# Synthesis of biodegradable cellulose acetate plastic from cellulose extracted from vegetable and fruits

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## Abstract

Our project aims to investigate whether different types of vegetables and fruits can be used to produce cellulose acetate plastic with high yield, as well as what solvents worked the best to make the plastic. The experiment involves the purification of the cellulose by removing the chlorophyll, the organic impurities and colourants, and finally treating it with a delignifying bath to obtain pure cellulose. The pure cellulose is then acetylated to give the desired cellulose acetate, before finally dissolved and moulded into plastic. Of the 10 vegetables and fruits tested, it is found that pistachio shells had the highest yield of cellulose, and that an equal volume ratio of acetone and ethyl acetate as the solvents worked the best to make the plastic.

## 1) Introduction

Plastic waste is an increasingly alarming issue due to its high toxicity. Many synthetic plastics, including polystyrene, polypropylene and polyethylene are non-biodegradable, and remain in the environment. Moreover, plastics like polystyrene can break down into its monomer, styrene, which is carcinogenic. (Vodicka, P., Koskinen, M., Naccarati, A., Oesch-Bartlomowicz, B., Vodickova, L., Hemminki, K., & Oesch, F. 2006) Some plastics, like polyvinyl chloride, have been known to emit formaldehyde, which is a known carcinogen and can lead to developmental problems.

Another problem with plastic waste is is increasingly greater amounts of waste and its low recycling rates. According to the NEA, the recycling rate for plastic in Singapore in 2017 was 6%, and 79% of plastic waste worldwide are in landfills (Waste Statistics and Overall Recycling. (n.d.).)

## 2) Objectives and Hypotheses

1. To determine which type of fruits and vegetables gives the highest yield of cellulose.
2. To determine which solvent gives the best tensile strength for the plastic.

Our hypotheses are that if we increase the quantity of synthesizable cellulose by using fruits or vegetables samples of higher cellulose yield, we can increase the quantity of cellulose acetate plastic produced, and that the solvent for the plastic will affect the physical properties of the plastic.

## 3) Methods and Materials

### 3.1) Materials:

| Making Cellulose | Making Cellulose Acetate | Making Plastic |
|---|---|---|
| 95% Ethanol | 50% Acetic Acid | Dichloromethane |
| Sodium Hydroxide | 98% Sulfuric Acid | Methanol |
| Sodium Sulfite | Iodine Crystals | Ethyl Acetate |
| 3.33% Sodium Hypochlorite | Hexane | Acetone |
| | | Acetonitrile |
| | | Glycerol Triacetate |

### 3.2) Methodology:

#### 3.2.1) Making Cellulose

A sample of 5.00g of the desired plant material was added to 100ml of 95% ethanol and boiled on a hotplate at a temperature of 80℃ for a duration of 30 minutes (Figure 1). The solution was then filtered through gravity filtration, and the residue was collected. This procedure was repeated three times for each 5.00g sample, until the colour of the residue is near to colourless. The purpose of this procedure is to remove the chlorophyll present in the plant material sample, which can potentially affect the results obtained if not removed.

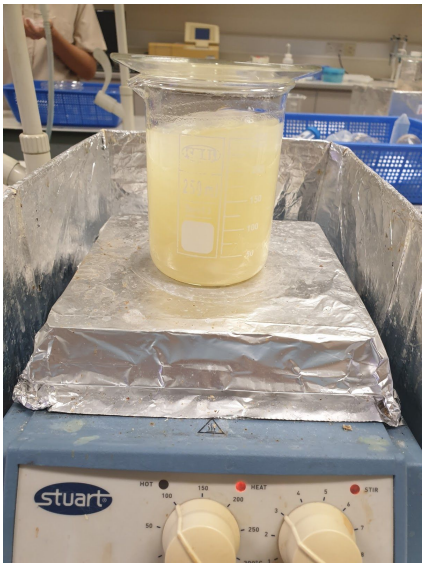


**Fig. 1: Vegetable sample being mixed with 95% ethanol on hotplate**

Next, the sample was then added to 100ml of 3.33% sodium hypochlorite solution, which was made by diluting 33ml of 10% sodium hypochlorite solution in 67ml if deionised water to make 100ml. The solution was stirred with a magnetic stir bar for 30 minutes. The solution was then decanted and the procedure was repeated 3 times. The sodium hypochlorite helps to destroy any impurities as well as to remove any remaining colour from the sample.

