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RECYCLING CITRUS AND GARLIC PROCESSING WASTES WITH DIVERSE POTENTIAL APPLICATIONS

by
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ABSTRACT
OF THE THESIS OF

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Annually, the world generates more than 1.3 billion tons of food loss and food waste and produces more than 300 million tons of plastic, 50% of which are single-use. While most of the food waste generated across the globe is suitable for composting or use as animal feed, others like citrus and garlic-processing wastes have been denoted as challenging to the environment.

Citrus peels are rich in oils and highly acidic, making them unsuitable for animal feed or composting as they harm the soil and prolong the composting process. As for garlic stalks, not only are they hard to digest by animals due to high quantities of lignin, they also cause soil pollution and add waste problems.

This study investigates the possibility of recycling citrus and garlic processing waste into a bio-based and biodegradable material with the potential to replace plastics and other non-renewable materials.

This work aims to develop and characterize the envisioned material in terms of mechanical, thermal, sorption and migration properties to assess its potential applications and compare it to conventional materials in an attempt to reduce human-induced environmental stresses.

The accomplished material was proven highly heat resistant, mechanically strong, and moldable. When immersed in a natural waterproof coating based on beeswax, it resisted absorption of food simulants for 7 minutes, without migration of any natural additive from the material formulation into the food simulant media. Moreover, the developed material has a density and thermal conductivity close to building materials. Applying an optimized coating to the developed material expands its commercial applications ranging from disposable tableware, coasters, and placemats to tiles and building materials.

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CHAPTER I

CURRENT ENVIRONMENTAL CHALLENGES

A. Plastic waste

In 2018, the global plastic production reached almost 360 million tons (Europe & EPRO, 2019), most of which was destined for single-use packaging applications. This trend has been causing plastic packaging to account for half of the plastic waste in the world, from which only 9% is being recycled (United Nations, 2018).

Plastics are highly durable and take hundreds of years to degrade in nature, meaning that every piece of plastic ever produced still exists today and has been accumulating in landfills, the oceans, and the environment, causing irreversible threats to human health and wildlife. Despite all the repercussions that come with the use of plastics, they are too valuable and useful to eliminate: their durability, lightweight, ease of processing, and low cost (Batori, 2019) render them as a preferred material for various commercial applications.

The need to find alternative renewable materials is crucial today more than ever and has been urging scientists and corporates to take action and find solutions on an international level.

B. Food waste and loss

It is estimated that one-third (or 1.3 billion tons per year) of the food produced for human consumption is lost or wasted worldwide throughout the food value chain (FAO, 2019). For fruits and vegetables, food loss and waste are their unused and unconsumed parts that are mainly disregarded due to the characteristics of their morphology or as a result of their improper handling (Sagar et al., 2018).

Usually, a vast amount of organic waste goes to landfills, releasing greenhouse gases into the atmosphere and adding more stress to the climate. In addition, landfills can have high running costs in many countries (Laufenberg et al., 2003) and are not a sustainable solution. Another traditional way is dumping food waste in the surroundings of a processing plant, which causes odors and environmental problems because of high water and nutrient levels that enable bacterial growth and fermentation (Van Dyk et al., 2013a). Incinerating food processing waste has a relatively low calorific value with adverse effects on the environment (Laufenberg et al., 2003).

Thus, a significant portion of food processing waste ends up as animal feed. However, most food wastes are low in protein and/or high in lignin, making them unsuitable for animal feed (Van Dyk et al., 2013b; Laufenberg et al., 2003). Consequently, one of the most sustainable disposal methods is composting, which allows food waste to be introduced back into the soil as a conditioner or fertilizer to enhance its nutritional properties (Schaub & Leonard, 1996). However, some types of food waste can harm the soil and may slow down the composting process.

C. Resource recovery and valorization

With the increasing concerns regarding food waste and loss, one of the proposed solutions to solve both plastic pollution and food waste is the use and recovery of ligno-cellulosic materials and waste from the agro-food industries to replace conventional waste and non-renewable plastics (Batori, 2019).

Instead of seeing food waste as "useless," "leftover," "unusable," or "unprofitable," now is the time to see these 1.3 billion tons per year as a valuable resource to alleviate the problems caused by both plastic pollution and excess food waste and loss as a step towards more sustainable and circular industries.

CHAPTER II

CITRUS AND GARLIC PROCESSING INDUSTRIES

A. The citrus processing industry

Citrus fruits are highly popular worldwide and are consumed either as fresh produce or processed into juice, marmalades, jams, jellies, potpourris, candied peel, flavoring agents, as well as oils and essences (Zema et al., 2018). It is estimated that 105 million tons of citrus fruits were globally produced in 2016 (Blasco et al., 2016).

1. Types of waste generated

Processing citrus fruits produce large amounts of different types of waste, including wastewater, semi-solid (vesicles, endocarp residual membranes), and solid residues (peels, membranes, and seeds) (Sharma et al., 2017). As seen in figure 1, the citrus peel is composed of the flavedo, albedo, and oil sacs, and accounts for 50% to 70% of the fruits' weight. Consequently, around 10 million tons of citrus peel waste is generated per year (Zema et al., 2018).

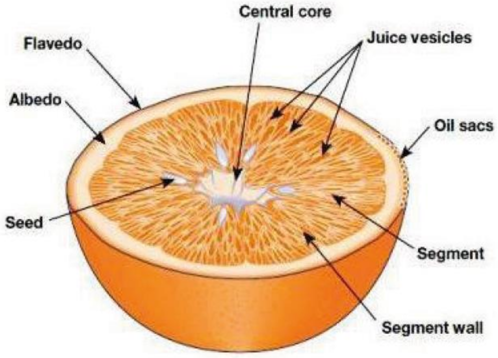


Figure 1. Inside an orange, (The orange fruit and its products, 2004)

2. Traditional disposal methods

When released into lakes, citrus peel waste causes pollution and may harm aquatic life (Sharma et al., 2017). Consequently, its majority is reused as animal feed being the cheapest and simplest disposal method (Chavan et al., 2018). However, citrus waste is low in nitrogen (Chen et al., 2019) and has low digestibility (Zema et al., 2018). Therefore, it requires supplementation with proteins, minerals, and vitamins for an optimized nutritional value. Besides, citrus peels are highly acidic, contain essential oils, and are high in moisture. This decreases their palatability to animals and promotes microbial growth and fast degradation (Chen et al., 2019). Drying the citrus waste may alleviate this issue but will increase the cost of this disposal method.

On another note, one can spread citrus peel waste directly on land or use it in compost. However, citrus waste may be very harmful to soil microorganisms due to the essential oils and many bioactive compounds it contains: the essential oils can damage yeasts and inhibit the development of beneficial soil microbiota (Zema et al., 2018). Nevertheless, and after adjustments, citrus compost can be beneficial to soil quality but would require additional treatment and longer composting times (Zema et al., 2018).

B. The garlic processing industry

Whether for consumption as a raw vegetable, for culinary purposes, or even for modern and traditional medicine, garlic is one of the most popular vegetables globally (Martins et al., 2016), with a worldwide production reaching 28 million tons in 2018 (FAO, 2020).

1. *Types of waste generated*

Harvesting and processing garlic generates different types of waste, including the stem, husk, unwanted bulbs, straw, and skins (El Mashad et al., 2019) as seen in figure 2. Garlic skins account for 8% to 10% of the original total weight of garlic (Alexander & Sulebele, 1973).

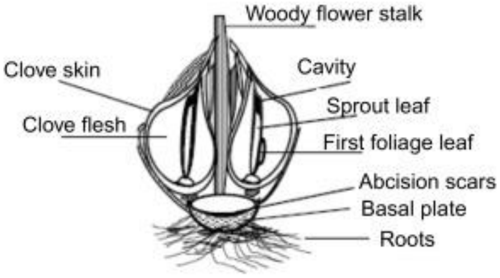


Figure 2. Major parts of garlic (Filaree Garlic Farm, 2012).

2. *Traditional disposal methods*

Nowadays, garlic waste is dumped in landfills or used as soil amendments, causing environmental pollution and plant toxicity (El Mashad et al., 2019). Moreover, it is not suitable for animal feed as garlic waste is rich in lignin and hard to digest (Laufenberg et al., 2003).

CHAPTER III

POTENTIAL OF CITRUS AND GARLIC PROCESSING WASTES

A. Chemical composition

Citrus (orange) peel waste is approximately composed of 33.98% cellulose, 20.9% pectin, 9.99% hemicellulose, 9% soluble sugars, 9% protein, 6.93% lignin, 4% flavonoids, 3.85% fat, and 2.46% ash (Rivas-Cantu et al., 2013). As for garlic stalks and skins are composed of 41-50% cellulose, 16-26% hemicelluloses, and 26-39% lignin (Reddy & Rhim, 2018).

B. Value-adding compounds

The chemical composition of citrus and garlic processing wastes shows remarkable amounts of cellulose, hemicelluloses, and lignin.

Cellulose is the most copious organic chemical available in nature. It is biocompatible, biodegradable, has remarkable mechanical properties, and very high durability (Sugave & Engineering, 2014). Cellulose is also insoluble in most common solvents due to its high polymer length and degree of polymerization (Olsson & Westm, 2013). The hemicelluloses are associated with cellulose fibrils to help strengthen the cell wall (Rowell et al., 2012). As for lignin, it is mainly composed of aromatic polymers that are highly complex and amorphous and are responsible for filling the spaces between the cellulose and hemicelluloses for higher strength (Rowell et al., 2012). Cellulosic plant fibers have remarkable mechanical properties, are lightweight, and have a low carbon footprint (Batori, 2019): three characteristics that are looked for in the development of biomaterials.

In addition, the essential oils present in citrus fruits hold antibacterial properties and, along with citrus flavonoids, offer antioxidant, antifungal, and antiviral effects (Sharma et al., 2017). Similarly, the garlic stalks hold Sulphur compounds with antimicrobial benefits (Sugave & Engineering, 2014). Accordingly, these compounds have the potential to increase the durability and shelf life of a proposed biomaterial.

