# Physical and Chemical Structural Analysis of Pistachio Shells

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**Abstract**

Pistachio shells were examined to determine structure and chemical composition. Structural analysis was completed using a differential scanning calorimeter (DSC), polarized light microscopy (PLM) and environmental scanning microscopy (ESEM). Chemical composition was quantified with Fourier transmission infrared spectroscopy (FT-IR) for organic components and electron dispersive spectroscopy (EDS) analysis for inorganic matter. The shells were found to have a layered, porous structure. Triglyceride fat and cellulose sugar accounted for most of the natural polymers present. The amount of fats increased inversely to the proportion of sugar closer to the outside surface of the shell, possibly accounting for the transport of nutrients into the shell as opposed to the strength needed from cellulose on the inside edge. Understanding the structure and its elemental derivatives will help in the future quantification of physical and mechanical properties.

Keywords: Pistachio, Cellulose, Biopolymers, Structure

## 1. Introduction

Nature is filled with polymers. Many are formed by cellulose, which is a compound formed from polymerized chains of glucose. Cellulose has a high degree of hydrogen bonding, creating a very strong, durable polymer[1] (Figure 1). As manufacturing costs for polymers increase due to the scarcity of petroleum, it is hoped that natural alternatives such as cellulose based materials can provide cheaper and more biodegradable products.

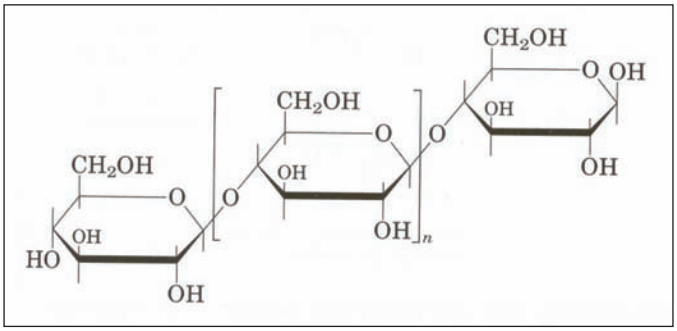


**Figure 1.** Cellulose, the group in brackets, is an individual glucose molecule2.

Pistachio shells are one example of a very tough natural polymer (Figure 2). The shells are extremely tough for a plant shell, which makes characterization intriguing. As opposed to the actual nuts, nothing was found in the literature about pistachio shells. Therefore, the shell was examined for both structural and chemical information. Analysis was completed on several different areas of the shell to determine if physical and chemical compositions varied with the depth of the shell. Quantifying structure and elemental make-up has the potential to explain many of the unique attributes of pistachio shells, such as their hardness and strength.

**Figure 2.** (L-R) Inside and outside of a pistachio shell.

## 2. Procedure

*2.1 Shell Preparation*

Shells were submerged in water for two weeks to remove salt and any other artificial treatments. Four of the shells were mounted in epoxy and polished up to 0.03 µm for microscopic examination. Two samples were of the cross-section of the shell, and two others were of the inside and outside shell surfaces. All the mounts except one cross-section were sputtered with gold for scanning electron microscope (SEM) and electron dispersive spectroscopy (EDS) analysis. The other cross-sectional sample was preserved and polished for polarized light microscopy (PLM).

*2.2 DSC Analysis*

Approximately 16 mg of ground shell sample was loaded in a platinum crucible under helium carrier gas in a differential scanning calorimeter (DSC). The sample was heated up to 400 °C and then cooled back to 30 °C at 10 K/min. DSC data was analyzed for structural information and mass loss.

*2.3 Microscopy*

Both EPI-polarized light microscopy and ESEM analysis were completed to determine the structure of the shells. Polarized light microscopy using EPI, or reflected, light was used for structural analysis of a cross-sectional sample. The other three samples, cross-sectional, inner shell and outer shell surfaces, were sputtered with a thin layer of gold for ESEM analysis. The inner and outer shell samples also underwent EDS analysis to uncover any inorganic chemical differences between the outside and inside of the shell.

*2.4 FT-IR Analysis*

Solid state FT-IR was performed on small shell fragments around 2-4 mm in diameter. Again, the inner and outer shell surfaces were examined for differences, yet this time in organic chemical composition.

## 3. Results and Discussion

*3.1 Physical Structure*

DSC analysis was the first test performed on the shells. This was done in the hopes of determining the glass transition temperature or Tg of the pistachio polymer. A Tg marks the temperature where a polymer transitions from crystalline to amorphous with the addition of thermal energy[3]. A Tg is not normally a fixed temperature, rather it is dependent upon processing[3].