Then, a 1L stock solution consisting of 2.5M sodium hydroxide and 0.4M sodium sulfite was prepared. The sample from the previous step was placed in a beaker, and 200ml of this stock solution was added. The mixture was then heated on a hotplate at 150°C for a duration of 4 hours, and constantly stirred with the usage of a stir bar (Figure 2). After 4 hours, the mixture is poured into 50ml centrifuge tubes to be centrifuged for a duration of 15 minutes. The settings of the centrifuge machine was adjusted to 7000rpm. When the centrifugation is complete, the supernatant is then decanted to obtain the cellulose from the plant material sample (Figure 3). The cellulose is then placed in the oven at a temperature of 70°C overnight to dry. These 2 procedures is not required for the control set-up, as pure cellulose is used for the control setup.

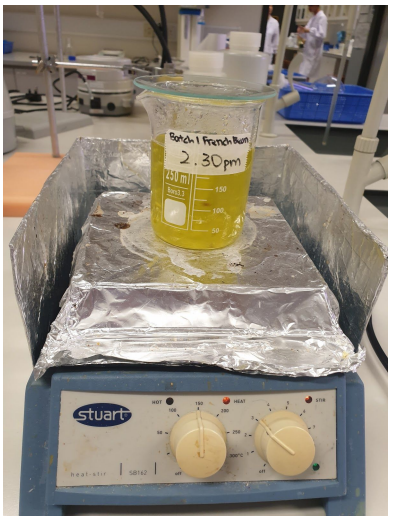


**Fig. 2: Mixture of washed vegetable sample**

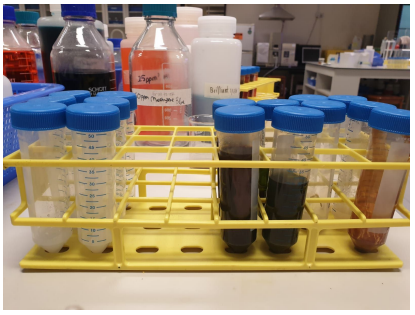

**Fig. 3: Different supernatents collected and decanted after centrifugation**

### 3.2.2) Making Cellulose Acetate:

A solution consisting of 30ml of hexane, 20ml of 50% acetic acid, and a few drops of 98% sulfuric acid was added into a 250ml round-bottom flask. 2.00g of dry cellulose obtained from the previous procedure was then added into the round-bottom flask, and 0.16g of iodine crystals was added into the round bottom flask. The iodine crystals, which was added into the mixture, serves the purpose of the catalyst. (Biswas, A., G. Selling, M. Appell, K.K. Woods,

J.L. Willett and C.M. Buchanan, 2007.) The iodine was allowed to dissolve in hexane present in the solution. A magnetic stir bar was added into the round-bottom flask before the mixture was refluxed for a duration of 1 hour, with a Dean-Stark apparatus to remove excess water that is collected during the process of reflux (Figure 4).

Iodine is used to form acetyl iodide in situ. The acetyl iodine reacts with hydroxyl groups, involving a nucleophilic attack on the acyl carbon center of the acetyl iodide molecule by a lone pair of the alcoholic hydroxyl group, followed by subsequent loss of hydriodic acid, to generate the ester. Hydriodic acid decomposes under heat to regenerate the catalyst.

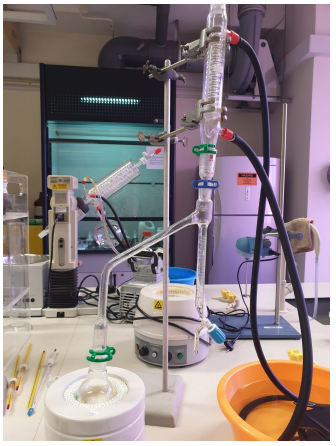

**Fig. 4: Dean-Stark Set-up**

After the reflux was completed, the round-bottom flask was left to cool. The solution is then decanted, and only the cellulose acetate residue is left in the round-bottom flask. Hexane was then added into the round-bottom flask and decanted off repeatedly until no more iodine is present in the cellulose acetate. The cellulose acetate was then washed with deionised water and left in a beaker to dry (Figure 5).