CHAPTER IV

RECYCLING CITRUS AND GARLIC PROCESSING WASTES INTO A BIOMATERIAL

A. Bioplastics

Petroleum-based polymers used for the production of plastic products are non-renewable and non-biodegradable. They have been continuously threatening the natural resources of the planet and harming human health. As a result, there has been growing interest in developing natural, bio-based, and biodegradable polymers to replace conventional ones.

"Bioplastics are a type of plastic that can be made from natural resources such as vegetable oils and starches" (Ashter, 2016). Their adoption on a large scale contributes to more sustainable production and consumption with increased resource efficiency (Batori, 2019).

B. Citrus and garlic processing wastes and bioplastics

1. Citrus peel waste

Studies by Batori in 2019, Shan in 2016, and Villanueva et al. in 2018, and other projects such as "*BioPeel"* have already implemented the conversion of citrus peel waste into biofilms and/or biomaterials.

In 2019, Batori developed 3D objects such as cups and fiberboards using 0.2-mm particle-sized orange waste powder and 30 % glycerol. Shaping and drying of these objects were done using compression molding, an energy-efficient method for their preparation (Batori, 2019). Batori (2019) also demonstrated that the properties of the objects produced from orange waste powder were compatible with potential commercial biomaterials. However, the developed biomaterial was very sensitive to water and had to be coated with a biodegradable waterproof coating such as plant waxes or polyhydroxyalkanoates to target wider applications (Batori, 2019).

Moreover, a design student from Brunel University London developed a biodegradable packaging from orange peels called "*BioPeel."* The product is strong and malleable but is not waterproof without an additional hydrophobic coating. The product has a rustic look that limits its application in many fields. The production process is simple and consists of molding, baking, and drying (Pilgrim, 2019).

Another way of recycling citrus peels for biodegradable packaging applications consists of pre-treating, drying, pulverizing, and molding the citrus peels into seedling plates and nutritional bowls. The powdered citrus peels are mixed with urea-formaldehyde resin and placed in a hot extrusion mold to produce the packages (Shan, 2016).

At the University of Sevilla, the project "*Miplascoe"* is developing a biomaterial with appropriate properties for profile extrusion and production of bottles by injection blow molding. It is based on extracting different monomers by microbial fermentation and the synthesis of bio polyesters (Villanueva et al., 2018).

Finally, when used as a reinforcement in bio-based and petrochemical materials, it was reported that orange waste improved the mechanical properties of both materials due to the presence of cellulosic fibers (Bátori et al., 2017).

2. Garlic stalks and skins

Limited research has been done on converting garlic stalks and skins into biomaterials. However, recent studies have focused on the characterization of garlic skin fibers, proving their high thermal and mechanical properties (Prasad Reddy & Rhim, 2014; Reddy & Rhim, 2018; Sugave & Engineering, 2014).

In 2018, Reddy & Rhim proved that cellulose microfibers extracted from garlic stalks and skins by alkaline extraction have higher heat stability than the crude fibers (247˚C compared to 235˚C for crude fibers) (Reddy & Rhim, 2018). Besides, they have higher mechanical properties and increased reinforcing abilities as a result of their high crystallinity index (69 to 70%) (Moreno et al., 2020).

In addition, reinforcing starch- based bio composites with garlic cellulose improved the tensile strength, modulus, and moisture resistance of the film (Agustin et al., 2013).

3. Synergetic biomaterial from citrus and garlic processing wastes

By-products or residues from different food processing industries, forest residues, and agricultural waste can contribute to the development of bioplastics. Previously, ligno- cellulosic wastes have been converted into various bioplastics by different bioconversion and bio-synthetization processes, which are rather expensive and challenging technologies. To compete with the convenience, affordability, and ease of processing of traditional plastics, it is pertinent to find ways to convert waste from the agro-food industry without separating its components (Batori, 2019).

As previously discussed, literature has shown that fibers from garlic processing waste are remarkably mechanically strong with high heat stability. In parallel, citrus peels contain several compounds that help improve strength and binding properties and offer antioxidant and antibacterial effects.

Consequently, this study aims to create and assess a synergistic material from both citrus and garlic processing wastes to replace non-renewable materials for diverse applications.

This solution will help reduce food waste and mitigate the use of plastics and other non-renewable materials while providing a performant yet biodegradable alternative. The biomaterial will be mechanically strong, heat resistant, flexible, visually appealing, and biodegradable. It can also be waterproof with an appropriate coating.

To achieve this objective, three main milestones were defined: developing and optimizing the formulation and production process of the material, testing its mechanical, thermal, sorption, and migration properties, and finally identifying and assessing its potential applications compared to typical materials.

CHAPTER V

METHODOLOGY

A. Development of the material

Citrus peels were procured from a local juice shop and garlic stalks and skins from a garlic peeling plant in the Matn District of Lebanon. The collected citrus peels were ground using a semi-automatic grinder and stored in vacuum bags at -20 °C until their use. The garlic stalks and skins were kept in their original form in a dry store at ambient temperature until their use.

1. Alkaline extraction (de-lignification)

A common pre-treatment step for the two types of waste is the alkaline extraction or de-lignification step. The wastes were immersed in a 15% sodium hydroxide NaOH solution for 4 hours at 60°C to remove the lignin, hemicelluloses, and other pectic substances. Then, they were neutralized with 1% acetic acid before being washed with distilled water (Agustin et al., 2013) and dried overnight at 60°C in a convective oven. The sodium hydroxide and acetic acid were acquired from Sigma Aldrich, Missouri, USA.

De-lignification is essential because lignin has a chemical structure that varies across plant species and is very reactive due to the hydroxyl and aromatic functional groups it carries on its backbone (Bertella & Luterbacher, 2020). Lignin might also react with glycerol (natural plasticizer used in the material formulation), causing an eventual darkening of the material (Batori, 2019). Furthermore, since the lignin is insoluble in water, it might hinder the interactions between the citrus and garlic processing wastes and the hydrophilic natural additives present in the material formulation (Watkins et al., 2015).

After the alkaline extraction, the treated citrus peels were ground using a blender (Braun Blender Multiquick MX2050, Braun, Germany) to obtain a powder as seen in figure 3. According to Batori (2019), using smaller particles of orange peel waste resulted in a higher strength of the end material. This can be attributed to the fact that smaller particles sizes and more regular shapes can pack up closer and help improve the propagation of stresses in composite materials (Mobarak et al., 1982; Batori, 2019).

Figure 3 Powdered citrus peel fibers

Unlike the treated citrus peel waste, the obtained garlic cellulosic fibers seen in figure 4 would directly be ready for incorporation in the material formulation without any further processing to maintain their ideal mechanical and thermal properties for an optimal reinforcing effect.

Figure 4 Garlic stalks and skins fibers

2. *Material formulation:*

Different natural additives, including starch, glycerol, agar-agar, and D-sorbitol, were added to the citrus and garlic processing waste fibers to develop the envisioned material for optimized mechanical and plasticizing properties. The selected additives were incorporated in different percentages to reach the optimum mix formula.

Starch is one of the most popular eco-friendly materials because of its rapid biodegradability, continuously renewable source, and availability at a relatively low cost (Liu et al., 2013). However, blends containing high starch concentrations become brittle and fragile (Vieira et al., 2011). Natural plasticizers are usually added to the blends to avoid the loss of value and use starch to replace petroleum-based products (Vieira et al., 2011).

The selection of a natural plasticizer for a specific application system depends on several factors, including the quantity required for proper plasticization, the processing characteristics, and the desired mechanical properties. Glycerol, xylitol, and sorbitol are usually used in biodegradable polysaccharide-based films (Vieira et al., 2011). Accordingly, glycerol and D-sorbitol were added to the newly developed material to help improve its flexibility and workability.

Agar-agar is soluble in hot water and can form a biodegradable film in the presence of an appropriate plasticizer (Shankar & Rhim, 2016). Using agar- agar as a base in biomaterials' development produced strong mechanical and physical properties, including flexibility, homogeneity, and ease of handling (Arham et al., 2016). Besides, when studying the physical and mechanical properties of agar-based films containing glycerol, it was demonstrated that increasing the concentration of agar resulted in the increase in the thickness, tensile strength, and elongation at break of the biofilm. Still, it decreased its solubility (Arham et al., 2016). Accordingly, agar was added to the material formulation to benefit from its offered advantages.

The glycerol was purchased from Fisher Scientific International Inc. (Pittsburgh, USA), agar-agar from Biolab Inc. (Budapest, Hungary), potato starch from Acros Organics B.V.B.A. (New Jersey, USA) and the D- sorbitol was acquired from Sigma Aldrich (Missouri, USA).

The ingredients were blended using a Thermomix TM5 (Vorwerk, Wuppertal, Germany) blender with controlled speed for every of the following mixing steps:

First, the potato starch was mixed with water for 20 minutes at 60˚C at a speed of 200 blade rotations per minute for proper gelatinization. Then, the glycerol, agar-agar, and D- sorbitol were added and mixed for another 10 minutes at 40˚C and the same speed. After a gel and foamy texture was obtained, the heating was stopped to add the citrus peel and garlic fibers and mix them at a speed of 3,100 blade rotations per minute. Finally, all the ingredients were mixed until full homogeneity and a paste-like material were obtained.

Figures 5 to 9 are examples of the final molded products developed.

Figure 5. Tile prototype.

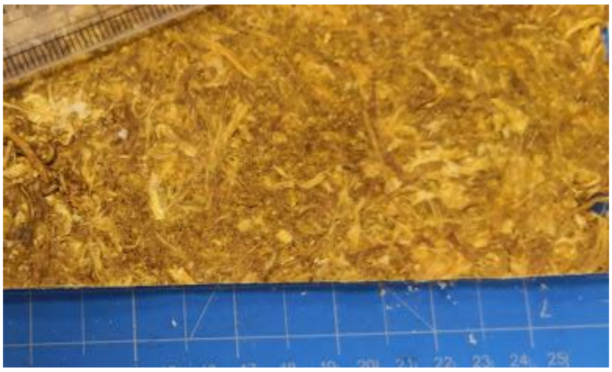


Figure 6. Material sheet prototype.

