

**Investigating the effect of esterification on the properties of biodegradable polymers  
synthesized from coffee silverskin-extracted cellulose.**

**Group 1-38**

**Abstract**

Current research in coffee silverskin waste is limited to composting and cosmetic applications, rather than in the field of bioplastics. Existing bioplastics face major development barriers due to the usually poor mechanical properties and high cost of synthesising them. Herein, we demonstrate a novel and low-cost method to convert coffee silverskin waste into cellulose acetate bioplastics. Cellulose was extracted from coffee silverskin through Schweizer's reagent (tetraamminediaquacopper dihydroxide), before undergoing an acetylation with iodine as a catalyst. The bioplastics produced had high water absorbency, making them suitable for use as drug delivery capsules and other applications. However, the films synthesized had low tensile strength, giving them limited applications for commercial use. The properties of the cellulose acetate bioplastic make it desirable for limited applications, but this can be remedied through the use of plasticisers.

**Introduction**

**Literature Review**

Recently, there has been growing interest in the research on bioplastics as a replacement for petrochemical plastics. Cellulose based polymers are one of the more popular types of bioplastics as it is a nearly inexhaustible raw material with fascinating structure and properties for the remarkable demand for environmentally friendly and bio-compatible products ( Osswald & García-Rodríguez, 2011) . One useful cellulose polymers is cellulose acetate. Its benefits

include low-cost, toughness, gloss, high transparency, natural feel, and other favorable aesthetic properties (Biswas et al, 2006).

A good source of cellulose is agricultural by-products as they are regarded as abundant, inexpensive, and readily available (Huang et al., 2011). Most related studies make use of agricultural byproducts like sugarcane bagasse and rice husk for the synthesis of cellulose acetate. Huang et al., (2011) have conducted successful chemical modification of SBC producing high-value-added cellulose derivatives and realizing the objective of turning waste into wealth. The acetylation of cellulose from corn fiber, rice hulls, and wheat straw was confirmed by proton NMR of the product cellulose acetate (Biswas et al., 2006).

However, these studies have yet to explore the use of coffee silverskin in the production of cellulose esters. According to Alghooneh, Asad Mohammad Amini, Fataneh Behrouzian and Seyed Mohammad Ali Razavi (2016) the high demand for coffee, resulted in considerable amount of residues generated in the industry. Coffee silverskin (CS), the thin segment of the outer layer of green coffee beans, is one of the major agro-industrial side-product generated worldwide. Therefore this study aims to make use of coffee silverskin extracted cellulose to synthesise cellulose acetate and investigate its properties to determine if it is suitable for the production of bioplastics.

## **Objectives**

We aim to:

1. Synthesize cellulose from coffee silverskin for the production of agro polymer
2. Investigate the effect of esterification on the properties of biodegradable polymers

## **Hypothesis**

1. Esterification affects the biodegradability of the plastic
2. Esterification affects the water resistance of the plastic
3. Esterification affects the tensile strength of the plastic

4. Biodegradable plastics can be synthesised from coffee silver skin

## **Methodology**

### **Preparation of coffee silverskin**

10g of CS was sieved, cleaned pneumatically, and washed with tap water three times. The CS was then dried using an air-forced oven at 60 °C, milled and sieved through a sifter with 0.3 mm aperture size. The dried powder was kept in polyethylene bags and in a cool and dry place prior to performing experiments.

### **Fat removal of CS**

A mixture of organic solvent ,hexane–methanol (2:1, v/v) and coffee silverskin was added to a 500ml round bottom flask. This mixture was put under reflux for 3 h at 60°C to remove the oil/wax etc. After extraction, the powder was dried in an oven.



**Figure 1 : Mixture put under reflux during fat removal process**

### **Extraction of cellulose from CS**

2g of copper(II) hydroxide was added to 100ml of 25% aqueous ammonia and the mixture was stirred till a dark blue solution is formed. 2.5g of defatted coffee silverskin powder was added to the solution and 30 min of reaction time was given. The solution was poured slowly into 100ml of 10% hydrochloric acid and cellulose precipitates. The product was filtered and the residue was collected. Cellulose was washed till pH is neutral before it was dried in the oven.



