Chitin: Fundamental Biopolymer Properties and Applications Discussion

Todd French[1] and Isaac L. Howard[2]

Acknowledgements

This white paper is part of the United States Department of Agriculture (USDA) Forest Products Laboratory (FPL) project 16-JV-11111129-088. Dr. Gregory Schueneman was the USDA-FPL Program Manager.

White Paper Number CMRC WP 23-1, December 2023

History

If cellulose and starch are lumped together, due in large part to both being made of glucose, then chitin (β-(1→4)-N-acetyl-D-glucosamine) is the second most abundant polymer on the Earth. Its function is similar to cellulose in that in nature chitin is a structural polymer and serves to reinforce structures (i.e. exoskeletons and cell walls). It is found in the exoskeleton of crustaceans (e.g. insects, crabs, shrimp, lobster, etc.), cell walls of fungi and yeast, and a slightly modified version is found in bacteria.

In 1998, the State of Mississippi processed 30,384,338 lbs of shrimp and in the process produced 7,334,242 lbs of waste containing chitin, proteins, lipids, etc. In 1995, 20,500,000 lbs of shrimp were processed in the State of Alabama producing an estimated 4,500,000 lbs of processing waste. Most Mississippi producers are transporting their processing waste to a meal manufacturer in Bayou La Batre, AL. The transportation cost for this waste was estimated to be between $140,000 - $150,000 dollars per producer per year (14 processors).[1] Based on information available through the NOAA website and Louisiana AgCenter[2] website, the 2003 shrimp, crab, and crawfish landing data for Alabama, Mississippi, Louisiana, and Florida is given in Table 1.[1]

Table 1. NOAA seafood landing data for Alabama, Mississippi, Florida, and Louisiana.

Product	Harvested (lbs)	Estimated Dry Waste (lbs)
Shrimp	197,505,023	41,871,064
Crab	64,384,469	54,726,799
Crawfish	85,000,000	63,750,000
Total	*346,889,492*	*160,347,863*

Between these states there are an estimated 160,347,863 pounds of processing waste that could be used as a feedstock for the conversion into value added products using biological conversion (*i.e.* bioprocessing). It should be pointed out that the chitin in this waste is being used as neutraceuticals, fertilizers, feed supplements, and seed coatings. Table 2 lists some of the known commercial uses for chitin/chitosan. Unfortunately, these uses only capitalize on a small fraction of the waste generated by US industries. The vast majority is simply landfilled. The inclusion of this material into appropriate building materials could be an excellent alternative to land disposal and aide in defraying disposal cost.

1 Professor, Chemical Engineering, Mississippi State University (MSU), french@che.msstate.edu
2 Director, Rula School of Civil and Environmental Engineering, MSU, ilhoward@cee.msstate.edu

Table 2. Known potential and commercial uses for seafood waste generated chitin/chitosan.

Application	Function	Reference
Chromatography	Absorbs chemicals	Datta, Basu, & Datta, 1984[3]
Chemotherapeutic Agent	Suppress tumor formation in mice	Hudson & Jenkins 2003[4]
Food	Protein Immobilization	Krajewska 2004[5]
Adsorbent	Industrial Pollutants Removal	Songkroah, C. et al. 2004[6]
Wound Care	Antimicrobial	Yusof, N.L. et al. 2003[7]
Oil Spill Cleanup	Crude oil adsorption	Barros, F.C.F. et al. 2014[8]

Of the uses, the adsorption and antimicrobial properties of chitin are very intriguing for use in paving materials. The inclusion of chitin could result in strengthening these materials while adding antimicrobial properties and retarding biofilm (e.g. fungi) buildup. The most potentially intriguing property is the hydrophobic property that allows it to be useful as a hydrocarbon adsorbent. Barros et al. tested chitin flakes, chitin powder, chitosan flakes, and chitosan powder for the adsorption capacity of crude oil.[8] The results of their work clearly showed that all of the chitin and chitosan samples adsorbed at least 0.2 g of oil/g of adsorbent. The best was chitosan flakes at 0.379 g of oil/g of adsorbent. Chitin flakes adsorbed 0.258 g of oil/g of adsorbent. Note that this absorbency would need to be tailored in a way as not to selectively absorb useful portions of asphalt binder to be advantageous.