Figure 7. Material coaster prototype.

Figure 8. Material tableware prototypes.

Figure 9. Material coaster prototypes.

3. ***Waterproof Coating***

To improve the hydrophobicity of the developed material, a natural coating material was prepared using beeswax and canola oil at a 1:1 w/w ratio. This coating provided a waterproof layer.

B. Characterization of the biomaterial

1. Mechanical properties

The developed material's tensile strength, bending behavior, and density were compared to existing and conventional materials.

a. Tensile Strength

The tensile strength of the material was measured using a Universal Testing Machine (Hounsfield H100 KS). Specimens of the material were prepared in a mold with the following dimensions: 80mm in length, 10 mm in width, 4 mm in thickness and 20mm gauge length. The tested specimens (after drying) were 74.6 ± 1.14 mm in length, 8.4 ± 0.55 mm in width, 3 ± 0.1 mm in thickness, and 20 ± 0.1 mm in gauge length. Then, they were stored for 96 hours in a hermetic container at room temperature until tested. The Generic Tensile with Laser Extensometer method was conducted at 5mm/ minute and a stress vs. strain graph was obtained for analysis.

b. 3- Point bending test:

Another mechanical test that is interesting to conduct is the 3- Point bending test force vs. deflection, to measure the material's behavior when subjected to simple beam loading where a complex combination of forces happens: tension, compression and shear forces. In this study, bending was performed using the Universal Testing Machine (Hounsfield H100 KS) at 5mm/ minute. The specimens were prepared using a mold with the following dimensions: 90mm in length, 8.0mm in width and 6mm. After drying, the tested specimens had the following dimensions: 86.4 ± 0.55 mm in length, 7 ± 0.1 mm in width, and 5 ± 0.1mm in depth.

c. Density

The density of a material is another important parameter to look at when determining the right applications for its use. For instance, a low density and lightweight material is preferred for protective packaging during transportation or to decrease the payload for air transit operations. In contrast, for other applications such as furniture or flooring, more dense materials are desired.

The density of the developed material was determined by weighing a known volume determined using the water displacement method (SCIENCING, 2020). Density measurements were conducted in five replicates.

2. Thermal properties

a. Thermal Gravimetric Analysis

Thermal and degradation properties are crucial and decisive during the assessment of a material. Thermal gravimetric analysis was performed on three replicates of the material to assess its thermal stability at a temperature ranging from 30°C to 550°C and a heating rate of 5K per minute in a nitrogen environment. A TGA-IR Tensor 27 Netzsch TG 209 F1 Libra thermo-gravimetric analyzer (Bruker Optics, Billerica Massachusetts, USA) was used for this measurement.

b. Differential Scanning Calorimetry

The natural waterproof coating developed and used as proof of concept in this study is based on beeswax, which has a relatively low melting point. The beeswax coating melting point was determined using a Differential Scanning Calorimetry (DSC), DSC Q2000 (TA Instruments Inc., New Castle, DE, USA). A temperature ramp of

10˚C/min from 35˚C to 120˚C under nitrogen was implemented. The melting point is critical to ensure the material does not fail during use. For instance, if used as biodegradable disposable tableware or coasters and placemats, products in contact with the coated material should not have a temperature higher than the coating's melting point to ensure it does not fail.

c. Thermal conductivity and thermal resistance

The thermal conductivity of the material was measured using a thermal conductivity unit manufactured by P. A. Hilton Ltd., Hampshire, England. The sample dimensions were 30.0 ± 0.5 x 30.0 ± 0.5 x 3.5 ± 0.5 cm.

3. *Sorption and migration studies*

One of the proposed applications for biomaterials is the production of disposable tableware as an attempt to reduce the production and consumption of single-use plastics. In the case of bio-based and biodegradable disposable tableware, sorption and migration studies are crucial to assess the behavior of the material and its coating in contact with food products. This is essential because migration of the material into the food or vice versa might affect the taste and smell of the foods, and the performance of the material.

According to the recommendation of the US Food and Drug Administration, the evaluation of the material's migration behavior was conducted in three different food simulant media: water, food oil (sunflower oil), and 10% ethanol. Respectively, these media simulate aqueous, fatty and acidic, as well as low-alcoholic foods that may be in contact with the material (USFDA, 2007) if used to produce disposable tableware.

To assess the efficiency of the natural coating, sorption tests were conducted on both coated (coating by immersion) and uncoated specimens for comparison. The produced specimens having dimensions of 30.2 ± 0.84 mm in length, 30.4 ± 2.7 mm in width, and 3.8 ± 0.45 mm in height were conditioned for 48 hours at a relative humidity of 55-60% and a temperature of 25˚C.

The water, oil, and 10% ethanol sorption were analyzed by measuring the difference in the weight of each sample before and after immersion in the concerned food simulant medium after 1, 3, 5, 7, 10,15, 30 and 60 minutes at both room temperature and 40˚C. The initial and final weights of each one of the five replicates were entered in the below formula to calculate the average percentage of the food simulant absorbed into the material specimens at each condition.

$$\%\,Sorption = \frac{Final\ weight - Initial\ weight}{Initial\ weight} \times 100$$

To see if the difference between the groups of specimens were significant, a univariate multi-factor analysis of variance (ANOVA) test was conducted on the data using SPSS version 23, having the percentage of sorption as the dependent variable and the time, temperature, coating and media as the four independent factors.

Following the sorption tests, qualitative migration studies were conducted on the group of coated specimens in contact with the food simulants at room temperature after 10, 15, 30, and 60 minutes. Actually, in this study, qualitative migration studies were done, as the possible migrants are all safe and edible (natural additive, beeswax coating, and fiber). Moreover, the group of coated specimens at room temperature was chosen because the material is strongly hydrophilic, and will unavoidably have to be coated before getting in contact with foods. Besides, the beeswax coating has a low melting point, and cannot be used in temperatures higher than ambient temperatures.

To identify the presence of starch as a possible migrant, the iodine test was conducted on the different solutions in three replicates: for every 2 to 3mL of solution, 1 to 2 drops of iodine solution were added. The iodine solution, that originally has a red/ brick color, reacts with the starch and turns into a blue/ black color. In the absence of starch, the iodine solution remains red. Therefore, the appearance of a blue/ black color is an indication of a positive starch identification test.

For the qualitative identification of glycerol in the concerned solutions, the Dunstan's test was performed in three replicates. According to Das (2005), adding 5 ml of borax solution in a test tube and adding one drop of phenolphthalein will form a vivid pink color. When a solution containing glycerol is added to the test tube while constantly stirring, the pink color will disappear and then reappear after heating. Therefore, the discoloration of pink and its reappearance after heating is a positive indication of glycerol in the solutions (Das, 2005).

As for the identification of D-sorbitol in water and 10% ethanol, it was based on a comparison with the water solubility of glycerol. In fact, starch/ plasticizer films made with glycerol were more hygroscopic than films prepared with sorbitol, as glycerol has a higher hygroscopicity (Müller et al., 2008). Accordingly, if Dunstan's test is negative for the presence of glycerol in the two aqueous food simulants, we can deduce that D-sorbitol did not migrate as well.

To identify the presence of the coating, agar, or fibers as migrants, the solutions were concentrated by evaporation before being observed under a microscope with image comparison to pure ingredients. The microscope used was an Olympus CH30 manufactured by Microscope Central, Pennsylvania, USA equipped with a microscope camera manufactured by Shenzhen Hayear Electronics Co, Ltd, Shenzhen, China using the scan focus. Images were compared via the S-EYE software.

CHAPTER VI

RESULTS

A. Characterization of the biomaterial

1. Mechanical properties

a. <u>Tensile strength</u>

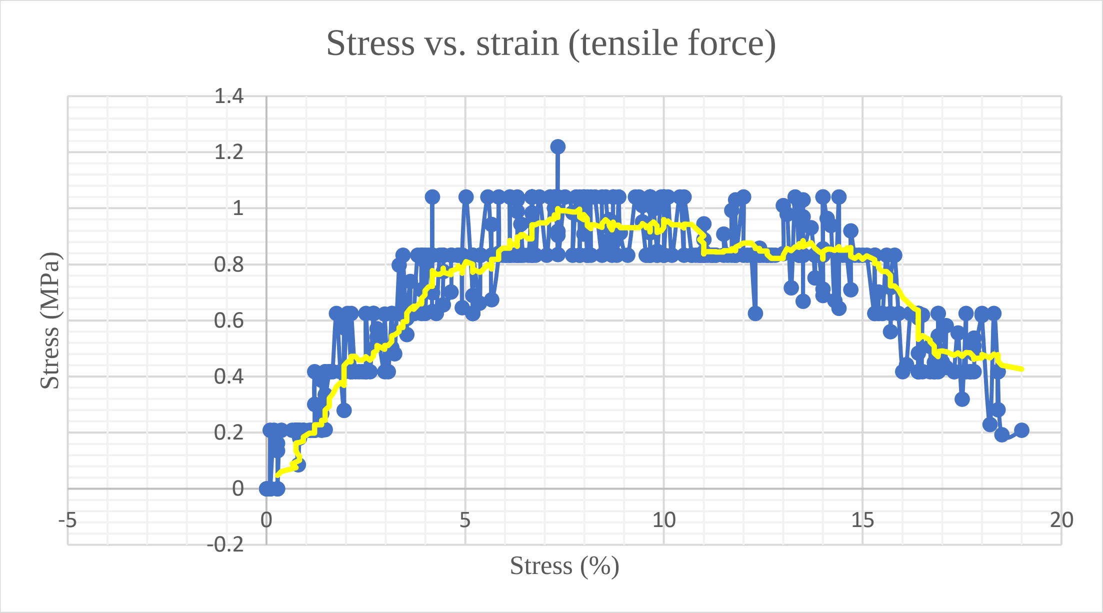


Figure 10. Stress vs. strain graph (tensile force)

Figure 10, showing the stress (mPa) vs. strain (%), represents the material's behavior when subjected to a tensile force. Four main points are identified on the curve: the proportionate limit, yield strength, the ultimate tensile strength point, and rupture point.