**Figure 2 :Cellulose that precipitated**      **Figure 3 :Vacuum filtration to remove water**

### **Acetylation of cellulose**

0.2 g of cellulose was taken into a 100 ml round bottomed flask fitted with a mechanical stirrer. 10 ml acetic anhydride was added in to the material and 0.3 g of iodine was added. The mixture was heated to 80°C and left for 300 min at 80 °C. At the end of every experiment, the reaction mixture was allowed to cool at room temperature and treated with 5 ml saturated solution of sodium thiosulphate with stirring. The colour of the mixture was changed from dark brown to colorless, indicating the transformation of iodine to iodide. The mixture was then transferred to a beaker containing ethanol (30 ml) and stirred for 60 min. The product was

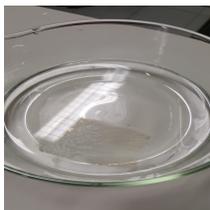
filtered and thoroughly washed with 75% (v/v) ethanol and distilled water to remove the unreacted acetic acid and byproducts. The solid material was then dried at 60 °C in an oven. The oven-dry materials was dissolved in methylene chloride and filtered. Cellulose acetate was formed as a film inside the flask after evaporating the filtrate. Ethanol was used to remove the film from the flask and filtered through a filter paper. The cellulose acetate collected on the filter paper was dried at 60 °C in oven for 24 h.

### **Tensile strength test**

The cellulose acetate film was cut into rectangular strips; 3cm by 1cm. A tensometer was used to conduct a tensile strength test on the cellulose acetate film.

### **Water absorption test**

A water absorption test was carried out on the cellulose acetate films produced based ASTM standards. The cellulose acetate film was cut into a square 6cm by 6cm. The square film was entirely immersed in a container of distilled water. At the end of 24h, the specimens were removed from the water one at a time, all surface water wiped off with a dry cloth, and weighed to the nearest 0.001 g immediately.



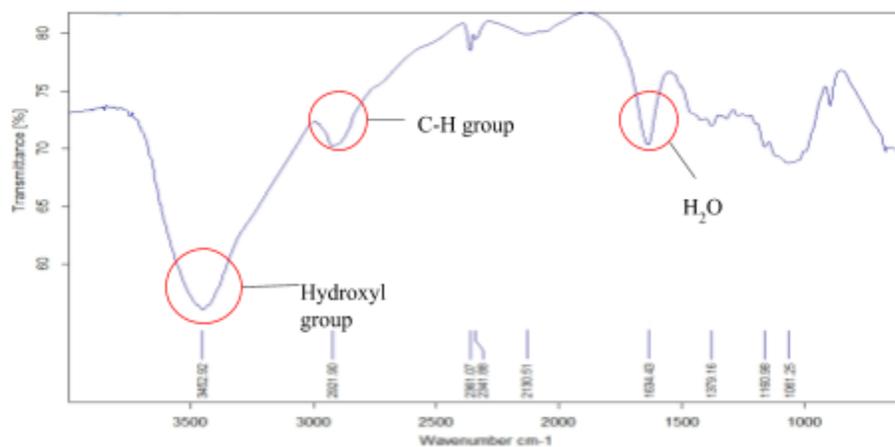
**Figure 4 :Cellulose acetate film immersed in water for water absorption test**

## FT-IR spectroscopy

Characterization of the acetylated product was examined by FT-IR spectroscopy. IR spectroscopic studies were performed using the KBr pellet technique to observe the ester peaks and hydroxyl group absorptions.

## Results and Discussion

### FT-IR Spectroscopy



**Figure 5: FTIR Spectroscopy of Cellulose**

From FTIR Spectroscopy of Cellulose (Figure 5), it is confirmed that synthesis of cellulose was successful. The broad peak at  $3453\text{ cm}^{-1}$  region is characteristic for stretching vibration of the hydroxyl (O-H) group in polysaccharides. This peak includes also inter- and intramolecular hydrogen bond vibrations in cellulose. The peak at  $2921\text{ cm}^{-1}$  is attributed to CH stretching vibration of all hydrocarbon constituents in polysaccharides. The peak located at  $1634\text{ cm}^{-1}$  corresponds to the vibration of water molecules absorbed in cellulose. The results are also similar to those found in other literature (Figure 6).

