ELECTRONIC SUPPORTING INFORMATION

**Electrospinning of Chitin Nanofibers Directly from an Ionic Liquid Extract of Shrimp Shells**

Patrick S. Barber,*a* Chris S. Griggs,*a,b* Jonathan R. Bonner,c and Robin D. Rogers*a*

a *Center for Green Manufacturing and Department of Chemistry, The University of Alabama, Box 870336, Tuscaloosa, AL 35467-0338*

*b* *US Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS, 39180-6199*

*c CFM Group, LLC. Tuscaloosa, AL 35401-1582*

*Experimental*

All materials were used as purchased. The ionic liquids used for chitin dissolution were 1,3-diethylimidazolium acetate [C2C2Im][OAc] from BASF (Florham Park, NJ) with 90% purity, and 1-ethyl-3-methylimidazolium acetate [C2C1Im][OAc] from IoLiTec Ionic Liquids Technologies Inc (Heilbronn, Germany). Practical grade chitin (PG chitin) obtained from crab shells (C7170) was purchased from Sigma (St. Louis, MO) and used directly without further purification. Dried shrimp shells were received from the Gulf Coast Agricultural and Seafood Cooperative in Bayou La Batre, AL and ground to a < 125 µm particle size before use. The ground material was dried in an oven at 80 ºC for 24 h.

*Preparation of the shrimp shell solution*

Chitin extraction from shrimp shell was performed using a domestic microwave oven (SHARP Carousel R-209KK, Mahwah, NJ) at full power. CAUTION: Care must be taken when using microwave heating because ILs are efficient microwave absorbers and heating occurs rapidly, which can easily lead to degradation of the ILs, cellulose, and chitin, or even explosions of sealed systems. All solutions were made in a similar fashion with an appropriate mass of chitinous sample being added to a mass of ionic liquid corresponding to a final weight percent (wt%). The mixture was heated in the microwave for a total of two min using 2-3 sec pulses. A detailed example follows:

0.200 g ground shrimp shell was dissolved in 9.80 g [C2C1Im][OAc] to give a total mass of 10 g to constitute 2 wt% shrimp shell loading (0.45 % chitin, assuming 100% extraction of shrimp shells consisting of 22 wt% chitin). The mixture was heated for a total of 2 min using 2-3 sec pulses with mechanical stirring between pulses with a glass stirring rod. The solution slightly darkened with time during the heating, most likely due to slight decomposition of the IL. After dissolution, the undissolved particles were removed through centrifugation and the supernatant was used for electrospinning experiments.

*Viscosity Measurements*

Viscosity measurements were taken at 30.0(1) ºC with a Cambridge Viscosity (Medford, MA) Viscometer, VISCOlab 3000. Approximately 2-3 mL of each solution was placed in the sample chamber. The correct sized piston corresponding to the expected viscosity range was added and the measurement was taken. The reported values were taken as an average of three measurements per reading as computed by the instrument.

*Electrospinning technique and equipment*

The chitin solution was subjected to electrospinning, which is schematically represented in Figure 1. All electrospinning experiments were conducted in a similar fashion. A 3 mL sample of the chitin solution was transferred to a syringe with a needle. A voltage was applied to the needle electrode with a grounded charge in the form of a stainless steel plate beneath the glass collection bath. The nozzle-to-ground target distance was fixed at certain distance. The chitin solution was delivered to the spinner head using air pressure from a syringe pump (New Era Pump Systems Inc., Farmingdale, NY) with a set flow rate. The coagulation solvent was water. A detailed example follows:

3 mL of 2 wt% shrimp shell loading in [C2C1Im][OAc] was transferred to a syringe with a 18.5 G needle. A voltage of 20 kV was applied to the needle electrode with the needle-to-ground target distance fixed at 10 cm. The syringe pump was set to a flow rate of 0.5 mL/min. The coagulation bath was filled with water. The solution was then subjected to electrospinning. Upon complete electrospinning of the 3 mL of solution, the resulting fibers were kept in the water bath overnight to ensure the complete removal of the ionic liquid. The fibers were then removed, washed with water, and dried upon the electron microscopy stubs for analysis.

*Optical and Electron Microscopy*

Fibers were characterized by optical and emission microscopy. An Olympus CH30 Light Microscope (Center Valley, PA) with attached camera was used for visualization of the fibers at 40X and 100X magnification. Emission microscopy was performed using a Hitachi S-2500 scanning electron microscope (Tokyo, Japan) with an accelerating voltage 10 kV. The dried samples were prepared by sputter coating with a gold/platinum alloy using a Technics Hummer Sputter Coater (Alexandria, VA). The coated samples were then placed on a pin-mount into the sample chamber where they were brought under high vacuum for the microscopy. Transmission electron microscopy samples were prepared by drying samples and loading unto a copper sample holder. The sample was loaded into the instrument's vacuum chamber, then once stabled inserted into the chamber for viewing.

*PXRD and FT-IR Spectroscopy*

Samples and reference materials were characterized by powder X-ray diffraction (PXRD) and infrared (IR) spectroscopy. The PXRD data were collected on a Bruker (Madison, WI) D2 Phaser powder X-ray diffractometer with Ni-filtered Cu Kα radiation. IR analyses were obtained by direct measurement of the neat samples by utilizing a Bruker Alpha FT-IR instrument, Bruker Optics Inc. (Billerica, MA) featuring an attenuated total reflection (ATR) sampler, and spectra were obtained in the range of νmax = 400–4000 cm-1.



Figure S1 Infrared spectra comparing shrimp shells, PG-Chitin, electrospun chitin fibers, and [C2C1Im][OAc]



Figure S2 Powder X-ray diffractograms comparing the electrospun chitin mats to PG-chitin and a calculated alpha-chitin pattern.