The first region of the curve is linear: this is the elastic region, throughout which the material obeys to Hook's law: stress and strain are directly proportionate. Up until a stress value of 0.76 MPa (proportionate limit) is applied on the material specimen, the body will behave as an elastic body and will return to its original dimensions once the force is removed. The slope of this linear curve represented in figure 11 is the modulus of elasticity E= 8.4271 MPa.

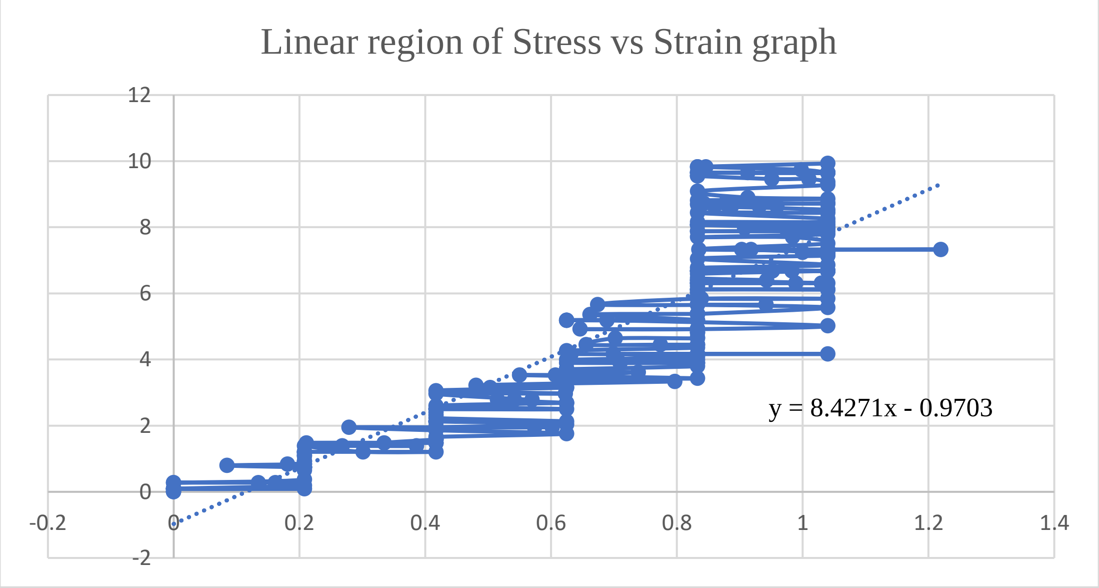


Figure 11. Graph representing the linear region of the stress vs. strain graph

Between the proportionate limit and the yield point (0.90 MPa), stress and strain are no longer directly proportionate; yet, at any force applied in this region, the body would still return to its original dimensions once the tensile force is removed. The yield point is also known as elastic limit and its corresponding stress value is the yield strength Ys= 0.90 MPa.

When the applied stress exceeds the material's yield strength Ys= 0.90 MPa, the strain starts to increase rapidly even for a small change in stress. This behavior continues until the ultimate tensile strength (UTS).

At any given point between the yield point and the ultimate tensile strength, the material will no longer regain its original dimensions once the load is removed. In this region, the body faces permanent deformation: even if the stress is equal to zero, the strain will happen: this is the plastic region of the material and accordingly corresponds to values of stress that go from 0.90 MPa to 1.00 MPa.

The Ultimate tensile stress is the y-axis stress point corresponding to the highest readings on the curve. In this graph, the Ultimate Tensile Stress of the material is 1.00 MPa, which is the maximum stress that the specimen can take in tension before completely breaking.

Beyond the ultimate tensile stress point, fracture occurs at the point where the curve starts to decrease drastically. In the case of this material specimen, the fracture occurred at a strain of 15%. Table 1 represents all the mechanical properties concluded from the stress vs. strain graph.

Table 1. Mechanical properties of the achieved biomaterial (tensile).

Ultimate tensile strength UTS (MPa)	*Proportionate limit (MPa)*	*Modulus of elasticity E (MPa)*	*Yield strength Ys (MPa)*	*Rupture point (strain %)*
1.00	0.76	8.4271	0.90	15

b. 3- Point bending:

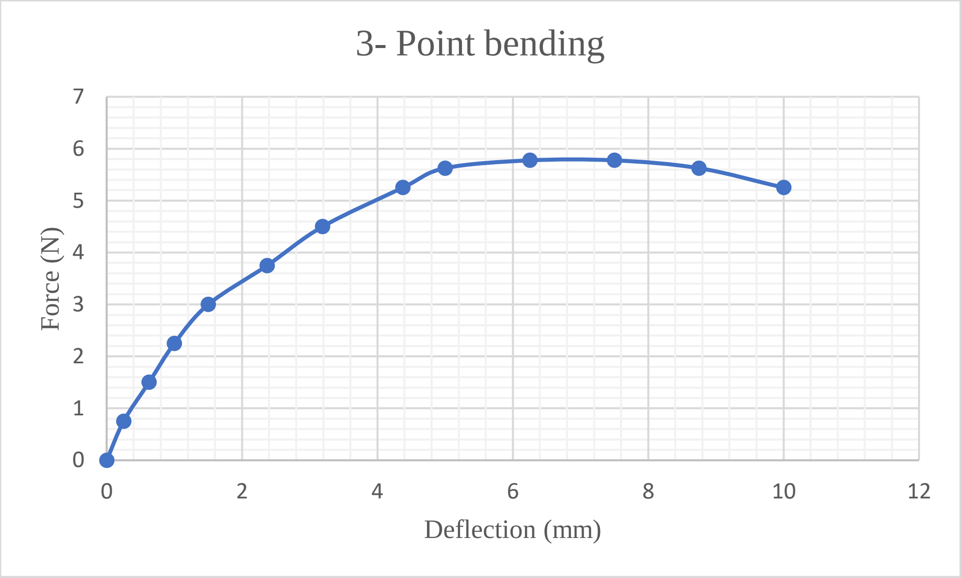


Figure 12. Graph representing force vs. deflection behavior of the biomaterial.

The above graph (figure 12) represents the influence of a certain force or load in Newton on the deflection of the specimen in mm. The results show that after bending, the maximum deflection achieved before rupture is equal to 10.125mm and that the specimen can withstand forces up to 5.775N. This indicates that the achieved biomaterial has a remarkable bending strength and can withstand up to 5.775N before rupture, proving that it has a strong bending behavior. Practically, one could suggest the use of this material to produce disposable tableware that, unlike disposable plastic or paper tableware, will not bend or deform once heavy or hot foods are poured inside of it.

c. Density

The material has an average density of 1.0197 g/ mL with a standard deviation of 0.125.

2. ***Thermal properties***

a. <u>Thermal Gravimetric Analysis</u>

As seen in figure 13, the TGA curve shows two main reductions in mass; a first mass change of an average of –7.4 wt % was observed between 30°C and 120°C. This corresponds to the evaporation of water residues around 100˚C and suggests that the moisture content of the material is approximately 7.4%.

A second reduction in mass was registered between 120°C and 550°C showing that the developed biomaterial lost an average of -68.17 wt % when subjected to these temperatures. Consequently, the remaining 24.43% of the sample are degrading at temperatures higher than 550°C.

Actually, the first derivative DTGA curve represented in figure 14 proves that there were three main peaks of degradation. A first peak at an average of 84.5˚C, a second peak at an average of 210.56˚C and a third one at 266.2˚C. The first peak represents the loss of water, the second one happening at 210.56 ˚C corresponds to volatile organic compounds and the third at 266.2˚C is representative of other organic compounds.

In conclusion, results from the thermal gravimetric analysis showed that the material is 7.4% water, 68.17% organic and volatile organic compounds, and 24.43% carbon and minerals.

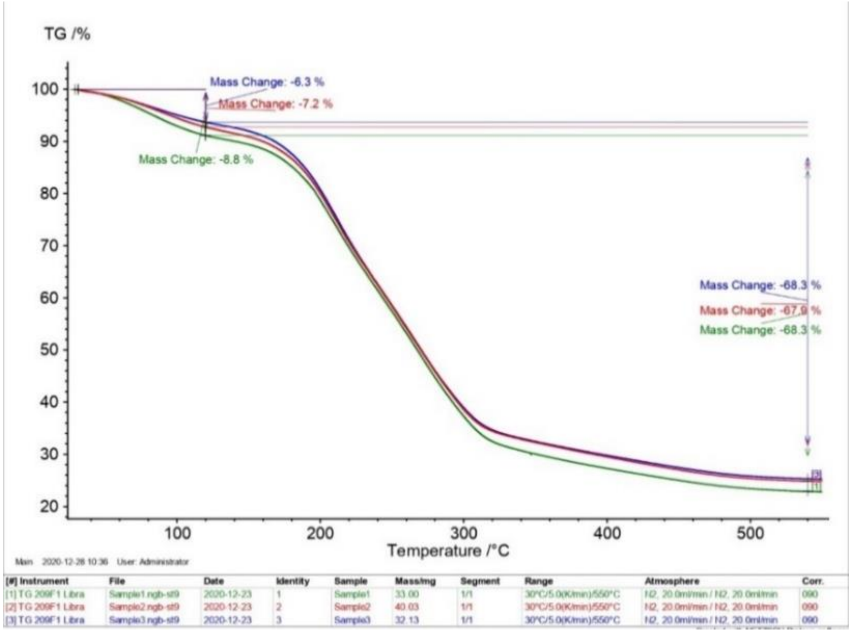


Figure 13. TGA graph representing the change in mass vs. temperature of the biomaterial.