Chitin has a distinct processing advantage over chitosan in that shrimp shells require fewer steps to produce. Chitin produced from shrimp shells requires the shells to be deproteinized via sodium hydroxide (NaOH) at temperatures up to 160 °C followed by demineralization using hydrogen chloride (HCl).[9] Chitosan on the other hand is produced via deacetylation of chitin which requires additional steps to remove the acetyl groups from the molecule by soaking the chitin in concentrated NaOH for additional time. The difference in chemical structure between chitin and chitosan is presented in Figure 1.

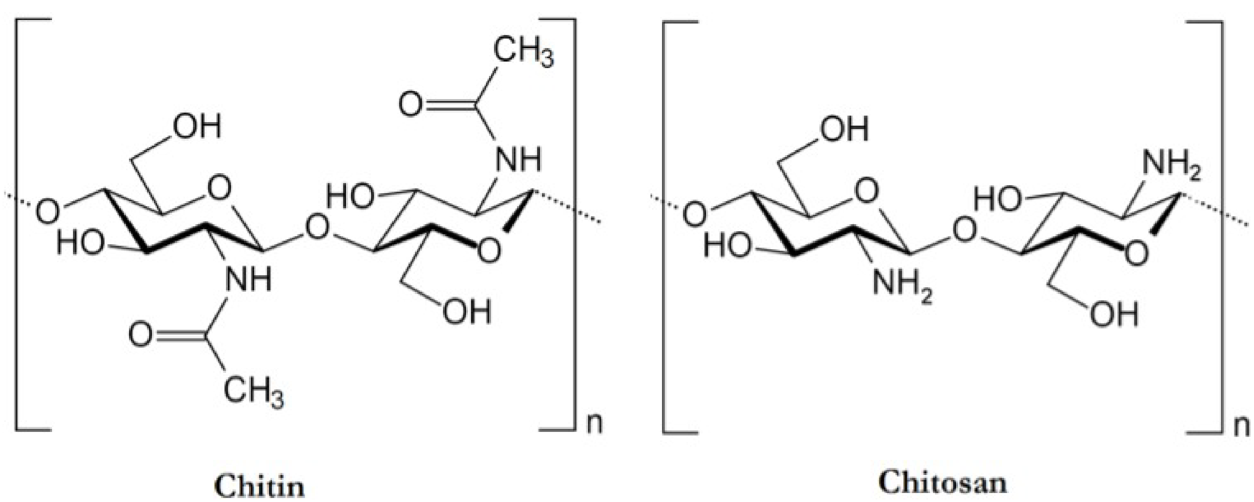

Figure 1. Comparison of Chitin and its deacetylation form Chitosan[13].

Since there is additional processing cost for producing chitosan from chitin without a significant increase in hydrocarbon adsorption, there might not be any real benefit that can be seen for adding the additional steps for the production of chitosan for use in road paving mediums. The use of shrimp or crab shells post seafood processing as is could potentially offer real savings to utilization for these types of applications. However, odor from the degradation of the proteins which would be still attached to the shells could present a significant problem.

Chemistry

Chitin is a polymer of N-acetylglucosamine (Figure 2). Chitin differs from cellulose in that the glucose monomer also contains an amide group. This gives chitin or the depolymerized form (chitosan) some antimicrobial activities. Chitosan is much more water soluble than the intact polymer or more acetylated chitosan.[10] Chitosans are also known to have an affinity for heavy metals such as Cu^{+2}, Hg^{+2}, Zn^{+2}, Cd^{+2}, Ni^{+2}, Co^{+2}, etc.[11] The addition of chitosan to a paving mixture could have the added benefit of sequestering any heavy metals. Since chitin and chitosan are safe for human consumption, the toxicity of these compounds is anticipated to be non-existent or negligible to the environment.

