

INVESTIGATING THE EFFECTS OF PLASTICISER TYPE ON THE MECHANICAL PROPERTIES AND SOLUBILITY OF BANANA PEEL-BASED BIOPLASTICS

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ABSTRACT

Bioplastics are plastics derived from biological sources including plants and food waste, rather than traditional plastics that are made from petroleum. In 2015, petroleum-based plastics contributed nearly 1.8 billion metric tons of carbon dioxide. As a result, bioplastics continue to become increasingly popular across the globe as governments, businesses and citizens alike make the switch to more sustainable ways of living and working. Plasticisers, which are substances that are added to synthetic polymers to make them more flexible, are used in all plastics: nanoscopic interactions between the layers of plastic and the plasticiser alter the physical properties of the plastic. The aim of this study was to study two physical properties of banana peel-based bioplastics prepared in the lab: mechanical strength and solubility (the ability of a substance to dissolve and form a solution), and to establish how these properties vary based on the type of plasticiser used to prepare the plastic. The findings confirm that plasticisers which form more intermolecular bonds produce bioplastics which have higher mechanical strength and resistance to breakage, while plasticisers with lower bonding tend to produce plastics which are more fragile and less flexible. Meanwhile, plasticisers that have a large molecular size significantly reduce the solubility of the bioplastic. Further investigation into the properties of bioplastics such as toxicity and biodegradability will provide valuable information that can be used to improve the quality of currently available bioplastics on the market.

INTRODUCTION

Contrary to their reputation today, petroleum-based plastics were once seen as a convenient and lightweight alternative to glass, wood, and other commercially available materials. Today, we know that petroleum-based plastics cause harm to the environment and human health from the very beginning of their life cycle. Their production involves mining for crude oil, which has detrimental effects on the environment including habitat destruction, oil spills, and deforestation (Borasin, 2002). Only 9% of plastic waste produced is recycled, 12% is incinerated, and the remaining 79% is discarded in landfills (Parker, 2022). Burning plastic can release carcinogenic and toxic fumes, reducing air quality and increasing the risk of large-scale fires (Plastic Soup Foundation, 2020).

The plastic that ends up in landfills can contaminate groundwater and release toxins into nearby ecosystems (The Watershed Institute, 2019). A large proportion of the plastic waste reaches the oceans, where it kills roughly 100,000 marine animals each year. These animals accidentally ingest the plastics or even get caught and get entangled in them, eventually drowning (WWF, 2021). For instance, in early May of 2022, a massive sperm whale was found dead on the coast of Florida, having consumed a large mass of plastic (Beavis, 2022). It is estimated that by 2050, plastic will outweigh fish in the ocean, making such incidents even more common in the future (Ellen McArthur Foundation, 2016).

Petroleum-based plastics and their ingredients have also found their way into our food: these plastics degrade into small fragments called microplastics, which can accumulate as they move up the food chain, which leads to the risk of these microplastics being ingested with food (Kuna and Sreedhar, 2019). This process is known as biomagnification. These microplastics have carcinogenic properties, making them detrimental to human health (Kumar, 2022).

Even though the risks and downsides of using petroleum-based plastics are evident, companies worldwide struggle to eliminate

their use because viable alternatives are not commercially available or as convenient in comparison. A crucial component of the success of plastics as a material for both packaging as well as everyday products is a substance known as a plasticiser, which is an additive commonly used to increase the flexibility of the plastic. The type and quantity of the plasticiser can induce different mechanical properties in the material. They work by embedding themselves between adjacent polymer chains to push them apart, thus decreasing the magnitude of forces holding the chains together, thus making the plastic more flexible. The plasticisers also allow for the layers of the plastic to slide over one another, thus further enhancing the plastic's flexibility (Godwin, 2000). Plasticisers are responsible for making petroleum-based plastics diverse enough to make a vast variety of products, ranging from plastic chairs to candy bar wrappers.