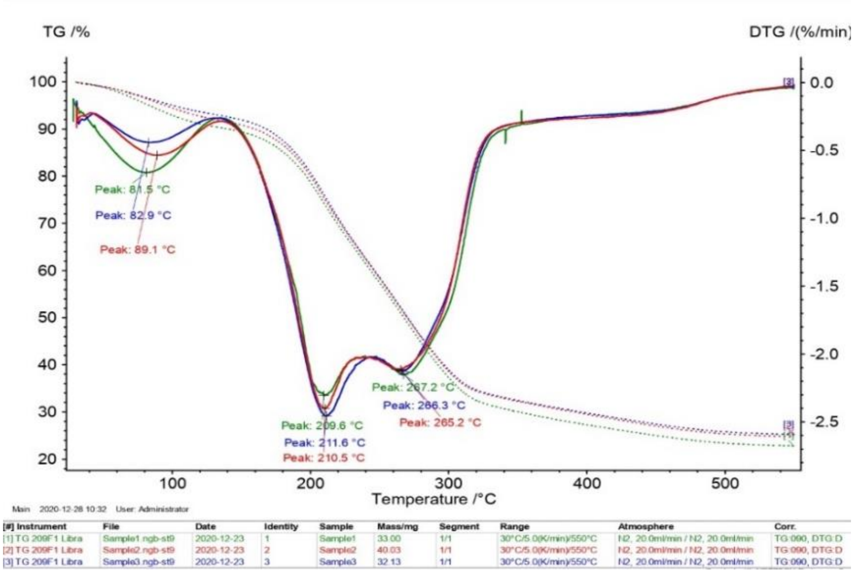


Figure 14. DTGA graph of the achieved biomaterial

b. <u>Coating melting point</u>

Results from the Differential Scanning Calorimetry (figure 15) showed that the coating mix based on beeswax and canola oil has an average melting point of 62.61±

0.77˚C. This demonstrates that when this specific coating is used, the material will fail in hot environments, especially if in direct contact with hot and wet products. However, if used with cold products, or products at room temperature, this coating should be enough to ensure a waterproof effect. Results obtained from sorption and migration studies will provide more clarity towards the behavior and the limitations of this natural coating as a function of time.

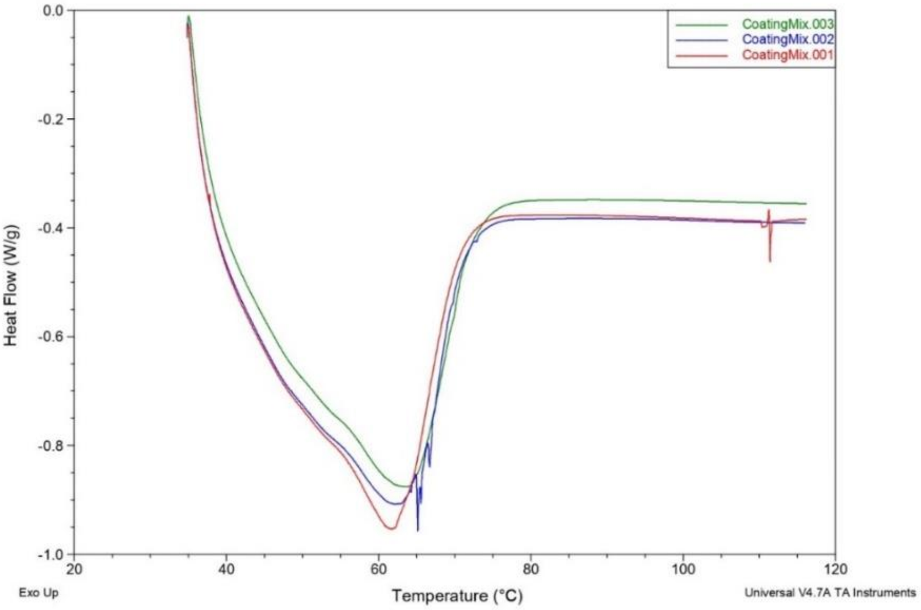


Figure 15. Differential Scanning Calorimetry graph of the tested coating mix.

c. Thermal conductivity and thermal resistance

The thermal conductivity is the "time rate of steady-state heat flow through a unit area of a homogeneous material induced by a unit temperature gradient in a direction perpendicular to that unit area, W/m·K" (C-THERM, n.d.).

Table 2 represents the hot, cold, and coolant temperatures, as well as the temperature difference between the two sides of the specimen, mean temperature, and the capacity of the heat flowmeter in Mv obtained at the end of the measurement.

Table 2. Thermal Conductivity Unit displayed parameters.

T_{hot} (˚C)	T_{cold} (˚C)	Coolant temperature (˚C)	Temperature difference (˚C)	Mean temperature (˚C)	Heat flowmeter (mv)
29.7	9.1	5.1	20.6	19.3	28.37

To calculate the thermal conductivity of the material, the following equation was used:

$$\lambda = [(l \times [(k1 + (k2 \times T)) + ((k3 + (k4 \times T)) \times HFM) + ((k5 + (k6 \times T)) \times \text{〖}HFM\text{〗}\ \hat{}2)])]/dT$$

Where λ is the thermal conductivity (W/m.K), l the thickness of the specimen (m),Dt the temperature difference (˚C), T the mean temperature (˚C), and HFM the heat flowmeter reading (mV).

Since the sides of the material were not perfectly smooth, rubber mats were used and the following calibration constants were included in the thermal conductivity formula:

K_1= -0.35.0998; k_2= 0.5455; k_3=7.4461; k_4=0.0182; k_5=0.0309; and k_6= -0.0006.

Accordingly, the thermal conductivity of the material is λ= 0.350 W/m.K.

The "Thermal resistance is the temperature difference, at steady state, between two defined surfaces of a material or construction that induces a unit heat flow rate through a unit area, K·m2/W." (C-THERM, n.d.).

$$R = \frac{\Delta T}{q} = \frac{L}{\lambda}$$

$$R = \frac{0.034}{0.350} = \ 0.097\ K \cdot m2/W$$

Where, L is the thickness of the specimen (m), T the temperature (K), q the heat flow rate (W/m2), and λ the thermal conductivity (W/m·K).

Table 3. Thermal conductivity and resistance of the achieved biomaterial.

Thermal conductivity (W/m.K)	Thermal resistance (K.m^2/W)
0.350	0.097

Table 3 summarizes the results and prove that the material has a relatively low thermal conductivity.

3. *Sorption and migration studies*

a. <u>Water Sorption:</u>

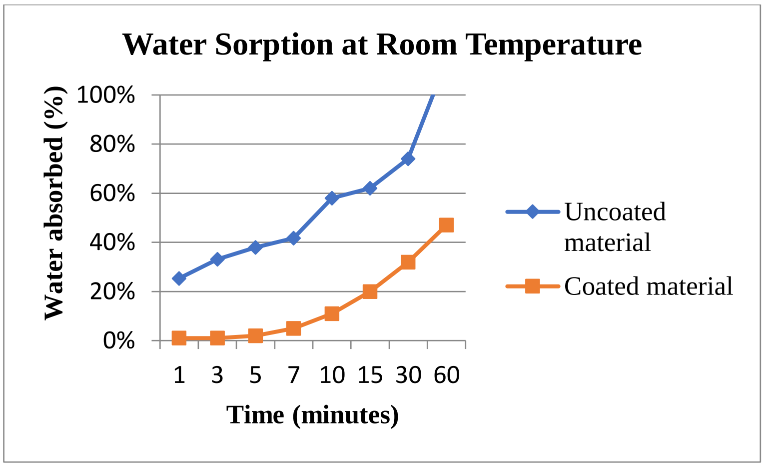


Figure 16. Graph representing the percentage of water sorption vs. time at room temperature.

Results from figure 16 show that the uncoated specimens absorbed an average of 25% of their weight after immersing them in water for 1 minute at room temperature. The percentage of sorption keeps increasing moderately for 7 minutes before reaching 42%. After the 7 minutes have passed, the water sorption percentage accelerates and finally reaches 114% of the samples' weight after 60 minutes.

In parallel, specimens enrobed in the natural waterproof coating absorb a mere 1% of their weight after immersion for 1 minute in water at room temperature. The sorption percentage is 5% after 7 minutes and reaches only 20% of absorption after 15 minutes. After 60 minutes of immersion, the sorption percentage reaches 47% of the specimens' weights.

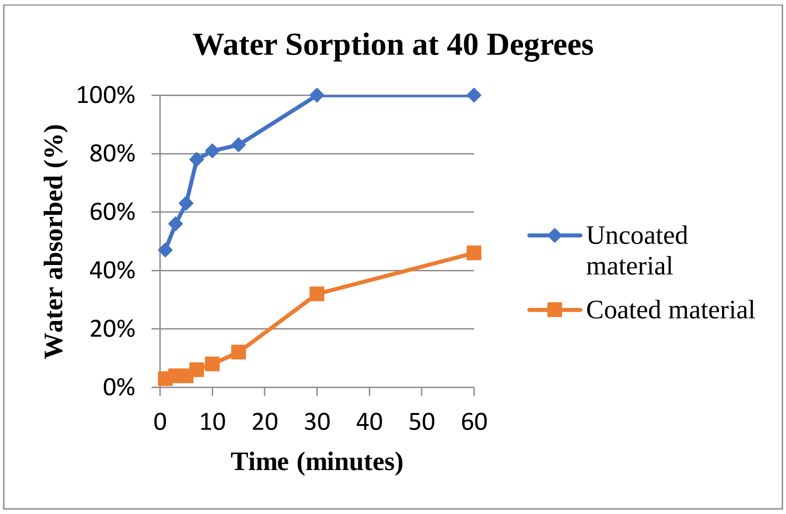


Figure 17. Graph representing the percentage of water sorption vs. time at 40˚ C.

The same trend is observed at 40˚C in figure 17. Here, the uncoated samples absorb 47% of their weight in water after just one minute whereas the coated ones only absorb 3%. After 15 minutes, the results show that the uncoated material degrades and starts to dissolve completely in the water.

