

Testing the Properties and Characteristics of Chitin Thin Films

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Abstract and Introduction:

Chitin, the second-most abundant polysaccharide found in nature, has increased biocompatibility and biodegradability compared to cellulose, the most abundant polysaccharide. Found in crustaceans, cephalopods and mushrooms, chitin can be used to create new polymeric devices and to reinforce pre-existing technologies for various applications [1]. In this project, chitin nanofiber thin films were fabricated and characterized to determine their material properties. The fabrication process used the highly-volatile solvent 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) [2]. As the HFIP slowly evaporated, chitin nanofibers self-assembled through hydrogen bonding to form a thin film sheet. The thin films were tested and measured for material properties: Instron 4505 (upgraded to 5500R) and dynamic mechanical analyzer (DMA) for mechanical properties, x-ray diffraction (XRD) for composition, thermomechanical analysis (TMA) for thermal properties, and a Porosimeter for physical characteristics. These fabricated thin films provide an avenue to create potential applications in wound healing, tissue scaffolds, and polymer reinforcement.

Experimental Procedure:

Chitin thin films were prepared from 0.5% (w/v) chitin/HFIP solutions. The solution was drop-casted and promptly covered to slow the evaporation of HFIP. A few holes were made in the cover to insure the complete evaporation of HFIP. The solution was placed in a fume hood and allowed to evaporate for 8-10 days. When the thin film was set, the characterization process began. First, TMA was performed to determine the coefficient of thermal expansion (CTE). The change in length was measured as temperatures were cycled from 25°C to 180°C and back down to 25°C three times.

To test mechanical properties, an Instron and DMA were employed. Both tests involved a simple tensile test on the sample, closely following ASTM D882-10 [3]. Kapton HN 100 sheets from DuPont were used as a control for both experiments. The Instron applied a maximum force of 20 N with an extension rate of 0.1 mm/min. Using the DMA, we performed a "Static Stress Test."

After calibration, the DMA applied a load that went from 110 mN to 5000 mN at 100 mN/min.

An XRD helped us determine the formation of our chitin. The test was performed on the samples by scanning from 2 θ at 3° to 55° with a 0.02 step-size following all necessary precautions while dealing with radiation equipment.

Lastly, a Porosimetry test was completed to determine the presence and characteristics of pores in the thin films. Multiple thin films, weighing a total of 0.0455 g, were loaded into the testing apparatus and mercury was intruded through the samples to determine the existence and size of the pores.

Results and Conclusions:

As previously noted, chitin self-assembles into nanofibers due to HFIP evaporation. This fabrication process helped yield 3 nm nanofibers in a thin film that ranges from 10 to 200 μ m in thickness [2].

The CTE values from the TMA test ranged from about 38 to 186 ppm/K, but literature states that the values should be closer to 9.8 ppm/K [1]. This discrepancy can be attributed to nanofiber alignment in a two-dimensional plane while experimentation was performed in the third dimension.

The Instron and DMA tests provided results for Young's Modulus (stiffness) that did not entirely match literature results. Our control Kapton® and chitin film were specified to have a stiffness of 2.5 GPa [1, 4], but our Instron results gave an average stiffness of 1.187 GPa. Nonetheless, chitin thin films were tested on the Instron and the chitin showed an average stiffness of 1.09 GPa with a large standard deviation of 815 MPa as seen in Figure 1. To double-check, DMA tests were carried out in hopes for more accurate and precise results. DMA tests showed Kapton and chitin stiffness at about 732 MPa and 307 MPa, respectively. These disagreements in values can be a result of the testing methods, testing equipment, and inconsistent samples. Interestingly enough, if outliers of the Instron tests were taken into account, the two experiments showed that Kapton was about twice as stiff as chitin.

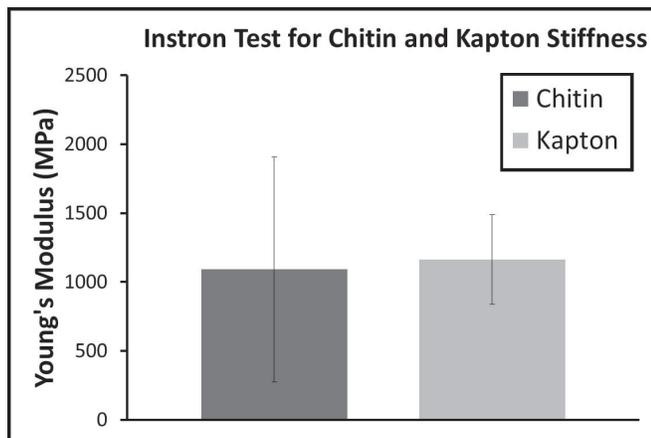


Figure 1: Kapton = 1.187 GPa with 325 MPa standard deviation. Chitin = 1.09 GPa with 815 MPa standard deviation.