**Fig. 5: Removal of iodine on cellulose acetate through using hexane**

### 3.2.3) Making Cellulose Acetate/Plastic:

2.0g of the purified cellulose acetate was dissolved in of 30ml of solvent respectively. 3ml, 5ml and 8ml of the solution of cellulose acetate was then measured with a measuring cylinder and then poured into beakers with the same base area (Figure 6). They were then

allowed to evaporate slowly until dry. Figures 7 and 8 shows the list of solvents which was used. In Figure 8, 4ml of Glycerol triacetate was used as a plasticizer in addition with 16ml of the respective solvents. Glycerol triacetate is used as a plasticizer in order to alter the plastic's physical properties, like flexibility and brittleness.

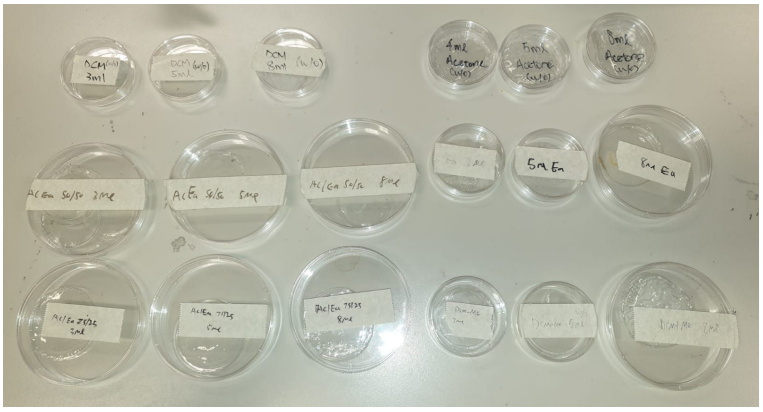

**Fig. 6: Different sets (3ml, 5ml and 8ml) of plastics for each solvent**

| | | | |
|---|---|---|---|
| 20ml of Acetone | 20ml of Ethyl Acetate | 15ml of Acetone and 5ml of Ethyl Acetate | 10ml of Acetone and 10ml of Ethyl Acetate |
| 5ml of Acetone and 15ml of Ethyl Acetate | 20ml of Dichloromethane | 18ml of Dichloromethane and 2ml of Methanol | 20ml of Acetonitrile |

**Fig. 7: List of solvents used for making cellulose acetate/plastic (Without Plasticizer)**

| | | | |
|---|---|---|---|
| 16ml of Acetone, 4ml of Glycerol Triacetate | 16ml of Ethyl Acetate, 4ml of Glycerol Triacetate | 12ml of Acetone, 4ml of Ethyl Acetate, 4ml of Glycerol Triacetate | 8ml of Acetone, 8ml of Ethyl Acetate, 4ml of Glycerol Triacetate |
| 4ml of Acetone, 12ml of Ethyl Acetate, 4ml of Glycerol Triacetate | 16ml of Dichloromethane, 4ml of Glycerol Triacetate | 14.4ml of Dichloromethane, 1.6ml of Methanol, 4ml of Glycerol Triacetate | 16ml of Acetonitrile, 4ml of Glycerol Triacetate |

**Fig. 8: List of solvents used for making cellulose acetate/plastic (With Plasticizer)**

## 4) Results and Discussion

### 4.1) Extraction Of Cellulose

Generally, the shells and pomace of the fruits and vegetables tended to produce a higher yield in cellulose. This is consistent with the fact that they tend to contain more cellulose which contributes to their hardness and rigidity. As observed in Figure 9, the yield of cellulose is the best for pistachio shells, followed by coconut husks and chinese cabbage. This further supports the conclusion that the hardness and rigidity are contributing factors to cellulose yield.