With the pistachio shell fragments, it was difficult to come up a well defined Tg. As seen in Figure 3, the blue line measuring thermal changes of state had several peaks, some better defined than others. This data provides evidence of a very complex structure. Following along to the right, the first couple upper, endothermic, peaks might be lower weight amorphous polymers that eventually transition into higher molecular weight, crystalline sections. To identify the peaks with more certainty, shell fragments would need to undergo x-ray diffraction at temperatures corresponding to the points of interest.

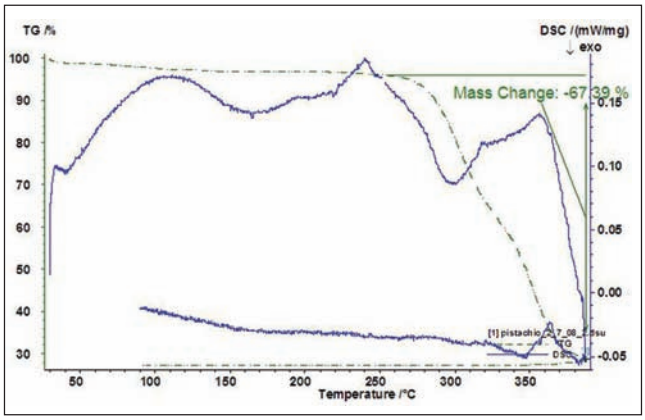


**Figure 3.** DSC graph for shell decomposition.

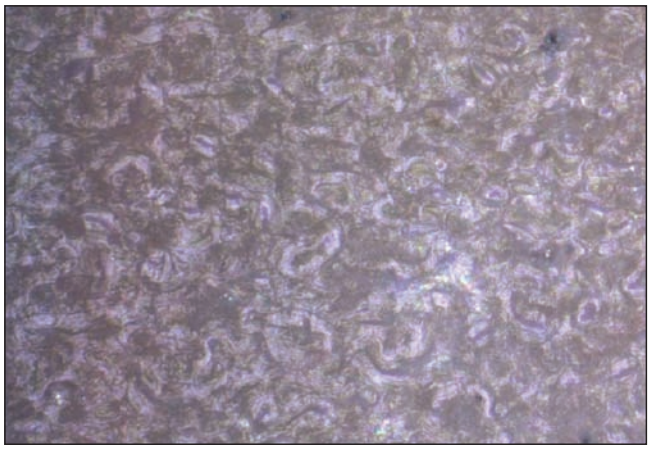

**Figure 4.** EPI-Polarized Light Microscopy at 20x.

Polarized light microscopy was the optical method used to examine a cross-section shell. Micrographs revealed a fibrous, porous structure. The shinier area towards the lower right corner of Figure 4 is thought to be a region of crystallinity. Analysis by ESEM provided a more in depth picture.

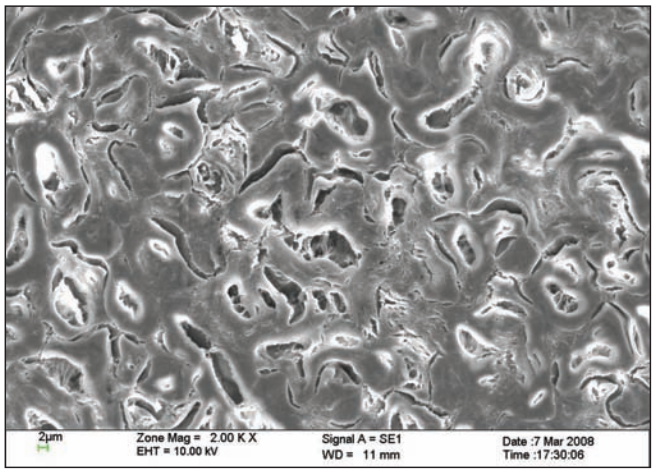


**Figure 5.** Overall structure from a cross-sectional sample – ESEM at 2000x.

Three samples were examined by ESEM, a cross-sectional slice of shell, the outside shell surface and the inside shell surface. Figure 5 provides a good example of a representative cross-sectional structure. The pores are probably due to the need to transport nutrients and oxygen to and from the growing pistachio nut.

