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Fabrication of porous chitin membrane using ionic liquid and subsequent characterization and modelling studies

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ABSTRACT

The application of green chemistry principles for the processing of biopolymers is a steadily increasing field of research. Chitin membranes were successfully prepared by using the ionic liquid 1-ethyl-3-methylimidazolium acetate ([C_2mim][OAc]) as solvent media. The resulting materials were thoroughly characterized, revealing that freeze drying produced membranes that were highly porous. The drying methods and the concentration of chitin used defined many of the membrane properties, such as mechanical strength, porosity, and water absorbency. From these data, an empirical model was generated which could be used to correlate the different membrane properties. The model could be used to predict the properties of the chitin membrane made with different wt% of chitin-IL solutions, and the predicted values aligned with the experimental results. This allowed for prediction of the properties of the chitin membrane (e.g., tensile strength) and gives the ability to tune the properties of the biomaterial. The methods and structures described here provide a starting point for the design and fabrication of a family of polysaccharide-based sustainable materials with potentially broad applicability.

1. Introduction

Chitin, a linear β-linked polysaccharide and the second most abundant natural biopolymer (after cellulose), has been widely studied due to its extensive applications in various fields (Bhatnagar & Sillanpaa, 2009; Dai et al., 2009; Hirano, 1999; Muzzarelli, 2009; Ragetly, Slavik, Cunningham, Schaeffer, & Griffon, 2010). The polymer has appealing properties for many biomedical applications, including acceleration of wound healing and tumor cell growth suppression, among others (Rinaudo, 2006; Silva, Mano, & Reis, 2010; Younes & Rinaudo, 2015). Despite the enormous availability of the polysaccharide and the desirable properties it possesses, like non-toxicity, biocompatibility, and being biodegradable, chitin has often been underutilized because it is insoluble in water and most common solvent systems (Arbia, Arbia, Adour, & Amrane, 2013). Chitin is known to be insoluble in water and most organic solvents, due to the presence of intra and intermolecular hydrogen bonding and close molecular chain packing (Kurita, 2006; Rinaudo, 2006). Harsh solvent systems like NaOH/urea (Wang et al., 2006), toxic solvents like DMAc-LiCl (*N,N*-Dimethylacetamide/lithium chloride) (Chen, Sun, & Zhang, 2004) and fluorinated acids (Kumar, 2000; Min et al., 2004) have often been used in chitin processing in order to manipulate and obtain a more "soluble" form of the biopolymer. These corrosive solvents can degrade the polymer upon even short exposures, and their removal and the subsequent complete recovery of the polymer can be difficult (Qin, Lu, Sun, & Rogers, 2010). Alongside rapid development in material science and the rise of environmental consciousness, there has been much interest in utilizing chitin for a diverse range of applications. An environmentally friendly solvent, which could readily solubilize chitin would be greatly beneficial in this area.

The dissolution of natural polymers like chitin in ionic liquids (ILs) could be seen as an alternative strategy to enhance their solubility and processability, without the use of harsh chemicals and solvents. Ionic liquids (ILs) are a group of salts that exist in liquid state at low temperatures, and are being examined as desirable green solvents (Rogers & Seddon, 2003) and have properties like stability over a wide range of temperatures, non-flammable, and tunable solubility properties (Pandey, 2006; Rogers & Seddon, 2003). ILs contain organic cations

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such as pyridinium, pyrrolidinium, imidazolium or ammonium derivatives (Wasserscheid, 2003), which can be associated with organic or inorganic anions such as CH_3COO^-, Cl^-, Br^-, I^- (Kumar, 2000). They have been found to be useful in dissolution of polar organic materials like biopolymers, which are otherwise difficult to dissolve (Rogers & Seddon, 2003). Using ILs, macromolecules can be dissolved, regenerated, functionalized, increasing their potential for exploitation.

Many ILs have been used to dissolve chitin, for example, 1-allyl-3-methylimidazolium chloride (AMIMCl), 1-Butyl-3-methylimidazolium chloride (BMIMCl), 1-Ethyl-3-methylimidazolium phosphate [EMIM][Me2PO4] (Wang, Zhu, & Wang, 2010), 1-allyl-3-methylimidazolium bromide (AMIMBr) (Kadokawa, 2013). 1-Butyl-3-methylimidazolium acetate [C4mim]OAc has also been used to dissolve 'native' chitin (Wu, Sasaki, & Sakurai, 2008). It has been reported that dissolution of chitin requires a more basic anion, such as acetate, due to the increased number of hydrogen bond donors and acceptors (Barber, Griggs, Bonner, & Rogers, 2013). Studies have also shown that chitin properties like its origin (i.e., from crustaceans, fungal cell walls, cuticles of insects etc.), polymorphic form, molecular weight, and degree of acetylation can also effect the dissolution of the polymer in ILs (Wang et al., 2010).