As a result, engineers and environmentalists have turned to a new family of materials in their search for a suitable replacement for petroleum-based plastics: bioplastics. These are plastics that are produced using biological sources that contain starch, such as corn and potatoes. These are regarded as crucial for the plan to shift towards the use of sustainable materials and eventually reducing plastic use and waste production (WWF, 2021).

Bioplastics can be of two types (Gibbens, 2018):

1. *Polyhydroxyalkanoates (PHAs)*: These use bacterial fermentation of starch.
2. *Poly(lactic acids) (PLAs)*: These are made by extracting starch from plant sources such as corn, which are processed and converted into PLAs. This branch of bioplastics is the one being investigated in this paper.

Certain bioplastics, particularly PLAs, need to be treated industrially in order to fully decompose, which requires an additional energy input (Gibbens, 2018). Despite this, bioplastics have a lower carbon footprint and a better ability to degrade, making them much more environmentally friendly

than petroleum-based plastics. There is also the argument, however, that bioplastic production has the potential to overtake farmland that was originally used to grow crops for food, leading to food scarcity (Gibbens, 2018). This paper therefore explores the idea of using banana peels as a source of starch for bioplastic production. Since banana peels are waste products, they could be a potential candidate for producing ethical and environmentally friendly plastics.

This study aims to explore the effects of using different plasticisers during bioplastic preparation on the resulting mechanical properties and solubility of banana peel-based bioplastics.

MATERIALS AND METHODS

Part 1: Preparing the bioplastic (Bilgin, 2013)

Six batches of banana peels, each containing 175g of peels, were taken. These peels were soaked in 5% $\text{Na}_2\text{S}_2\text{O}_5$ (sodium thiosulfate solution) for fifteen minutes (Figure 1)—this prevents decay and gives the bioplastic a longer shelf life.



Figure 1: Soaking the peels in sodium thiosulfate.

Each batch was then placed in a beaker containing 800cm³ of boiling water for 30 minutes (Figure 2).



Figure 2: Placing the peels in boiling water over a tripod stand and Bunsen burner.

The water was decanted, and the peels were then turned into a fine paste using a blender. The paste for each batch was added to their respective beakers. 12 cm³ of 5% HCl solution was then added to each of the six beakers: this is done because bioplastics

are prepared by reacting an acid with starch, which is a polysaccharide (i.e., a carbohydrate with long chains made of glucose molecules). This breaks down starch and produces water as a by-product, a process called hydrolysis.

To beakers 1-5, the following five plasticisers were added (one per beaker): glycerol, sorbitol, linoleic acid, glycerol triacetate and caproic acid. To the sixth beaker, no plasticiser was added as this was the control sample.

12 cm³ of 5% NaOH solution was added to each beaker in order to neutralise the pH of the mixture by reacting with any unreacted HCl that was left behind from the hydrolysis reaction. This step is crucial as a low pH could affect the bioplastic's resulting properties.



Figure 3: The final mixture.

The paste for each batch (Figure 3) was transferred to their respective petri dishes (two per batch, labelled 'Part 2' and 'Part 3' respectively, for the two tests to be performed) while maintaining a thickness of 1cm. The petri dishes were placed in an oven preheated to 130°C for 30 minutes. To eliminate any remaining moisture, the petri dishes were left in the sun to dry (Figure 4).



Figure 4: Drying the plastic samples in the sun.

Part 2: Mechanical Testing

The bioplastic samples labelled 'Part 2' were removed from the petri dishes using a stainless-steel blade and a spatula and each sample was cut into six even 1cm-wide strips.

A Newton meter was hung from a clamp and stand, and the hook at the base was attached to the strip being tested. A camera

was placed in front of the apparatus and a video of the process was recorded. The tip of the plastic was held and slowly pulled downwards until it snapped. The video was replayed and the reading on the Newton meter at the exact force required for failure was recorded and was used to find its tensile strength. Six values were found for each batch of plastic, for which the average value with an uncertainty was calculated.