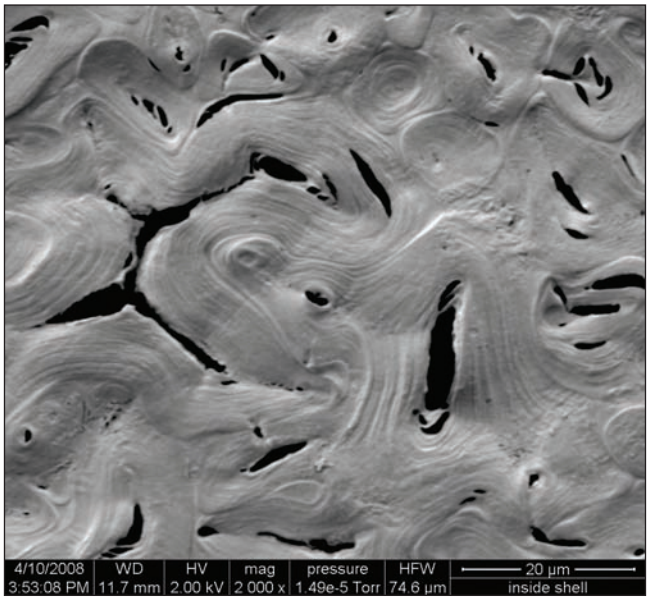


**Figure 6.** Inside shell structure – ESEM at 2000X.

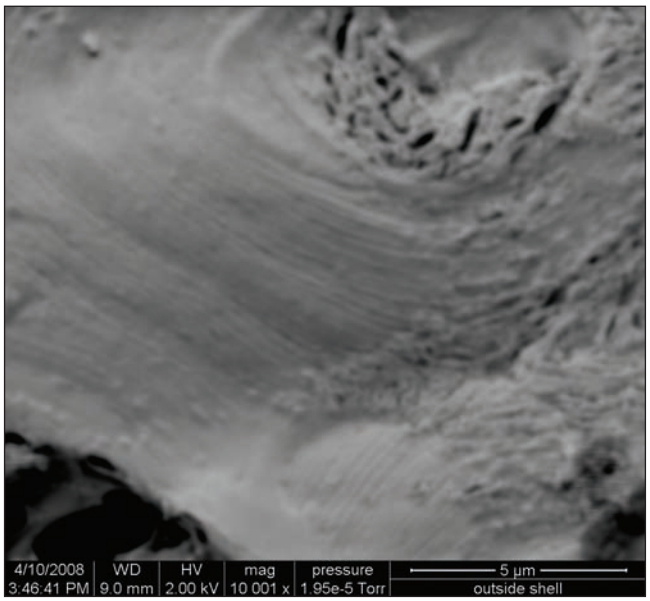


**Figure 7.** Outside shell with laminar features – ESEM at 10000X.

Figure 6 shows a large pore with its surrounding inside shell surface. As seen in Figure 6 and in more detail in Figure 7, layering was very evident producing a laminar structure flowing around the pores. This reflects common polymeric growth of sections of different polymers bordering on each other[4]. However, the sample was very sensitive to the ion beam from the ESEM at high voltage. This caused problems as the samples visibly deformed under high magnification. Therefore, it was impractical to try EDS analysis or any other sort of close examination to find out whether the structure in Figure 7 is a compilation of layers of different polymers or the same polymer folded on top of itself.

*3.2 Chemical Analysis*

Also, the chemical composition of the shell was examined. IR analysis revealed a make-up of fats and polysaccharide cellulose carbohydrates. Cellulose provides strength and organization to the shell, whereas fats help to dissolve nutrients and vitamins necessary for plant growth[1]. Fat peaks[5] generally show up by detection of C-H bonds around 3000-2800 $cm^{-1}$ and C=O bonding between 1745-1725 $cm^{-1}$. Carbohydrates such as polysaccharide cellulose have defining peaks in spectra at 3000-2800 $cm^{-1}$ for C-H bonds and 1400-800 $cm^{-1}$ from bonds between glucose polymer chains[5]. The spectra of the inside shell showed the definite presence of cellulose and carbohydrates with sharper, better defined peaks in the 3000-2800 $cm^{-1}$ range and a multitude of peaks starting at 1700 $cm^{-1}$. This may note the linkages between glucose polymer chains to create cellulose. Some protein was also detected with amine peaks between 1700 and 1600 $cm^{-1}$. The lower spectra in Figure 8 is the result for the outside shell. The spectra of the outside shell surface appears to have a higher concentration of fat with sharp peaks at 2920 cm-1 and 1720 $cm^{-1}$ as seen in the top graph in Figure 8.