| Type of Vegetable | Initial Mass/g | Average Mass of Cellulose Extracted/g | | | | Percentage Yield |
|---|---|---|---|---|---|---|
| | | $Mass_1$ | $Mass_2$ | $Mass_3$ | $Mass_{ave}$ | |
| Pistachio (Shell) | 5.00 | 4.03 | 4.04 | 4.00 | 4.02 | 80.4% |
| Coconut (Husk) | 5.00 | 3.57 | 3.60 | 3.57 | 3.58 | 71.6% |
| Chinese Cabbage | 5.00 | 3.53 | 3.38 | 3.50 | 3.47 | 69.4% |
| Cucumber (Flesh) | 5.00 | 3.33 | 3.38 | 3.40 | 3.37 | 67.4% |
| Cucumber (Skin) | 5.00 | 3.36 | 3.35 | 3.31 | 3.34 | 66.8% |
| Gingko Nut (Shell) | 5.00 | 2.99 | 3.07 | 2.97 | 3.01 | 60.2% |
| Gingko Nut (Flesh) | 5.00 | 2.85 | 2.90 | 2.89 | 2.88 | 57.6% |
| Kang Kong | 5.00 | 2.87 | 2.86 | 2.82 | 2.85 | 57.0% |
| French beans | 5.00 | 2.64 | 2.61 | 2.64 | 2.63 | 52.6% |
| Edamame (Shell) | 5.00 | 1.53 | 1.48 | 1.49 | 1.50 | 30.0% |

**Fig. 9: List of vegetable samples used to extract cellulose, and respective cellulose yield.**

### 4.2) Yield of Cellulose Acetate

Figure 10 shows how the percentage yield of cellulose acetate varies with the different vegetables and fruits. As it can be seen, there is no significant difference in the percentage yield as the cellulose extracted from the different plants had a similar purity, as confirmed by an FTIR of cellulose and cellulose acetate (Figure 11). The Broad band in the region 3448-3417 $cm^{-1}$ indicates the presence of free O-H stretching which is evident of cellulose. The presence of three ester bonds at 1751 $cm^{-1}$ (CO ester bond), 1369 $cm^{-1}$(CH

bond in acetyl group) and CO stretching band of acetyl group at 1220 $cm^{-1}$ indicates that cellulose acetate is present.