Part 3: Solubility testing

The samples labelled 'Part 3' were taken and removed from their respective petri dishes. The plastic was cut into small, even pieces using a stainless-steel blade, and 1.00g of the pieces was taken and placed into 100 cm³ of distilled water and was stirred. This was done six times per batch. The apparatus was set aside for 30 minutes, after which the sample was filtered and the remaining liquid, the filtrate, was decanted. The bioplastic sample, the residue, was removed from the filter paper and was placed onto a dry piece of filter paper and was set aside. Once completely dry, the residue was weighed to find the mass of undissolved bioplastic, which will be used to find its solubility and will provide insight into its response to water. Once again, six values were found for each batch of plastic, for which the average value with an uncertainty was calculated.

Limitations and Scope

Throughout this study, six trials were taken for each measured value (as summarized in the appendix) to limit the effects of random experimental errors on the results, ensuring accuracy.

Possible sources of error and uncertainty include:

Sorbitol and glycerol have hygroscopic properties, which refers to their tendency to retain water in their structure. This may have led to extra water molecules being retained in the structure of the plastic during the solubility test. This is may have made the final mass of the plastic after drying appear greater than it actually was, thus leading to a systematic error, pushing the solubility values for these two plasticisers towards the lower side.

Additionally, the use of a Hounsfield tensiometer and data logger to record the results for the mechanical testing section could have provided further insight into the material's behaviour, allowing one to plot a stress-strain curve for the samples and to find their Young's Modulus.

Tables and figures may span either one or two columns, or an entire page, depending on their width and level of detail. See the 'Graphics' section below for more on this.

RESULTS

Table 1: Tensile strength and solubility of bioplastics produced using different plasticisers (see Appendix for calculations)

Plasticiser	Tensile strength (±0.01 MPa)	% Solubility (±1%)
Glycerol	0.18	37%
Sorbitol	0.26	27%
Caproic acid	0.24	27%
Glycerol triacetate	0.17	16%
Linoleic acid	0.15	6%
No plasticiser	0.12	9%

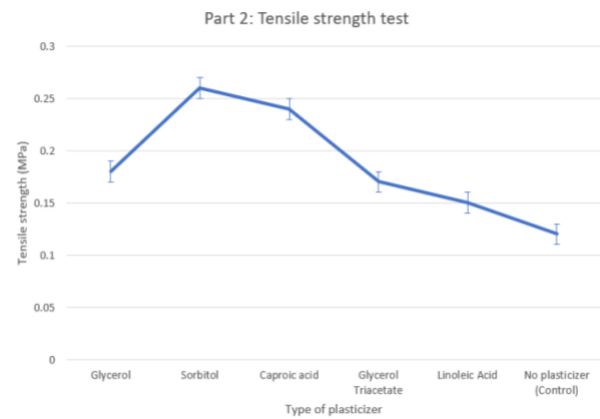


Figure 5: Mechanical testing results.

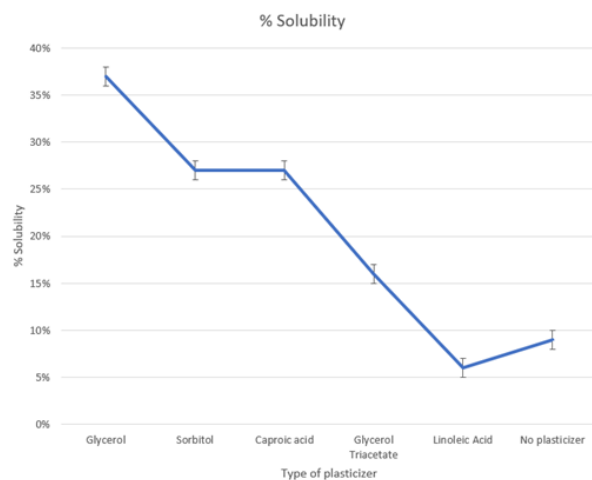


Figure 6: Solubility testing results.

