2016. Proceedings of the Indiana Academy of Science 125(2):87–90

MECHANICAL AND THERMAL PROPERTIES OF CHITIN FROM DIVERSE SOURCES

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ABSTRACT. Chitin is an abundant polysaccharide that can be found in the exoskeletons and sloughs of many different organisms. Commercially, chitin is extracted from shrimp exoskeletons and used in applications ranging from thickening agents to wound dressing. Previous studies in our group showed that other sources of chitin (lobster, crawfish, and the sloughs of cicada) can be extracted in a similar manner but produce chitin with varying degrees of acetylation and protein content. In this study, chitin from a cicada, lobster, and shrimp source materials was studied to determine their mechanical and thermal properties. The chitin to chitosan ratio of the resulting product also was altered through a reaction with sodium hydroxide at differing temperatures or for differing time periods. The three source materials produced films with similar mechanical strength and thermal properties. Likewise, each responded similarly to changes in the degree of acetylation.

Keywords: Chitin, chitosan, cicada, lobster, shrimp, TGA, mechanical properties

INTRODUCTION

Chitin, a naturally occurring biopolymer, is second only to cellulose in abundance in the biosphere (Zeng et al. 2012). Chitin can be found in the exoskeletons of a number of organisms such as shrimp, lobster, and cicada. Chitin and its deacetylated derivative, chitosan, have many known functions that range from cosmetics (Sahoo et al. 2009) to food (Aranaz et al. 2009) to biomedicines (Ding et al. 2014). Despite the wide variety of uses and wide variety of possible sources, the majority of chitin is derived from two sources, i.e., fungi and shrimp.

In many of its uses, chitin and chitosan are added to other materials as mechanical fillers or thickening agents. Studies have shown that the mechanical properties of these materials can vary greatly depending on the processing of the chitin and/or chitosan and the type of solvent used (Fernandez-Pan et al. 2010). However, even though the processing conditions of chitin have been well-documented in numerous studies, the effect of the source material has not been fully explored. It has even been reported that chitin can be found and extracted from many unique sources ranging from honeybees (Draczynski 2008) to crawfish (Mendez et al. 2015), but evidence for the usefulness of these sources in mechanical applications is lacking. In this study, a comparison of the mechanical and thermal properties of chitin prepared from differing source materials is presented along with the effect of differing ratios of chitin to chitosan.

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METHODS

Source material.—Fresh samples of lobster shells and shrimp shells were collected from restaurants in Columbus, IN. Cicada sloughs were collected from the campus of Indiana University – Purdue University Columbus. All fresh source materials were cleaned with deionized water and allowed to dry. After drying, samples were ground into a powder and stored in sealed containers until the extraction process.

Chitin extraction.—The chitin from the raw powder samples was extracted in a multi-step process to remove minerals and other organic materials. The first step was to stir the samples in 2 M sodium hydroxide at reflux for 1 h at a concentration of 40 mg/ml. Once removed from the sodium hydroxide, the sample was brought back to a neutral pH using multiple washes of deionized water and allowed to dry in a desiccator. In the second step, the sample was placed in 2 M hydrochloric acid at room temperature and stirred for 1 h. The sample was returned to a neutral pH using multiple washes of deionized water. The lobster samples were then washed with acetone to remove the astaxanthin, which gives the shell its red

Table 1.—Temperature and time specifications used to prepare each sample. All samples were stirred at 100 °C while heated and 23 °C when unheated.

Sample source	Degree of acetylation (%)	Stir time (Days)	Heat time (Hours)
Shrimp	32.4	3	5
Shrimp	45.7	7	10
Shrimp	47.6	10	30
Shrimp	54.3	9	20
Lobster	37.7	2	10
Lobster	39.0	1	5
Cicada	39.5	2	10
Cicada	49.8	9	20

coloring. The final step for all samples was a wash in 4% sodium hypochlorite for 5 min for discoloration. These samples were dried in a desiccator for 24 h before being stored for future use.