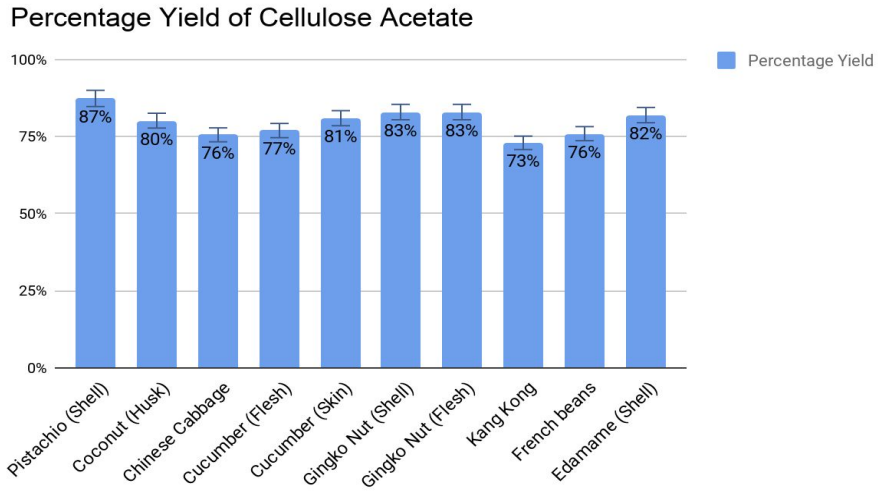


**Fig. 10: Graph of yields of cellulose acetate from cellulose content of each vegetable type**

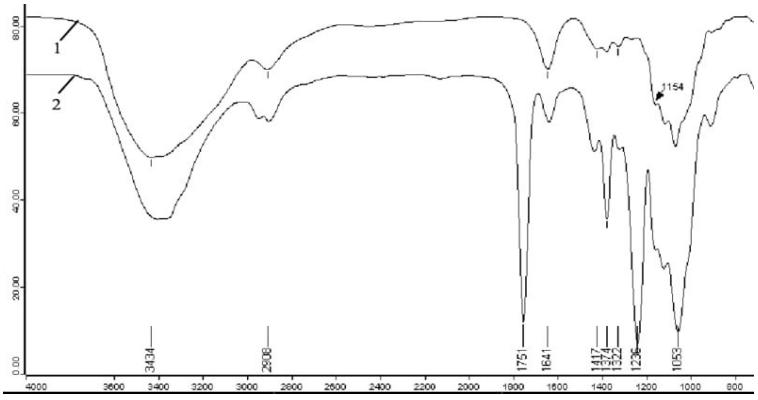


**Fig. 11: FTIR of cellulose and cellulose acetate(1-Extracted Cellulose, 2-Cellulose acetate)**

## 4.3) Degree Of Substitution

The Degree of Substitution (DS) of the cellulose acetate was determined by proton Nuclear Magnetic Resonance(NMR). The degree of substitution of a polymer is the average number of substituent groups attached per base unit, hence in this case, the average number of acetyl groups attached to one unit of cellulose. The ratio of the seven anhydrocellulose proton absorbance in the range of 3.5-5.2 ppm to the absorbance of three methyl proton of acetyl group in the range of 1.9 and 2.2 ppm is used. The DS of the acetyl group was hence calculated by the ratio of spectral integrals of acetyl moiety and repeating unit. It was found that the DS of crude cellulose acetate was calculated to be 1.69. This is consistent with the fact that the cellulose acetate formed is soluble in acetone, which dissolves cellulose acetate with degree of substitutions around 55%.