DISCUSSION

The following section analyses the results obtained based on the 3 types of van der Waals forces, also known as intermolecular forces:

1. *Hydrogen bonding*: This occurs in polar molecules (i.e., molecules in which a separation of electrical charges has taken place, leading to some regions being positively charged and others being negatively charged) containing the elements oxygen, nitrogen and fluorine. This leads to forces of attraction between the hydrogen atoms of one molecule and the oxygen, nitrogen and fluorine atoms of adjacent molecules. Hydrogen bonding is the strongest amongst all three van der Waals forces.
2. *Permanent dipoles*: This occurs in polar covalent molecules where one atom attracts the shared electrons towards itself, making one side of the molecule negatively charged, leaving the other side positively charged. As a result, there are forces of attraction between negatively charged side of one molecule and the positively charged side of the adjacent molecules. Permanent dipoles are weaker than hydrogen bonding, but stronger than London dispersion forces.
3. *London dispersion forces*: These occur in non-polar, covalently bonded molecules. These are forces of

attraction between adjacent molecules that occur due to an unequal distribution of electrons around an atom as they constantly move around atoms present in a molecule. These are the weakest of the three types of van der Waals forces.

Mechanical Testing

In increasing order of tensile strength, the results have been analysed:

1. No plasticiser (control experiment) (0.12 MPa)

The control experiment had the least tensile strength because of its lack of plasticiser, making the forces holding the polymer chains together stronger. This makes this batch of plastic brittle and less flexible.

2. Linoleic acid (0.15 MPa)

There is one hydroxyl group present in linoleic acid, which allows for very minimal hydrogen bonding to take place. There are also weak London dispersion forces present. Both these forces allow for better bonding between this plasticiser and the plastic, making it slightly stronger and less brittle than if no plasticiser was added. Therefore, linoleic acid is the least effective of all the plasticisers.

3. Glycerol triacetate (0.17 MPa)

Glycerol triacetate is non-polar, which prevents dipole-dipole interactions from taking place. None of glycerol triacetate's hydrogen atoms are bonded to oxygen, nitrogen or fluorine atoms, making both hydrogen bonding and dipole-dipole interactions impossible. Since glycerol triacetate is a relatively large and branching molecule, the London dispersion forces present in this batch of plastic are the highest amongst all the other batches.

4. Glycerol (0.18 MPa)

There are 3 hydroxyl groups present in glycerol, which allows for the formation of a lot of hydrogen bonds. Glycerol is polar, which leads to the production of dipole-dipole interactions. Weak London dispersion forces are also present. The presence of all of these forces between the plastic and glycerol results in a relatively high tensile strength.

5. Caproic acid (0.24 MPa)

Caproic acid contains one hydroxyl group, which allows for very minimal hydrogen bonding to take place. Being an acid, it is polar, allowing for lots of dipole-dipole interactions to occur. Weak London dispersion forces are also present. All of these forces occurring between caproic acid and the plastic combined result in the relatively high tensile strength of this batch of plastic.

6. Sorbitol (0.26 MPa)

Sorbitol is a polar molecule, which allows it to undergo dipole-dipole interactions with the plastic. It also contains 6 hydroxyl groups (the most amongst all the plasticisers), allowing for the greatest number of hydrogen bonds to be present in this batch of plastic. Weak London dispersion forces are also present in this batch of plastic. All three of these forces make it the most effective amongst all the plasticisers, giving this batch of plastic the highest tensile strength.