After 10 minutes, the results showed that the coated samples had only reached 5% of sorption, compared to the uncoated specimens that had reached 81% of their weight in additional water absorbed. It is clear that the coating is really providing the material with an efficient waterproofing effect as the coated specimens absorb a mere 14% of their weight in water after the full 15 minutes have passed, compared to the uncoated ones that reached 84%. However, the coating starts to lose its efficiency after 15 minutes, where the sorption of water accelerates. A better waterproofing effect was recorded when the coated specimens were immersed in water at 40˚C especially at minutes 15 and 30. This could be because the coating was starting to melt and spread to areas that were not completely covered during the coating step.

b. Oil Sorption:

Immersing the specimens in sunflower oil at both room temperature and 40˚C showed low percentages of oil sorption for both the coated and the uncoated samples in figure 18.

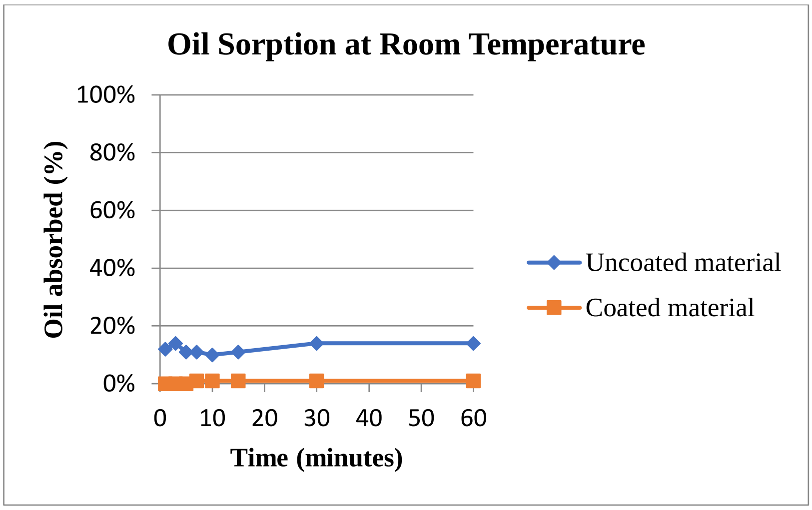


Figure 18. Graph representing the percentage of oil sorption vs. time at room temperature.

At room temperature, the uncoated specimens maintained an average of 12% of their weight in oil sorption for the whole 60 minutes. In comparison, the coated samples absorbed barely anything throughout the full 60 minutes of immersion in sunflower oil (average of 1%). This is due to the fact that the material formulation is majorly hydrophilic and will not absorb oil.

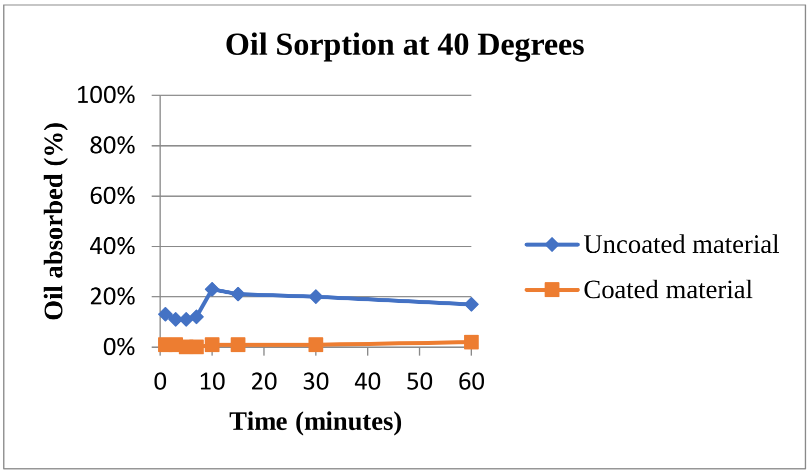


Figure 19. Graph representing the percentage of oil sorption vs. time at 40˚C.

Similar results were observed at 40˚C (figure 19), where the uncoated samples absorbed an average 12% of their weight in oil throughout the first 7 minutes and increased towards an average sorption of 20% starting 10 minutes. As for the coated specimens, they maintained a mere 1% of oil sorption throughout the full 60 minutes.

c. <u>10 % ethanol Sorption:</u>

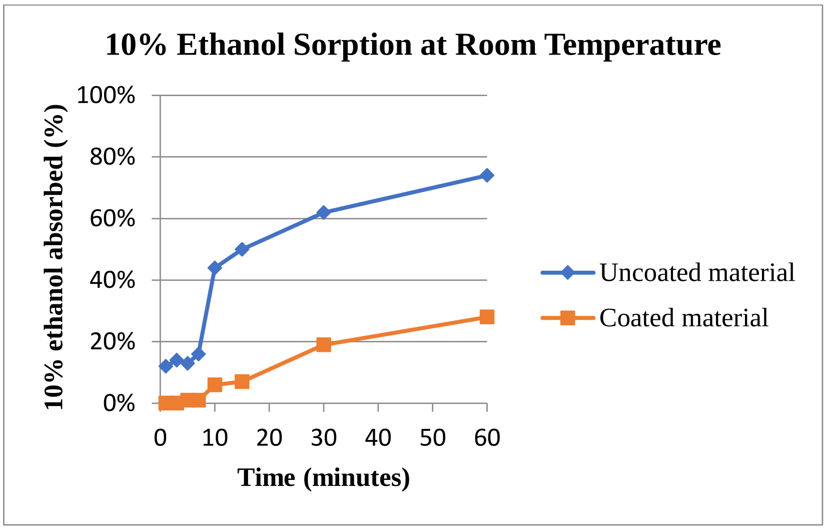


Figure 20. Graph representing the percentage of 10% ethanol sorption vs. time at room temperature.

The results of the sorption test in 10% ethanol, represented in figure 20, showed that at room temperature, the uncoated material samples absorbed 12% of their weight in 10% ethanol after 1 minute, and reached 16% after 7 minutes. A sharp increase in sorption is recorded after 10 minutes reaching 44% and finally 74% after 60 minutes. In parallel, the coated specimens maintained a maximum of 1% for 7 minutes, before respectively reaching 6% and 7% after 10 and 15 minutes, and finally 28% after 60 minutes.

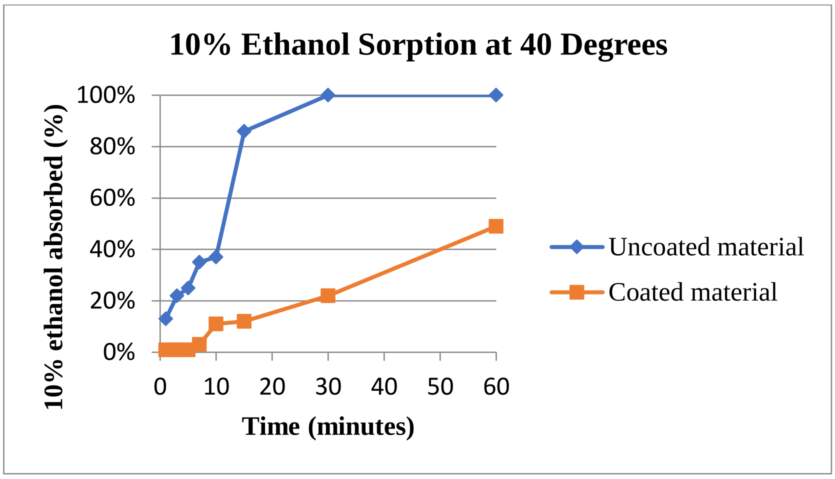


Figure 21. Graph representing the percentage of 10% ethanol sorption vs. time at 40˚C.

At 40˚C (figure 21), the uncoated samples absorb 13% of their weight in in 10% ethanol after 1 minute and reach 53% after 15 minutes before starting to dissolve and degrade in the 10% ethanol after 15 minutes have passed. As for the coated ones, they maintain 1% of sorption for 5 minutes, before reaching 12% of their weight absorbed after the 15 minutes have passed. After 60 minutes, the sorption percentage reaches 49% for the coated specimens.

Based on all of the above results and their analysis, we can deduce that coating the material with a layer of beeswax and canola oil by immersion can protect the material when in contact with food at room temperature for 7 minutes with a maximum sorption of 5%. At 40˚C, it can withstand food for 5 minutes before the sorption percentages exceed 5%.

This proves that coating the material with this natural waterproof coating is sufficient for a contact of around 7 minutes, as long as the foods do not exceed the melting point of the coating (Refer to DSC results).

Regarding the uncoated material, the curves show that it absorbs a very small amount of oil at both room temperature and 40 ˚C (a maximum of 20% at 40˚C after 10 minutes). However, when it is in direct contact with an aqueous medium, it starts to absorb as soon as the contact begins. We can deduce that for optimal results, the uncoated material should be used with dry products but can withstand oily ones.

To see whether or not the percentages of sorption at the different conditions are significantly different or not, a univariate multi-factor analysis of variance (ANOVA) test was conducted on IBM SPSS version 23. The dependent variable is the percentage of sorption and the four independent factors are the media, temperature, time and coating (alpha= 0.05). It is also interesting to explore the interactions between the different independent factors and see if they significantly affect the percentages of sorption at the respective testing conditions.

One limitation of this analysis is the absence of normality seeing that the sample size is lower than 30 (five replicates). Yet, the assumptions of independency of the observations and equal variances across groups are met.

As seen in Table 4, the p-value is lower than $\alpha = 0.05$ in all cases except the replication which is expected, and highlights the replicability of our results. This proves that there is significant difference between the sorption behavior of the material between all of the different studied conditions (coating, time, temperature, and media). The interactions between the independent factors are also significantly different across all of the possible combinations of interaction. To recognize which of the conditions actually differ, Post- Hoc comparisons were run.

Post- Hoc multiple comparisons were not performed for coating and temperature because they are fewer than three groups. For media and time, tables 5 and 6 represent their respective multiple comparisons (Bonferroni).

Table 4. Multi- factor univariate ANOVA.