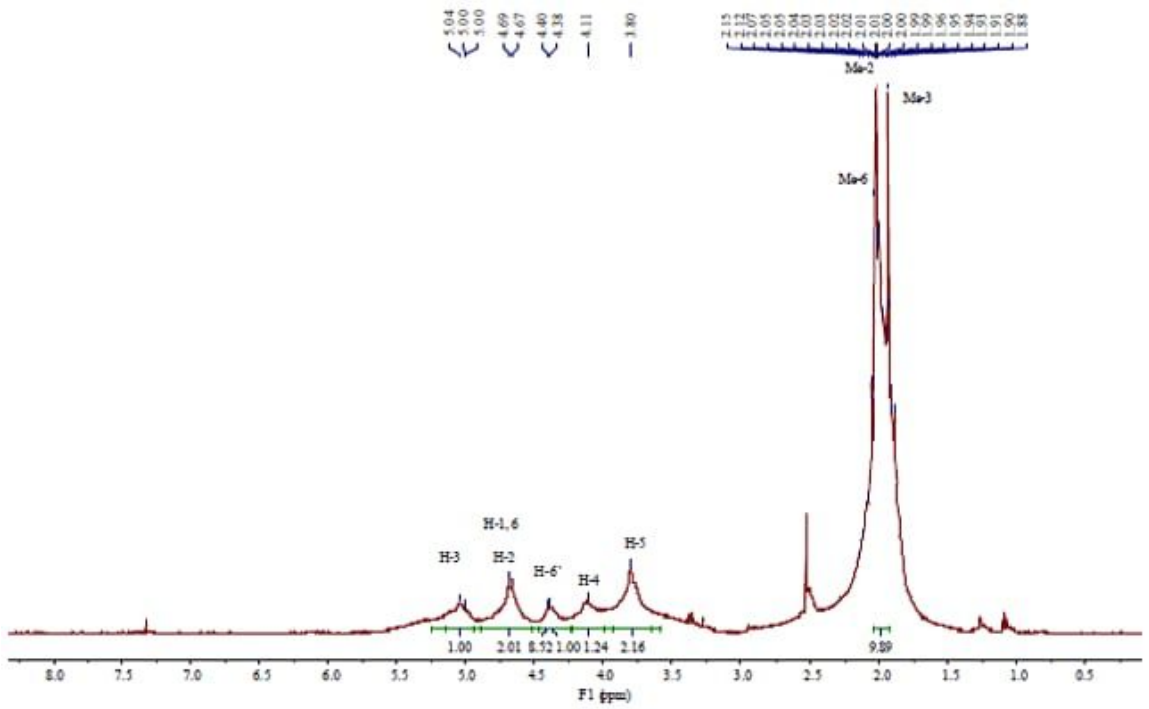


**Fig. 12: NMR for cellulose acetate**

### 4.4) Yield Of Plastic

For the various sets without the plasticizer, the plastics of varying thicknesses and tensile strength is successfully formed. With each type of solvent, we produced respective results for 3ml, 5ml and 8ml sets of plastic formed by pouring the respective amounts into petri dishes with the same base area to vary the thickness. The tensile strength of pure cellulose acetate given as 12-110MPa. As observed in Figure 13, it can be concluded that the following two solvents are the most suitable to synthesise plastic: 18ml DCM and 2ml Methanol mixture; and 10ml Ethyl Acetate and 10ml Acetone mixture, as they have the highest tensile strength of 101.7MPa and 108.4MPa respectively.

| Solvents | Thickness/mm | | | Tensile Strength/MPa | | |
|---|---|---|---|---|---|---|
| | 3ml | 5ml | 8ml | 3ml | 5ml | 8ml |
| DCM/Dichloromethane (20ml) | 1.22 | 1.35 | 1.84 | 9.5 | 10.9 | 12.2 |
| DCM (18ml) and Methanol (2ml) | 0.15 | 0.19 | 0.23 | 97.3 | 98.3 | 101.7 |
| Acetone (20ml) | 0.24 | 0.33 | 0.40 | 59.3 | 63.8 | 67.1 |
| Ethyl Acetate (20ml) | 0.12 | 0.22 | 0.28 | 62.9 | 65.8 | 68.2 |
| Acetone (5ml) and Ethyl Acetate (15ml) | 0.11 | 0.25 | 0.31 | 80.7 | 83.6 | 87.9 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Acetone (10ml) and Ethyl Acetate (10ml) | 0.09 | 0.22 | 0.27 | 103.5 | 105.9 | 108.4 |
| Acetone (15ml) and Ethyl Acetate (5ml) | 0.08 | 0.15 | 0.23 | 82.8 | 84.6 | 88.9 |
| Acetonitrile (20ml) | 0.15 | 0.21 | 0.35 | 88.3 | 89.7 | 91.2 |

**Fig. 13: List of thickness and tensile strength of plastic formed by each solvent, respective to 3ml, 5ml and 8ml groups.**

However, the addition of 4ml of plasticizer, glycerol triacetate, did not aid in the process of making plastic. Instead, the addition of glycerol triacetate resulted the plastic to soften, and thus leaving a viscous, sticky gel like layer on the petri dish. This might be due to the low vapour pressure of the plasticizer causing it to remain in the petri dish along with the cellulose acetate, making it viscous. When added to Dichloromethane, the plastic does not completely dissolve, owing to its slow hydrolysis in air to form very fine insoluble cellulose, which cannot dissolve in such solvents.

## 5) Conclusion and Recommendations for future work

In conclusion, it is possible to create biodegradable plastic from discarded vegetable parts. Of all the vegetables and fruits tested, it is evident that the pistachio shell gives the best yield at 4.02g and with a percentage yield of 80.4%. The plastic made is not only biodegradable, but also prevents food wastage. Of the solvents tested, it is evident that 3ml of 50/50 ethyl acetate and acetone solvent gives the highest tensile strength at (108.4MPa).

In the future, it is possible to find alternatives to such solvents that are more environmentally green and also less damaging to human health. It is also possible to explore how to potentially scale up the process into an industrial scale so as to assess its viability to produce the plastic on a commercial scale at a low price. Considerations could also be made to reduce the amount of waste produced by this process or to reduce the amount of solvents used.

## 6) References


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