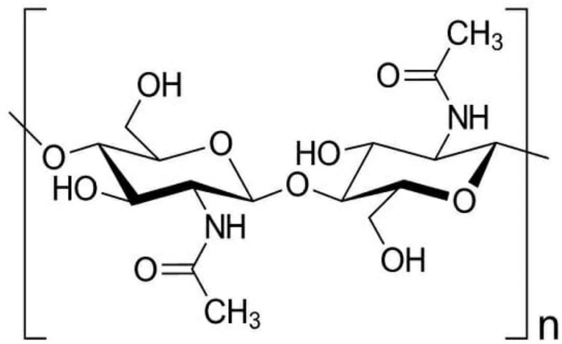

Figure 2. Chitin is a polymer of the monomer N-acetylglucosamine[13].

Chitin in nature exists in primarily two allomorphic structures, α and β. α-Chitin is the most abundant form of chitin occurring in crabs, yeast, and shrimp shells.[12] β-Chitin is much rarer, can be highly swollen in water by mixing, and has been found in squid pens. Therefore, for paving materials α-chitin would be the targeted polymer. It would be abundant in the seafood processing waste generated by the seafood industries.

Summary

There is an abundance of waste which contains the second most abundant natural polymer (chitin) on the planet and it present a significant disposal cost to many seafood processors along the gulf coast as well as other sections of the US. Chitin has been demonstrated to have many unique polymers in structural stability. Some of these properties might be beneficial for building materials such as hydrophobicity and antimicrobial characteristics. These biopolymers have potential and could warrant further investigation. The purpose of this white paper was to summarize their potential for building materials.

References

1. https://www.st.nmfs.noaa.gov/commercial-fisheries/publications/index
2. https://www.lsuagcenter.com/portals/our_offices/departments/ag-economics-agribusiness/extension_outreach/budgets/2015/projected-costs-for-crawfish-production-in-louisiana-2015
3. Rhazi, M., Desbrieres, J., Tolaimate, A., Rinaudo, M., Vottero, P., Alagui, A., El Meray, M., 2002. Influence of the nature of the metal ions on the complexation with chitosan. Application to the treatment of liquid waste. European Polymer Journal. 38:1523-1530.
4. Datta, P.K., Basu, P.S., Datta, T.K., 1984. Isolation and Characterization of Vicia faba lecticn affinity purified on chitin column. Preparative Biochemistry and Biotechnology 14:373- 387.
5. Judson, S. M., Jenkins, D. W. 2003. Chitin and chitosan. In: Mark H.F., editor, EPST. Vol. 1. 3rd ed. New York: Wiley; 569 – 580.
6. Krajewska, B. 2004. Application of chitin- and chitosan-based materials for enzyme immobilizations: a review. Enzyme and Microbial Technology. 35:126-139.
7. Songkroah, C., Nakbanpote, W., Thiravetyan, P., 2004. Recovery of silver-thiosulfate complexes with chitin. Process Biochemistry. 39:1553 -1559.
8. Yusof, N.L., Wee, A., Lim, L.Y., Khor, E. 2003. Flexible chitin films as potential wound-dressing materials: wound model studies. Journal Biomedical Material Research A. 66A: 224-232.
9. Atkins, E.D.T. 1985. Conformation in polysaccharides and complex carbohydrates. Journal of Biosciences 8:375-387.
10. Freitas Barros, F.C.F., Vasconcellos, L.C.G., Técia Vieira Carvalho, T.V., Nascimento, R. F. 2014. Removal of Petroleum Spill in Water by Chitin and Chitosan. Orbital: The Electronic Journal of Chemistry. Vol.6 No.1 January-March.
11. Younes, I., Rinaudo, M., 2015. Chitin and Chitosan Preparation from Marine Sources. Structure, Properties and Applications. Marine Drugs. 13 1133-1174.
12. Aiba, S. 1991, Studies on chitosan: 3. Evidence for the presence of random and block copolymer structures in partially N-acetylated chitosans. International Journal Biological Macromolecules. 13:40-44.
13. Lambertus A.M. van den Broek, Rutger J.I. Knoop, Frans H.J. Kappen, Carmen G. Boeriu, Chitosan films and blends for packaging material, Carbohydrate Polymers, Volume 116, 2015, Pages 237-242