Solubility Testing

In increasing order of solubility, the results have been analysed:

1. Linoleic acid (0.06g dissolved)

Linoleic acid, being made up of fatty acids, is hydrophobic, which explains the fact that this batch of plastic has the lowest solubility in water. Linoleic acid has the largest structure amongst all the plasticisers used in the experiment, with 18 carbon atoms. The length of the hydrocarbon affects its solubility too because in order for a substance to dissolve in water, it must overcome the naturally occurring forces in the water using energy. This energy is paid back after the substance dissolves and forms new intermolecular forces with the water molecules, provided the magnitude of these new forces is sufficient. In very large covalent compounds, such as linoleic acid, its large carbon chain prevents hydrogen bonding from occurring on either side of the molecule, preventing energy from being paid back, thus preventing solubility. Linoleic acid also contains one hydroxyl group, allowing for very minimal hydrogen bonding to take place.

2. No plasticiser (control experiment) (0.09g dissolved)

The control experiment didn't dissolve as much due to the strong hydrogen bonding holding the layers of plastic together. As these hydrogen bonds are very strong due to the lack of a plasticiser, a lot of energy is required to overcome these hydrogen bonds, which isn't paid back, causing there to be very minimal solubility. The control had a greater solubility than that of the linoleic acid plastic as it contained no hydrophobic materials in it, making dissolving easier.

3. Glycerol triacetate (0.16g dissolved)

This plasticiser is a relatively large molecule, with 9 carbon atoms, which will reduce its solubility. The molecule is non-polar and none of hydrogen atoms are bonded to oxygen, nitrogen, or fluorine atoms, making both hydrogen bonding and dipole-dipole interactions not possible. Only London dispersion forces can occur, which aren't sufficient to overcome the hydrogen bonds present in the water, making it only slightly soluble in water, thus resulting in its relatively low solubility.

4. Caproic acid (0.27g dissolved, same as sorbitol)

This is a relatively short molecule, with 6 carbon atoms. It contains only one hydroxyl group, which allows for minimal hydrogen bonding to take place. Being an acid, it is polar, allowing for dipole-dipole interactions to take place, promoting solubility.

5. Sorbitol (0.27g dissolved, same as caproic acid)

This is a relatively short molecule, with 6 carbon atoms (just like caproic acid). This promotes its ability to dissolve. It has 6 hydroxyl groups, which can form hydrogen bonding with the water molecules, thus promoting solubility. It is also a polar molecule which allows for dipole-dipole interactions to take place, promoting solubility. (Caproic acid contains less hydroxyl groups than sorbitol, while sorbitol contains a lot more hydroxyl groups; however, caproic acid, being an acid, has the property of dissociating into its constituent ions when it comes into contact with water, while sorbitol cannot do this, making dissolution more difficult for sorbitol. Overall, these two properties cancel each other out, making the solubilities of caproic acid and sorbitol turn out to be equal.

6. Glycerol (0.37g dissolved)

Glycerol is the shortest of all the plasticisers, with 3 carbon atoms, which means it can easily dissolve in water. Its 3 hydroxyl (-OH) groups present in glycerol allow for the

formation of hydrogen bonds with the water molecules, increasing solubility. It is a polar molecule, which allows for the formation of dipole-dipole bonds, increasing solubility.

CONCLUSION

In Figures 5 and 6, a positive correlation can be seen between the number of intermolecular bonds formed by the plasticiser and the resulting tensile strength and solubility. There is a negative correlation between the size of the plasticiser and the solubility of the bioplastic. Based on results, sorbitol appears to be the most ideal plasticiser for industrial purposes, as it has the highest tensile strength and a low solubility (a high solubility would cause the plastic to dissolve if it is used to hold food items.) The behaviour of plasticisers when more than one kind

of plasticiser is added to a bioplastic could be researched. Since different kinds of plasticisers behave differently, manufacturing companies can make bioplastics with the properties desired by mixing a combination of different plasticisers.

The bioplastics developed in this paper aren't viable biodegradable alternatives yet and require further enhancement through research. However, this paper provides an insight into the relationship between plasticiser types and the bioplastic's resulting mechanical properties as well as its behaviour when exposed to water. This information could be used for the development of new and improved bioplastics that are suitable for replacing petroleum-based plastics, reducing and gradually eliminating plastic waste production.

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APPENDIX**Table A:**

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