The use of ILs can help us to overcome the challenge of processing chitin from marine sources (Barber et al., 2013). This strategy combines green chemistry principles, such as use of environmentally friendly solvents (ILs) and bio-renewable feedstocks (natural biopolymer like chitin). The direct processing of chitin out of nonhazardous, nontoxic solvents could give access to a sustainable material that has the potential to be used in a number of applications, such as tissue engineering (Jayakumar et al., 2011), wound dressings (Wu et al., 2004), and vascular implants (Muzzarelli, 2009). An often-ignored fact is that most reports claiming preparation of chitin as a material for biomedical applications actually use chitosan (Fan et al., 2005; Freier, Montenegro, Shan Koh, & Shoichet, 2005; Hirano, Nakahira, Nakagawa, & Son, 1999) or other water soluble derivatives of chitin (Szosland & East, 1995). Also, most studies use chitin extracted by traditional chemical processing techniques that involve the use of harsh acids and caustic soda at elevated temperatures that can cause degradation of the chitin structure, thus changing the properties of the biopolymer (Arbia et al., 2013; Jung, Kuk, Kim, & Park, 2005).

Previous studies have shown that dissolution of chitin in IL can produce membranes with different properties (Rogers, 2016). A mathematical model could be used to correlate and predict different polymer properties like tensile strength, which would lead to the ability to tune the properties of the biomaterial. Rayleigh's method is often used to develop an expression in the form of an exponential equation to show the functional relationship for a variable that depends on other independent variables (Mendoza, 1994). All physical properties are expressed in terms of basic or fundamental dimensions such as mass (M), length (L), and time (T).

This study focusses on the dissolution of chitin using the IL 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]), to produce chitin membranes with different properties. This work includes the characterization and evaluation of mechanical properties of IL solvent-cast chitin membranes and proposes a novel model to relate and predict various properties of the biomaterial. To the best of our knowledge, there have not been any studies that have produced an empirical model to predict the properties of chitin membrane.

2. Materials and methods

2.1. Chemicals and materials

The IL 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc], purity > 95%) was purchased from Sigma-Aldrich Co. LLC (St. Louis, MO, USA). Dried, ground lobster shell waste powder was a generous gift from Gloucester Seafood Processing Inc. (Gloucester, MA, USA) and was stored at room temperature until used.

2.2. Preparation of chitin membrane

The chitin used in this study was extracted from lobster shells using biological treatment. Briefly, lobster shells were treated by incubation with a co-culture of *Serratia marcescens* strain db11 and *Lactobacillus plantarum*. The main carbon source for the bacterial co-culture was 5% glucose, and the culture was incubated at 37 °C for six days. The microbial activity in the culture assists in removing protein and minerals from the shell biomass, producing purified chitin, as has been shown in a similar experiment by Zhang, Jin, Deng, Wang, and Zhao, (2012). Chitin obtained by this method was washed and dried overnight in an oven at 80 °C, and ground to a fine powder for further use.

The dissolution of chitin in the 1-ethyl-3-methylimidazolium acetate ([C2mim][OAc]) ionic liquid (IL) was performed by adding the polysaccharide to ([C2mim][OAc]) in a loosely-capped glass vial along with a magnetic stir bar, followed by heating the mixture at 80–90 °C with continuous stirring until full dissolution of chitin was achieved. Different chitin-IL solutions, with concentrations of 2 wt%, 2.25 wt%, 2.50 wt%, 2.75 wt% and 3 wt% chitin, were prepared by dissolution in ([C2mim][OAc]). The dissolution time varied (from 4 to 8 hrs) with the weight percentage of the chitin polymer added to the ionic liquid. After complete dissolution of the chitin in IL, the solution became homogeneous, viscous, and turned an amber color.

The chitin-IL solution was then transferred to a cultivation plate (50 mm in diameter). Once the solution was allowed to settle to a uniform thickness, the culture dish was placed into a deionized (DI) water bath to allow membrane coagulation. The cultivation plate was carefully removed, and the DI water was replaced a few times to wash away the IL from the membrane. The IL was considered washed out after about 6–8 washes; after which the IL was no longer visible in the bath. The membrane was removed from the solution by sliding a piece of wax paper underneath and carefully lifting the paper from the water, with the membrane on the wax paper. The chitin membrane was then transferred to non-stick parchment paper for drying. This process is shown schematically in Fig. 1 below.

2.3. Drying methods

Four different drying methods were examined: air, press, methanol, freeze dry. For air drying, the wet membrane was placed onto a piece of parchment paper and then left exposed to room air on the laboratory bench until it was dry to the touch. Press drying was achieved by placing the membrane between two pieces of parchment paper, topped by absorbent paper (i.e., Kimwipe). This setup was then placed under a flat weight (5 lbs). The membrane was left under the weight until it was dry to the touch, and then carefully removed. For the methanol method, the membrane was dipped into a mixture of methanol and water (1:1 vol/vol). The membrane was then washed several times with the methanol

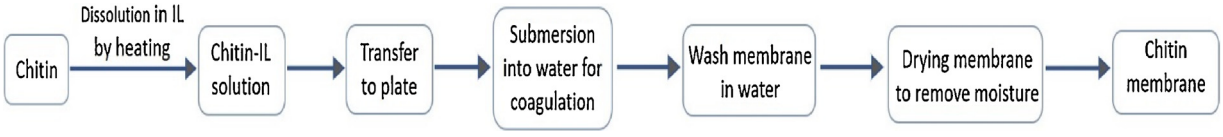

Fig. 1. Schematic diagram showing steps for chitin membrane preparation.