Tests of Between-Subjects Effects

Dependent Variable: Sorption

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	429701.432[a]	99	4340.419	74.948	.000
Intercept	312380.782	1	312380.782	5394.051	.000
*Media * Coating*	29205.785	2	14602.892	252.156	.000
*Media * Temperature*	3352.240	2	1676.120	28.942	.000
*Media * Time_min*	37509.490	14	2679.249	46.264	.000
*Coating * Temperature*	6612.795	1	6612.795	114.187	.000
*Coating * Time_min*	11937.864	7	1705.409	29.448	.000
*Temperature * Time_min*	1585.976	7	226.568	3.912	.000
Media	88717.014	2	44358.507	765.963	.000
Coating	138367.925	1	138367.925	2389.275	.000
Temperature	9040.766	1	9040.766	156.112	.000
Time_min	82533.424	7	11790.489	203.593	.000
Replication	462.476	4	115.619	1.996	.094
*Media * Coating * Temperature * Time_min*	1993.473	14	142.391	2.459	.002
*Media * Coating * Temperature*	1956.385	2	978.193	16.891	.000
*Media * Coating * Time_min*	7909.667	14	564.976	9.756	.000
*Coating * Temperature * Time_min*	2772.299	7	396.043	6.839	.000
*Media * Temperature * Time_min*	4775.711	14	341.122	5.890	.000
Error	21890.771	378	57.912		
Total	765630.955	478			
Corrected Total	451592.203	477			

a. R Squared = .952 (Adjusted R Squared = .939)

Table 5. Multiple Comparisons table for Media (Bonferroni).

Multiple Comparisons							
Dependent Variable: Sorption							
	(I) Media	(J) Media	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Bonferroni	10% ethanol	Oil	21.77*	.858	.000	19.71	23.84
		Water	-10.99*	.858	.000	-13.05	-8.93
	Oil	10% ethanol	-21.77*	.858	.000	-23.84	-19.71
		Water	-32.76*	.855	.000	-34.82	-30.71
	Water	10% ethanol	10.99*	.858	.000	8.93	13.05
		Oil	32.76*	.855	.000	30.71	34.82
Based on observed means. The error term is Mean Square (Error) = 58.516.							
*. The mean difference is significant at the 0.05 level.							

At the 0.05 significance level, there is evidence in table 5 that there is a statistically significant difference between the percentages of sorption across the three different food simulant media (p-values< 0.05).

Table 6. Multiple comparisons table for time in minutes (Bonferroni).

Multiple Comparisons

Dependent Variable: Sorption

	(I) Time_min	(J) Time_min	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
Bonferroni	1	3	-2.37	1.397	1.000	-6.76	2.02
		5	-3.40	1.397	.428	-7.80	.99
		7	-6.80*	1.397	.000	-11.19	-2.40
		10	-19.34*	1.403	.000	-23.75	-14.93
		15	-19.98*	1.403	.000	-24.39	-15.57
		30	-29.08*	1.397	.000	-33.47	-24.69
		60	-38.53*	1.397	.000	-42.92	-34.14
	3	1	2.37	1.397	1.000	-2.02	6.76
		5	-1.03	1.397	1.000	-5.43	3.36
		7	-4.43*	1.397	.046	-8.82	-.03
		10	-16.97*	1.403	.000	-21.38	-12.55
		15	-17.61*	1.403	.000	-22.02	-13.20
		30	-26.71*	1.397	.000	-31.10	-22.32
		60	-36.16*	1.397	.000	-40.55	-31.77
	5	1	3.40	1.397	.428	-.99	7.80
		3	1.03	1.397	1.000	-3.36	5.43
		7	-3.39	1.397	.436	-7.79	1.00
		10	-15.93*	1.403	.000	-20.35	-11.52
		15	-16.58*	1.403	.000	-20.99	-12.17
		30	-25.68*	1.397	.000	-30.07	-21.28
		60	-35.13*	1.397	.000	-39.52	-30.73
	7	1	6.80*	1.397	.000	2.40	11.19
		3	4.43*	1.397	.046	.03	8.82
		5	3.39	1.397	.436	-1.00	7.79
		10	-12.54*	1.403	.000	-16.95	-8.13
		15	-13.19*	1.403	.000	-17.60	-8.77
		30	-22.28*	1.397	.000	-26.68	-17.89
		60	-31.73*	1.397	.000	-36.13	-27.34
	10	1	19.34*	1.403	.000	14.93	23.75
		3	16.97*	1.403	.000	12.55	21.38
		5	15.93*	1.403	.000	11.52	20.35
		7	12.54*	1.403	.000	8.13	16.95
		15	-.64	1.408	1.000	-5.08	3.79
		30	-9.74*	1.403	.000	-14.15	-5.33
		60	-19.19*	1.403	.000	-23.60	-14.78
	15	1	19.98*	1.403	.000	15.57	24.39
		3	17.61*	1.403	.000	13.20	22.02
		5	16.58*	1.403	.000	12.17	20.99
		7	13.19*	1.403	.000	8.77	17.60
		10	.64	1.408	1.000	-3.79	5.08
		30	-9.10*	1.403	.000	-13.51	-4.69
		60	-18.55*	1.403	.000	-22.96	-14.14
	30	1	29.08*	1.397	.000	24.69	33.47

		3	26.71^{*}	1.397	.000	22.32	31.10
		5	25.68^{*}	1.397	.000	21.28	30.07
		7	22.28^{*}	1.397	.000	17.89	26.68
		10	9.74^{*}	1.403	.000	5.33	14.15
		15	9.10^{*}	1.403	.000	4.69	13.51
		60	-9.45^{*}	1.397	.000	-13.84	-5.06
	60	1	38.53^{*}	1.397	.000	34.14	42.92
		3	36.16^{*}	1.397	.000	31.77	40.55
		5	35.13^{*}	1.397	.000	30.73	39.52
		7	31.73^{*}	1.397	.000	27.34	36.13
		10	19.19^{*}	1.403	.000	14.78	23.60
		15	18.55^{*}	1.403	.000	14.14	22.96
		30	9.45^{*}	1.397	.000	5.06	13.84
Based on observed means. The error term is Mean Square (Error) = 58.516.							
*. The mean difference is significant at the 0.05 level.							

As seen in table 6, there is evidence that there is no statistically significant difference between the sorption percentages after 1 minute and 3 minutes, 3 and 5 minutes, 5 and 7 minutes, 7 and 10 minutes, and 10 and 15 minutes.

Beforehand, results of the sorption tests established that the coated material was capable of resisting 7 minutes with maximum sorption of 5% of its weight in food. Yet, conducting the Post- Hoc comparisons provided evidence that there were no statistically significant difference between 7 and 10 minutes of immersion.

This suggests that prolonging the contact with foods from seven to ten minutes will not significantly affect the sorption of the coated material.

The same conclusion works for the coated specimens at 40˚C that can now sustain 7 minutes instead of 5 minutes without a significant difference in sorption levels.

a. Migration studies:

i. Starch, Iodine test:

After conducting the iodine test on 3 replicates of each one of the solutions recuperated from the sorption tests of the coated specimens at room temperature, the results displayed in table 7 show that starch was not migrating into any of the three food simulant mediums after 10, 15, 30 and 60 minutes of immersion. These results suggest that the starch present in the material formulation will not migrate into food at room temperature when the material is coated with the natural waterproof coating used in this study.

Table 7. Results of iodine test (starch identification).

Blanks	***Concentration of starch***	***Color***	***Presence of starch***
B1	1%	Green/ black	+
B2	5%	Blue/ black	+
B3	10%		+
B4	15%		+
Media	***Immersion duration (min)***		
Water	10	Orange	-
	15		-
	30	Orange/ red	-
	60		-
Oil	10	Orange/ red	-
	15		-
	30		-
	60		-
10% ethanol	10	Orange	-
	15	Orange/ red	-
	30		-
	60		-

ii. Glycerol, Dunstan's test:

Results from table 8 prove that the glycerol present in the material formulation will not migrate into food at room temperature when the material is coated with the natural waterproof coating used in this study.

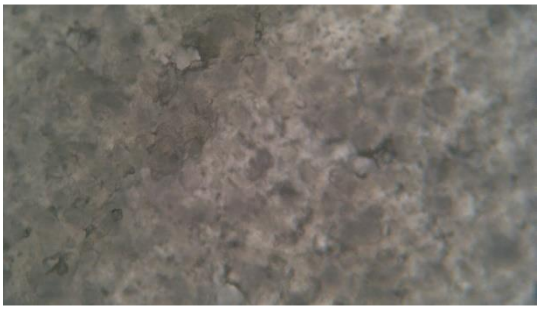
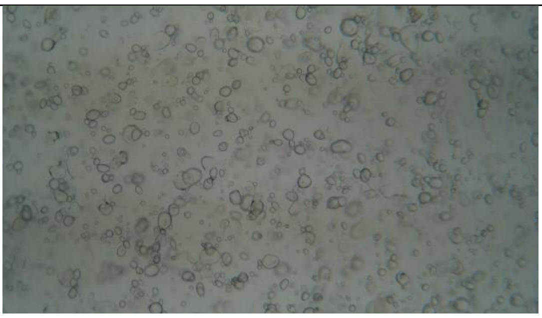
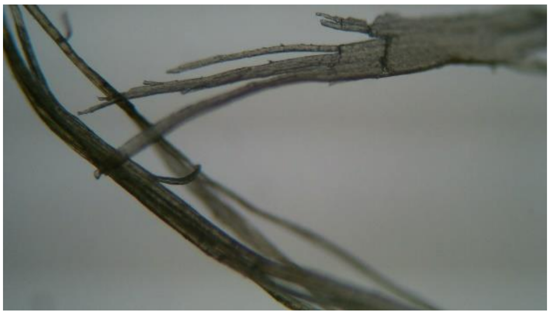
The establishment that glycerol did not migrate into the aqueous food simulants suggests that D- sorbitol did not as well. This assumption is backed up by the fact that films made with glycerol were significantly more soluble in water than films made with sorbitol (Müller et al., 2008). Accordingly, since the Dunstan's test shows that glycerol did not migrate, it is safe to assume that the D-sorbitol did not as well. The oil sorption results of the coated material at room temperature showed a mere 1% in sorption even after 1 hour of immersion in the oil. In addition, both glycerol and D-sorbitol are hydrophilic sugar alcohols, and the Dunstan's test for the identification of glycerol in the oil solutions was negative for the studied time intervals. Accordingly, there is evidence that D-sorbitol did not migrate into the food oil even after 60 minutes of direct contact.