Chitosan conversion.—Each chitin sample (with a concentration of 3 mg of sample per ml of sodium hydroxide) was heated to 100 °C and allowed to stir for a predetermined time. Once the predetermined time was met, the heat was turned off and the samples were allowed to stir at room temperature for another predetermined time (Table 1). The samples were transferred into centrifuge tubes and spun 10 min so that all solid settled to the bottom of the tube. The supernatant was discarded and deionized water was added. Tubes were mixed thoroughly before being placed back into the centrifuge for 10 min. This wash process was repeated until the samples reached a neutral pH. The deacetylated samples were then dried in the desiccator 24 h before being cast into films.

Infrared microscopy.—The selected deacetylated sample was added to enough 1 M acetic acid to reach a concentration of 5 mg/ml. This solution was sonicated for 30 min in a Branson 2800 sonicator to ensure a uniform dispersion. Films were cast overnight under ambient conditions to a thickness of approximately 0.06 mm and then measured utilizing a Nicolet IR100 FT-IR (Fig. 1). The absorbance of the carbonyl peak at 1655 cm^{-1} (only present in chitosan) was compared to the hydroxyl peak at 3600 cm^{-1} (present in both chitin and chitosan) to give an accurate ratio of chitin to chitosan (Czechowska-Biskup et al. 2012).

Young's Modulus.—Films were cut into small strips approximately 5 mm wide with a thickness of 0.06 mm. A single strip was clamped into an Instron Mechanical Tester (model # 2716-020). The maximum load was set at 100 N with a speed of 40 mm/min. The Young's Modulus for each sample was determined by taking the linear slope of the elastic region of the stress/strain curve. A minimum of 10 measurements were taken for each sample to obtain an average value.

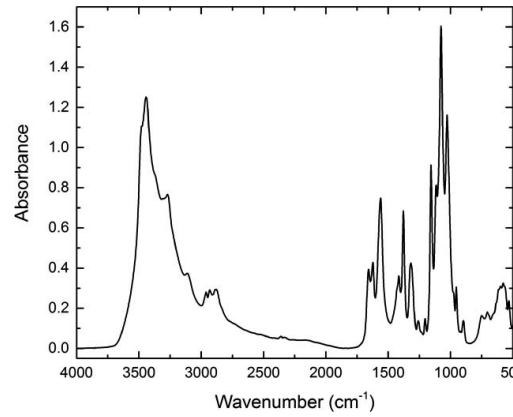

Figure 1.—Representative IR obtained from lobster with a degree of acetylation (DA) of 24.9%.

Transmission electron microscopy (TEM).—A Tecnai G2 12 Bio Twin transmission electron microscope was used to obtain detailed images of individual chitin fibers. The instrument was run at 80 kV with magnifications ranging from 18,500 to 250,000×.

Thermogravimetric analysis (TGA).—Thermogravimetric analysis was performed on representative chitin samples from each source material on a TA Instruments Q50 TGA instrument. The temperature was ramped from 20° C to 500° C for each sample.

RESULTS AND DISCUSSION

As expected, the three sources in this study produced chitin with very little modification of the extraction process necessary. Chitin fibers appear similar under TEM (Fig. 2) with cicada fibers showing a slightly higher aspect ratio compared to fibers extracted from lobster or shrimp (Table 2).

The thermal stability of chitin did not vary significantly with the source material. Results from the TGA show degradation occurring between 370° C and 390° C for each sample (Fig. 3), consistent with literature sources (Zeng et al. 2010).

