1-ethyl-3-methylimidazolium acetate soln. of chitin extd. from dried shrimp shell. Such a technol. obviates the need not only for the many chems. and the energy used in industrial isolation of chitin from crustacean shells but also saves the chems., energy, and time needed to prep. chitin spinning dopes.

49. Compositions containing recyclable ionic liquids for use in biomass processing
By Daly, Daniel T.; Rogers, Robin D.; Qin, Ying
From U.S. Pat. Appl. Publ. (2012), US 20120245336 A1 20120927,



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 CO2 at a flow rate of 70 cm3/min at 40° for up to 24 h gave ppt. which could be isolated.





50. 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.

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.

51. Electrospun chitin nanofibers for uranyl absorbant materials
By Griggs, Chris S.; Barber, Patrick S.; Kelley, Steven P.; Gurau, Gabriela; Rogers, Robin D.
From Abstracts of Papers, 244th ACS National Meeting & Exposition, Philadelphia, PA, United States, August 19-23, 2012 (2012), I+EC-58.

It has been recently shown that ionic liqs. (ILs) allow the dissoln. of biopolymers without the loss of the important high mol. wt. of the natural polymer which leads to improved strength. Electrospinning polymers produces high surface area fibers which can be functionalized with selective ligands for preferential complexation of the uranyl ion. Here we will present our efforts to prep. electrospun nano and micron sized chitin fibers directly from the dissoln. of shrimp shells in the IL 1-ethyl-3-methylimidazolium acetate. The results of this single step process suggest that chitin can be extd. with higher mol. wt. and purity over current processes that result in chitin with a lower d.p. We will discuss the correlation of phys. properties and electrospinning conditions with the surface morphol. and size range of the fibers.

52. 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.

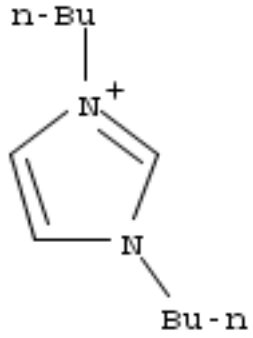
53. Ionic liquids and shrimp shell waste - emerging technologies for the manufacture of nanochitin materials
By Gurau, Gabriela; Rogers, Robin D.
From Abstracts of Papers, 243rd ACS National Meeting & Exposition, San Diego, CA, United States, March 25-29, 2012 (2012), IEC-117.

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.

54. 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,

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.



• Cl⁻

55. 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,

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.

56. Dissolution or extraction of crustacean shells using ionic liquids to obtain high molecular weight

purified chitin and direct production of chitin films and fibers
By Qin, Ying; Lu, Xingmei; Sun, Ning; Rogers, Robin D.
From Green Chemistry (2010), 12(6), 968-971. DOI:10.1039/c003583a

1-Ethyl-3-methyl-imidazolium acetate can completely dissolve raw crustacean shells, leading to recovery of a high purity, high mol. wt. chitin powder and to fibers and films which can be spun directly from the ext. soln.

57. 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.

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.

58. Ionic liquids as benign solvents for extraction of astaxanthin and solubilization of chitin
By Spear, Scott K.; Reichert, W. Matthew; Swatloski, Richard P.; Rogers, Robin D.
From Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), IEC-412.

Research priorities laid out in the Vision 2020 Technol. Roadmap for Renewable Resources include biosepns. The sepn. processing of biomass into a series of distinct chems. poses many challenges because of the high diversity of chem. components present in living materials. Ionic liqs. are an interesting new class of solvents exhibiting solvating abilities of biol. materials and biomoecules. This presentation will focus on our exploratory progress to study ionic liqs. as novel solvent systems for the extn. of astaxanthin and solubilization of chitin from decalcinated shrimp shells.

59. Solubilization and 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, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001 (2001), IEC-052.

Research priorities laid out in the Vision 2020 Technol. Roadmap for Renewable Resources include the use of biorenewables. In the shellfish industry more then 85% of the waste produced is in the form of insol. shells, whose major component is chitin. Ionic liqs. have been shown to be excellent replacements for traditional org. solvents in liq./liq. extns. Recently we have seen that RTILs can also act as novel solvents in the dissoln. of chitin, the major component in the shells. This presentation will focus on the methods of dissolving refined and processed chitin and some derivatization of the chitin, e.g., chitosan a water-sol. form of chitin.