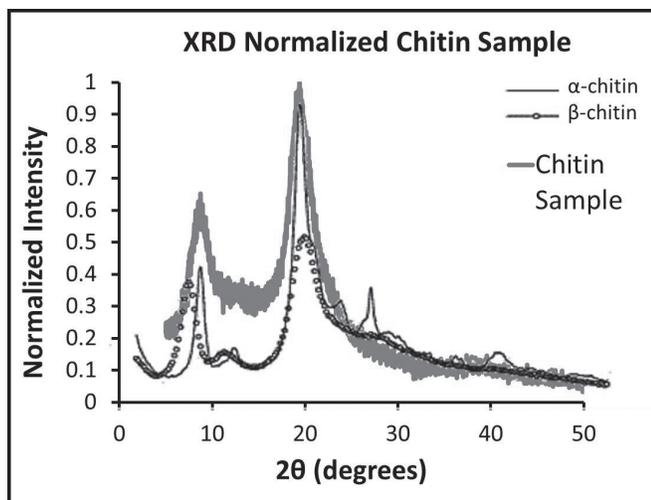


Figure 2: XRD of chitin thin film compared to α - and β -chitin.

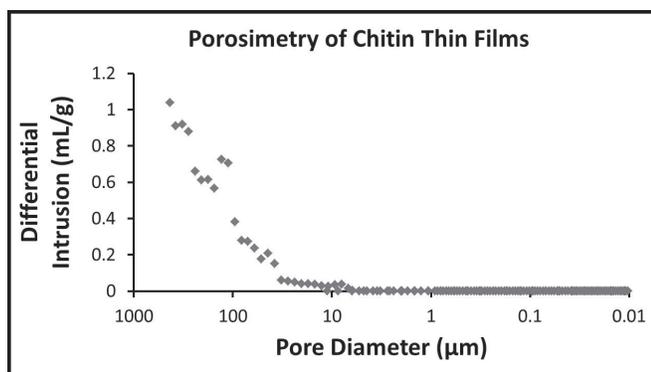


Figure 3: Porosimetry results of chitin thin film test.

XRD results, in Figure 2, were fairly conclusive in showing that our chitin thin films exhibited α -chitin (nanofibers are aligned parallel and antiparallel [5]). This orientation caused the nanofibers to pack closer together due to hydrogen bonding. This transformation of β -chitin in the chitin powder to α -chitin in the thin film was a result of the HFIP evaporation process.

The graph of the Porosimetry results, represented in Figure 3, shows spikes that occur at a higher pore diameter, a result of mercury filling the voids in between the different thin film samples. But with smaller pore diameters, the mercury could not penetrate through the thin films, meaning that if pores are present, they are smaller than 10 nm.

Future Work:

In the future, we will try to test our chitin thin films on equipment specifically designed for thin films testing. Hopefully, this will reveal better results for our stiffness values. Another aspect we would like to test is how the concentration of chitin/HFIP solution affects chitin thin film properties. Lastly, we will try to formulate sample preparation methods that yield consistent thin films.

Acknowledgements:

I acknowledge Professor Marco Rolandi, Dr. Jungho Jin, and the entire Rolandi Research Group for giving me an opportunity to help conduct this research and teaching me scientific research skills. I would also like to thank MSE User Facility and Nanotechnology User Facility personnel for their help and advice. Lastly, I wish to thank the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program and National Science Foundation for allowing me to participate in such an intellectual program.

References:

- [1] Ifuku, S., Green Chemistry, 13, 1708, (2011).
- [2] Zhong, C., Soft Matter, 6, 5298, (2010).
- [3] ASTM Standard D882-10, ASTM International, West Conshohocken, PA, (2010), www.astm.org.
- [4] DuPont, kapton.dupont.com.
- [5] Lavall, R. L., Bioresource Technology, 98, 2465, (2007).