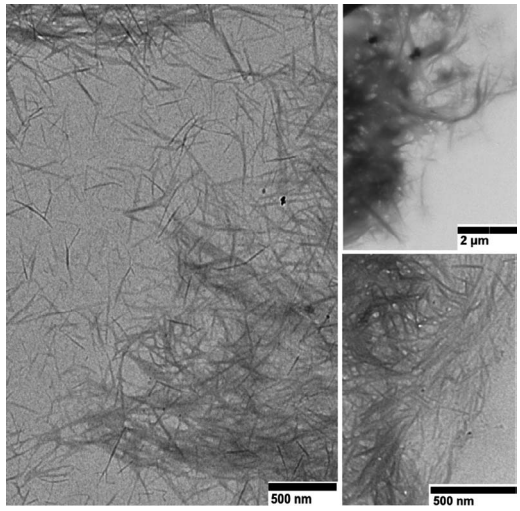

Figure 2.—TEM of chitin from cicadas (left), lobster (top right), and shrimp (bottom right).

Comparing the Young's Modulus of the chitin to chitosan ratio shows a clear relationship between these two properties (Fig. 4) with the median values comparable to other studies (Aklog et al. 2015). However, the source material does not show any significant effect on the Young's Modulus.

Conclusion.—There is always a tradeoff between the chitin to chitosan ratio and mechanical properties. With strong hydrogen bonding between fibers, chitin is a mechanically strong material but these same strong intermolecular forces also decrease solubility. Deacetylating the chitin to chitosan increases solubility but lowers the mechanical properties. The results presented above confirm this and show that the Young's Modulus increases with an increased degree of acetylation (percentage of chitin).

While the degree of acetylation does correlate with Young's Modulus, the source material does not. Additionally, the aspect ratio and thermal stability also show very little relation to source material. Taken together, this lack of significant difference demonstrates the viability of these different materials as potential commercial sources for chitin production.

Table 2.—Aspect ratio and standard deviation of chitin fibers.

	Aspect ratio	Standard deviation
Cicada	15.8	3.7
Lobster	8.3	2.7
Shrimp	7.4	4.4

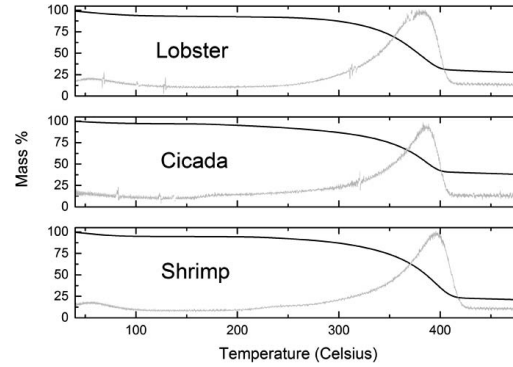

Figure 3.—Thermograms (black with derivative in gray) of chitin from lobster (top), cicada (middle), and shrimp (bottom).

CONFLICTS OF INTEREST

The authors have no conflicts of interest to report.

ACKNOWLEDGMENTS

The authors would like to thank Red Lobster in Columbus for the donation of lobster shells, the biology classes of Barbara Haas-Jacobus for gathering cicada sloughs, and Caroline Miller with the Electron Micros-

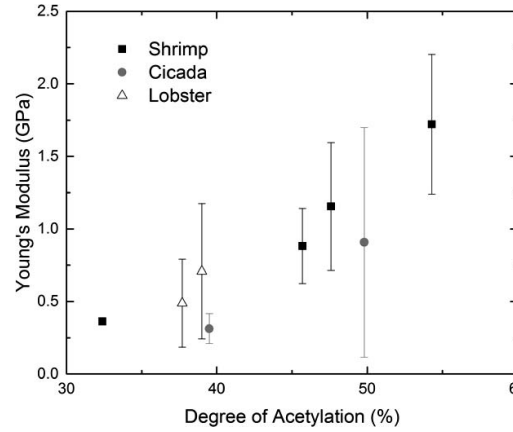

Figure 4.—Young's Modulus of chitin samples from shrimp (black squares), cicada (gray circles), and lobster (white triangles) at various degrees of acetylation.

copy Center at IUPUI for assistance with the TEMs. The authors would also like to thank Emma Parks and Heather Johnson for their assistance in the early stages of the experiment.

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Manuscript received 18 August 2016, revised 11 January 2017.