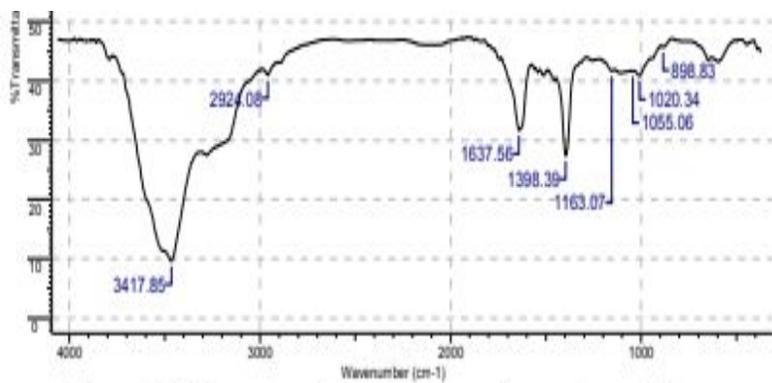


Figure 6 : FTIR spectra of original cotton cellulose

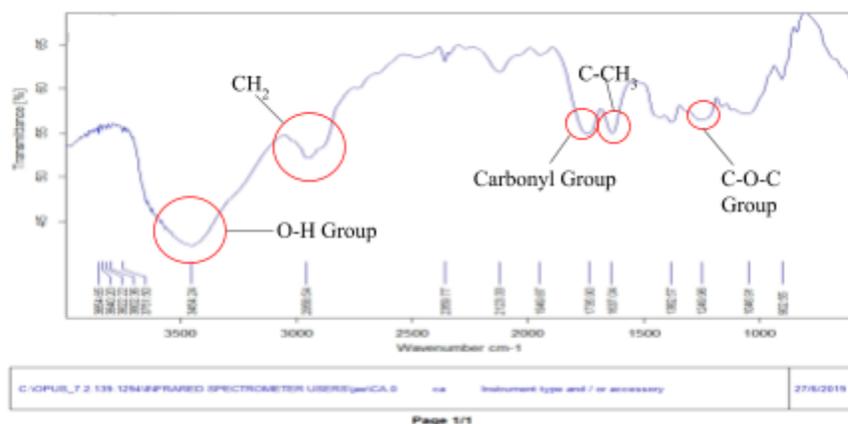


Figure.7 : FTIR Spectroscopy of Cellulose acetate synthesised from cellulose extracted from coffee silverskin

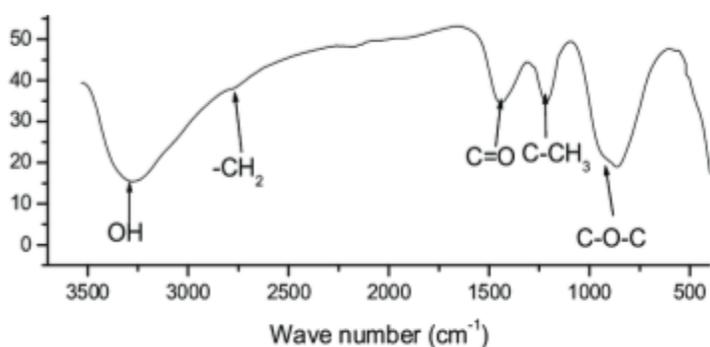
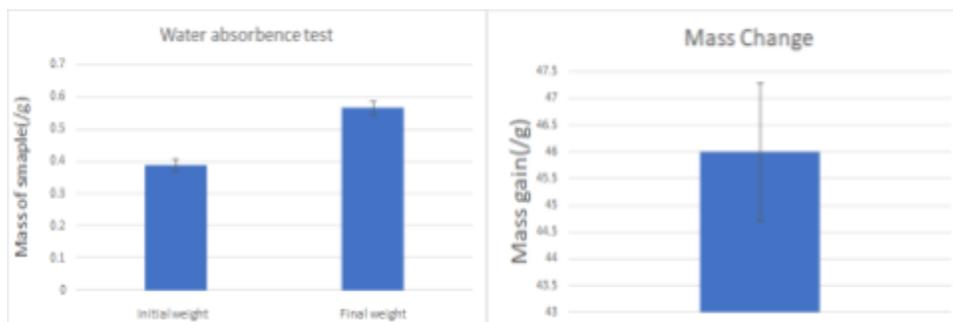


Figure 8 : FTIR spectra for free CA nano-fiber

FTIR spectroscopy of cellulose acetate (Figure 7) confirmed our hypothesis that cellulose acetate was synthesized. There were a few major changes in the spectrum of acetylated cellulose

as compared to cellulose on acetylation. Firstly, there was a decrease in the hydroxyl (OH) stretching band at  $3322\text{ cm}^{-1}$ , corresponding to the acetylation of hydroxyl groups. However, there were some hydroxyl groups remaining, suggesting that cellulose did not undergo complete esterification. Secondly, there was an increase in the carbonyl (C=O) stretching band at  $1736\text{ cm}^{-1}$ , which corresponds to the introduction of a carbonyl group into cellulose during esterification. Thirdly, the new peak in  $903\text{ cm}^{-1}$  corresponds to the COC group. This result corresponds to the FT-IR spectrum from literature as shown in (Figure 4).