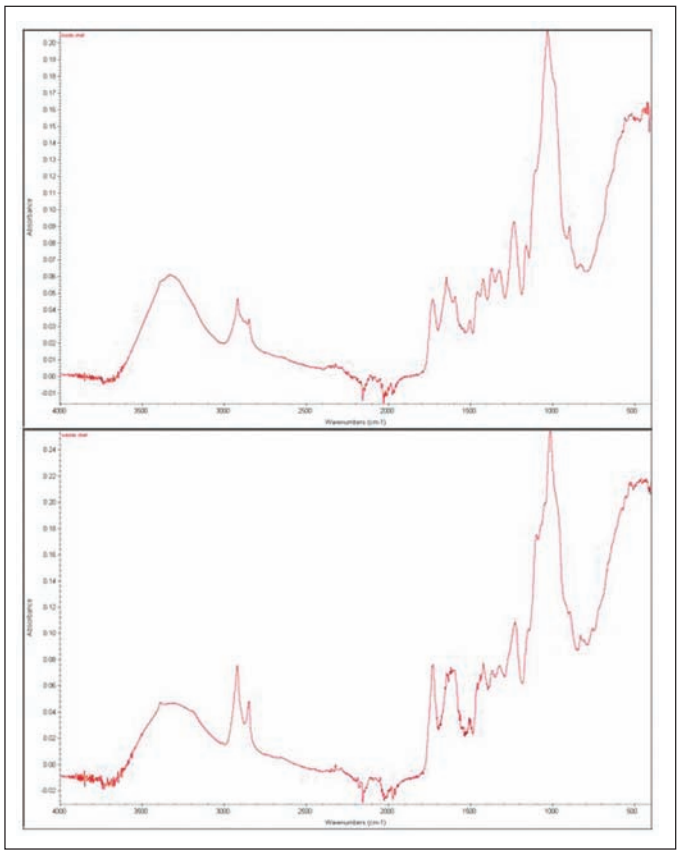

**Figure 8.** IR analysis for inside shell surface (top) and outside shell surface (bottom).

The change in composition between shell surfaces probably accounts for the need for a strong, protective structure

provided on the inside of the shell by cellulose. In contrast, fat on the outside of the shell helps dissolve vitamins and nutrients for transport to the nut. Traces of protein and further fats found on the inside surface may be related to the protective membrane formed around the nut.

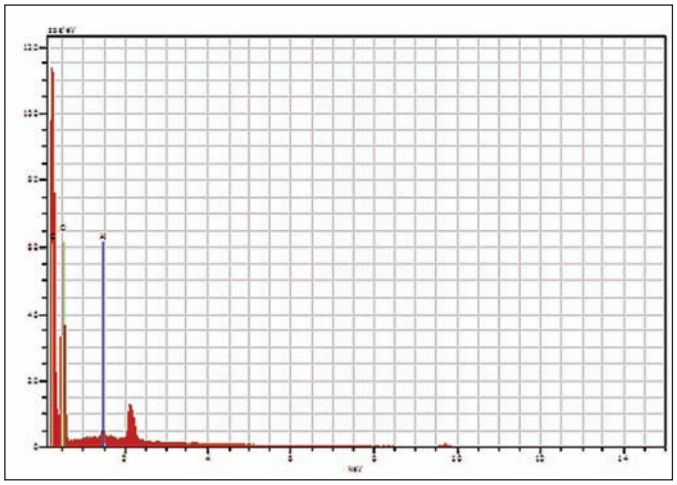

**Figure 9.** Example EDS analysis of inside shell surface.

EDS results from the ESEM showed no measureable traces of inorganic matter in the shell, no matter the surface. As shown in Figure 9, the only elements detected were carbon and oxygen. The aluminum present is probably due to the near impossibility of removing all alumina from the polishing process from such a porous sample.

## 4. Conclusions

In conclusion, pistachio shells have a very fibrous structure with a combination of amorphous and crystalline polymers. From microscopy, the shells were found to have laminar polymer layers wound around pores. Chemically, pistachio shells appear to be made from triglycerides and cellulose with no trace inorganic compounds. The concentrations of triglyceride and cellulose vary as per the depth of the shell in accordance with the function of the shell at that depth. These results, especially those quantifying the physical structure, provide a good foundation for explaining the results of future mechanical testing.

## Acknowledgements

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## Reference

[1] R. M. Brown Jr., et al., "Molecular and Structural Biology;" Springer: Dordrecht, 2007.

[2] Weblink:http://erkki.kennesaw.edu/schem219/sc00029.htm Lesson four: polysaccharides and carbohydrate digestion., part of online resources for chemistry courses at Kennesaw State University, accessed on 29th Apr. 2008.

[3] W. D. Callister Jr.; "Materials Science and Engineering: An Introduction," Wiley, New York, 2007.

[4] Weblink:http://www.doitpoms.ac.uk/tlplib/polymers/index.php Crystallinity in Polymers, part of materials science focused teaching packages from the University of Cambridge, accessed on 18th Apr. 2008.

[5] B. Stuart, "Infrared Spectroscopy: Fundamentals and Applications;" Wiley, Sussex, 2004.

## About the Author

Jessica Piness is a junior in Materials Science and Engineering and Chemistry at Virginia Tech with a focus in polymers. She enjoys research and working in the laboratory.