### Water Absorption Test



**Figure 9 : Graph of initial weight, final weight and % mass gained**

The average increase in weight/water absorbance for the cellulose acetate film is 45.99%, with an average standard deviation of 1.38. This is far from that in commercial cellulose acetate films, which have a water absorption of only 1-3%, and is similar to other plant based bioplastics such as rice starch-based bioplastics, which have a water absorbance of 30-40%. This gives cellulose acetate film limited applications as a high water absorbance can compromise mechanical strength and other physical properties. As the cellulose acetate film is non-homogenous and the edges were cut, this could increase water absorbance. The cellulose acetate film also has a high number of hydroxyl groups as shown in the FTIR results, which

interacts with the water molecules, causing more water to be absorbed. However, the water absorbance of the film can be modified significantly through the addition of plasticizers and by molding it using an extruder, which would make it much more attractive for commercial use.

### Tensile Strength test

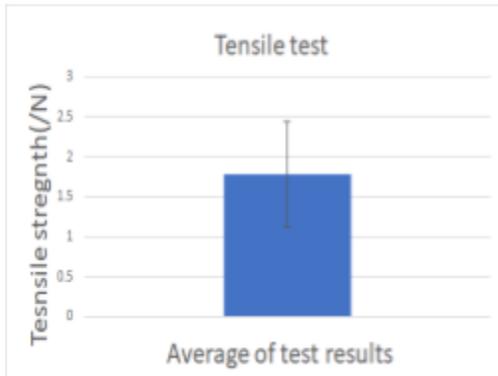


Figure 10 : Graph of ultimate tensile strength

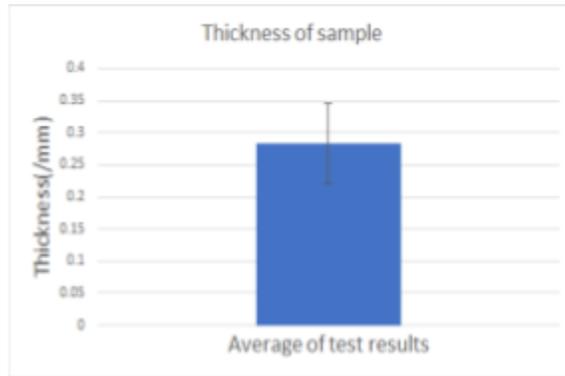


Figure 11: Graph showing thickness

The average ultimate tensile strength of the cellulose acetate film produced is 26kPa. This value is much lower in comparison to that of other commonly used petrochemical plastic products like Polystyrene, Polypropylene, Polyimide, Polyethylene and Acrylonitrile butadiene styrene which have ultimate tensile strength of 40MPa, 40MPa , 85MPa, 15MPa, and 40Mpa respectively. (“Tensile Property Testing of Plastics,” 2008). Though the disparity is not as great when compared to industrial grade cellulose acetate which has an ultimate tensile strength of 4MPa (“Properties: Cellulose Acetate,” 2013) it is still very far from the required industrial quality, giving very few applications.

The first possible reason for the low ultimate tensile strength is the film’s thickness. The average thickness of the film was 0.28mm, which makes it much weaker as the properties of reinforced thermoplastics are affected by the amount of skin and core developed within the film during the injection molding process. Since the thickness of a film greatly influences the amount

of skin and core developed within a molded part, thickness also affects the properties of reinforced thermoplastics (Pechulis & Vautour, 1988 ). Thus, the ultimate tensile strength can be improved by increasing its thickness and this can be done by adding a greater volume of cellulose acetate solution into the mold .

Another possible reason for the low ultimate tensile strength is its relatively high water absorbance. Water sensitivity is one of the important criteria in many applications and it was verified that the mechanical properties are also dependent on the moisture content (Rahmatiah, Sujuthi & Liew, 2016). One of the main physical properties affected by the high water absorbance is tensile strength. This is because the high water absorbance means that there are more spaces for water to penetrate and also high amount of porous tubular structures in fibres that cause the plastic film to break easily. (Rahmatiah, Sujuthi & Liew, 2016).

## **Conclusion**

Cellulose of high purity was synthesized from coffee silverskin through an effective two-part process which involves defatting by 2:1 (w/w) Hexane/methanol mixture and cellulose extraction with the use of Schweizer's reagent . Cellulose was successfully esterified under solvent-free conditions in presence of Lewis acid catalyst (iodine). Characterisation by FT-IR spectroscopy proved that synthesis of cellulose acetate from coffee silverskin was successful. Although the ultimate tensile strength of the synthesized product was low, areas of improvement have been identified. This includes the use of plasticisers and increasing the thickness of the plastic film produced. Currently, the poor physical properties of the film gives it very few industrial applications but we believe that through further research and improvements to the molding process a better product can be produced.

## References

Ali Alghooneh, Asad Mohammad Amini, Fataneh Behrouzian & Seyed Mohammad Ali Razavi (2016). Characterisation of cellulose from coffee silverskin. *International Journal of Food Properties*, 20, 2830-2843. DOI: 10.1080/10942912.2016.1253097

Alexander Ach (1993). Biodegradable Plastics Based on Cellulose Acetate. *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, 30, 733-740. DOI : 10.1080/10601329308021259

Atanu Biswas , Badal C. Saha , John W. Lawton , R.L. Shogren & J.L. Willett (2006). Process for obtaining cellulose acetate from agricultural by-products. *Carbohydrate Polymers*, 64, 134-137. DOI: 10.1016/j.carbpol.2005.11.002

Braun, D., Cherdrón, H., Rehahn, M., Ritter, H., Voit, B (2013). Modification of Macromolecular Substances. Springer Science & Business Media, *Polymer Synthesis: Theory and Practice: Fundamentals, Methods, Experiments* (pp. 334-335). Retrieved from <https://www.springer.com/gp/book/9783642289798>

Cheng, H., Dowd, M. K., Shogren, R., & Biswas, A. (2011). Conversion of cotton byproducts to mixed cellulose esters. *Carbohydrate Polymers*, 86(3), 1130-1136. doi:10.1016/j.carbpol.2011.06.002

Guozhi Fan, Min Wang, Chongjing Liao, TaoFang, Jianfen Li & Ronghui Zhou (2013). Isolation of cellulose from rice straw and its conversion into cellulose acetate catalyzed by phosphotungstic acid. *Carbohydrate Polymers*, 94, 71-76. DOI: 10.1016/j.carbpol.2013.01.073

Isabelle Vroman & Lan Tighzert (2009). Biodegradable Polymers. *Materials* , 2, 307-344. DOI:10.3390/ma2020307

Pechulis, M., & Vautour, D. (1998). The Effect of Thickness on the Tensile and Impact Properties of Reinforced Thermoplastics. *Journal of Reinforced Plastics and Composites*, 17(17), 1580-1586. doi:10.1177/073168449801701706

Properties: Cellulose Acetate. (2013). Retrieved from <https://www.azom.com/properties.aspx?ArticleID=1461>

Ragab, T. I., Wasfy, A. A., Amer, H., El-Gendi, A., Abdel-Hady, M., & Liebner, F. (2014). Synthesis of Cellulose Acetate Membrane from the Egyptian Rice Straws. *Journal of Applied Sciences*, 14(24), 3424-3435. doi:10.3923/jas.2014.3424.3435

Rahmatiah Al Faruqy M Sujuthi. (2016). *Properties of Bioplastic sheets made from different types of starch incorporated with recycled newspaper pulp*. e-VIBS, Faculty of Science and Natural Resources.

Retrieved from <http://www.malrep.uum.edu.my/rep/Record/oai:eprints.ums.edu.my:19229>

Tensile Property Testing of Plastics. (2008). Retrieved July 29, 2019, from <http://www.matweb.com/reference/tensilestrength.aspx>

Tim A. Osswald & Sylvana García-Rodríguez (2011). History of Sustainable Bio-based Polymers. Sanjay K Sharma, Ackmez Mudhoo, *A Handbook of Applied Biopolymer Technology Synthesis, Degradation and Applications* (pp. 1-21). Retrieved from <https://pubs.rsc.org/en/content/ebook/978-1-84973-151-5>

*Figure 6.* FTIR spectra of original cotton celluloses. Adapted from “Amorphous Cellulose – Structure and Characterization ,” Diana Ciolacu, Florin Ciolacu and Valentin i. Popa., (2010), *Cellulose Chemistry and Technology*, 45(1). 13-21. Retrieved from [https://www.researchgate.net/publication/279897864\\_Amorphous\\_cellulose\\_-\\_Structure\\_and\\_characterization](https://www.researchgate.net/publication/279897864_Amorphous_cellulose_-_Structure_and_characterization)

*Figure 8.* FTIR spectra for free CA nano-fiber. Adapted from “Fabrication of novel magnetic zinc oxide cellulose acetate hybrid nano-fiber to be utilized for phenol decontamination,” by Hassan, Elkady, Ahmed, Alaa & Abd-Elhamid A., *Journal of the Taiwan Institute of Chemical Engineers*, 78. doi: 10.1016/j.jtice.2017.06.021.