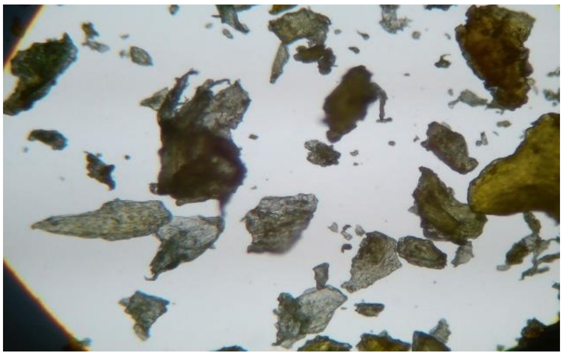
Table 8. Results of Dunstan's test (identification of glycerol).

Blanks	***Concentration of glycerol***	***Color observed***	***Presence of glycerol***
B1	1%	Clear pink	+
B2	5%	Transparent with a hint of pink	+
B3	10%	Transparent	+
B4	15%		+
Food simulant	***Immersion duration (min)***	***Color observed***	***Presence of glycerol***
Water	10	Pink	-
	15		-
	30		-
	60		-
Oil	10	Pink	-
	15		-
	30		-
	60		-
10% ethanol	10	Pink	-
	15		-
	30		-
	60		-

iii. Agar, coating, and other:

Table 9. Table representing the pure potential migrants as seen on the microscope.

Reference	***Microscope image***	***Description***
Coating (beeswax and canola oil)		Yellowish and opaque medium sized to large circular particules
10% agar		Pattern of large square shaped particules
10% potato starch		A regular pattern of small circles
Garlic fibers		Fibrous and incolore structures

Powdered citrus fibers		Geometric and medium- sized yellowish particles. The bigger the particle, the more opaque, the smaller the more translucid.

To study the migration of the rest of the material components into the different food simulants, the concentrated solutions recuperated from sorption tests were compared with the reference microscope images from table 9.

- Water after 10 minutes:

The microscope images in figures 22 and 23 suggest the presence of small particles from the coating, as well as small and thin citrus, and garlic fibers.

Figure 22. Microscope image of water solution after 10 minutes.

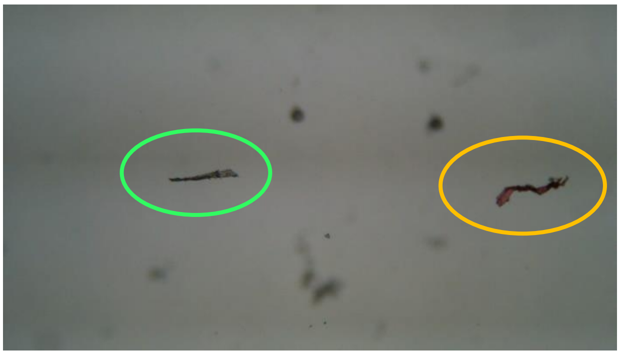


Figure 23. Microscope image of water solution after 10 minutes (2).

- Water after 15 minutes:

Figure 24 shows the presence of circular and opaque particles, which indicate the migration of the coating.

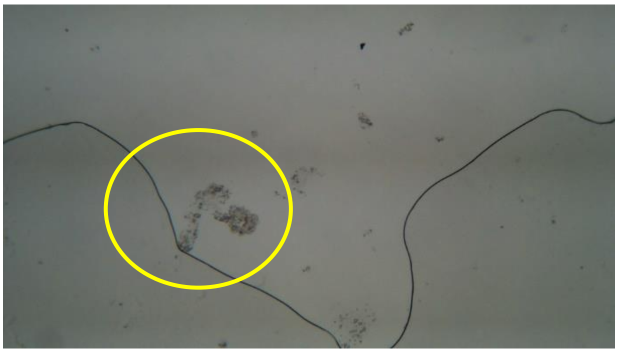


Figure 24. Microscope image of water solution after 15 minutes.

- Water after 30 minutes:

The presence of a long and thin fiber in figures 25 and 26 prove that some of the garlic fibers are migrating into the water after 30 minutes at room temperature. Yellowish, circular and opaque structures are from the coating.

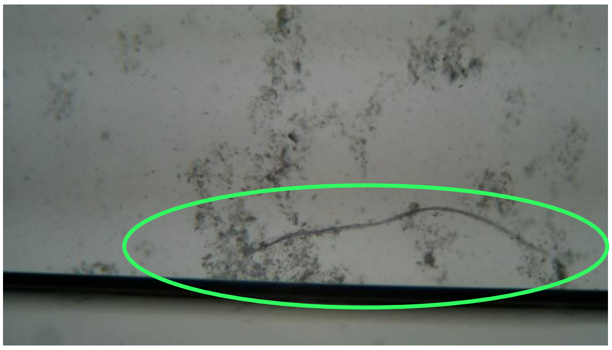


Figure 25. Microscope image of water solution after 30 minutes.

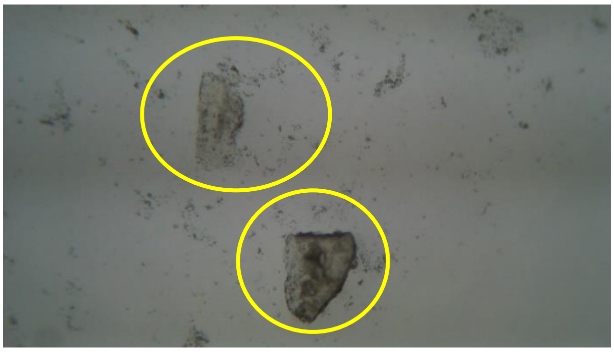


Figure 26. Microscope image of water solution after 30 minutes (2).

- Water after 60 minutes:

Fibrous structures in figure 27 are the garlic fibers that are migrating into the water after 60 minutes. Yellowish particules in figure 28 prove the presence of coating.

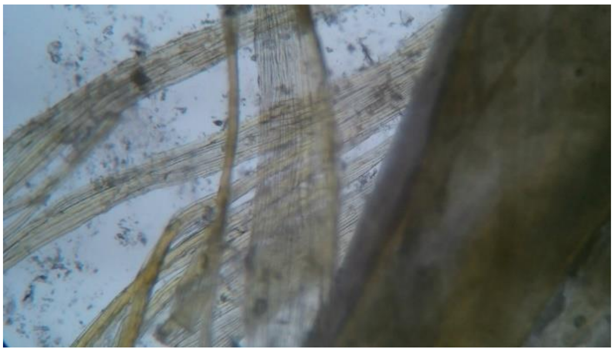


Figure 27. Microscope image of water solution after 6o minutes.

Figure 28. Microscope image of water solution after 60 minutes (2).

- Oil after 10 minutes:

The presence of a small geometric particle in figure 29 could be from the powdered citrus fibers, while the thin fibrous one seen in figure 30 is a garlic fiber.

Figure 29. Microscope image of oil solution after 10 minutes.

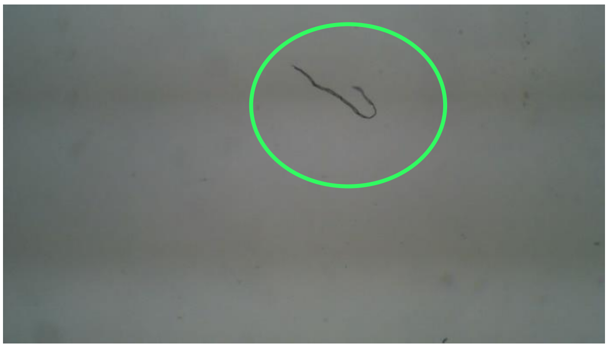


Figure 30. Microscope image of oil solution after 10 minutes (2).

- Oil after 15 minutes:

A small and thin garlic fiber is seen in figure 31.

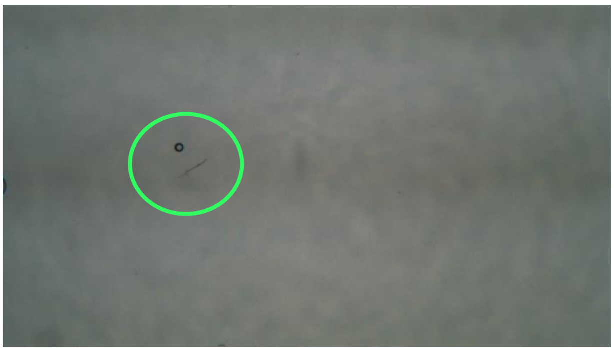


Figure 31. Microscope image of oil solution after 15 minutes.

- Oil after 60 minutes:

The microscope images in figures 32 and 33 prove that some of the garlic and powdered citrus fibers are migrating into the oil after 60 minutes.

Figure 32. Microscope image of oil solution after 60 minutes.

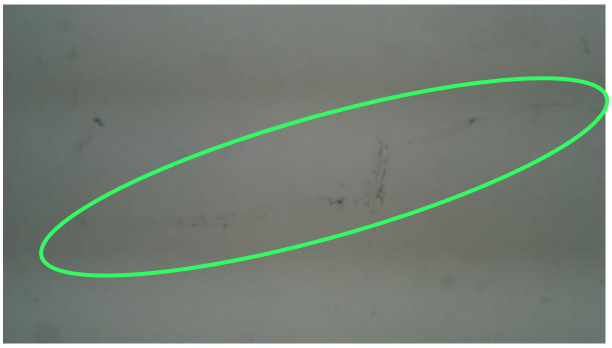


Figure 33. Microscope image of oil solution after 60 minutes (2).

- 10% ethanol after 10 minutes

Citrus and garlic fibers are seen as migrants in figure 34.

Figure 34. Microscope image of 10% ethanol solution after 10 minutes.

- 10% ethanol after 15 minutes

Garlic fibers and particles from the coating are migrating into 10% ethanol after 15 minutes as seen in figures 35 and 36.

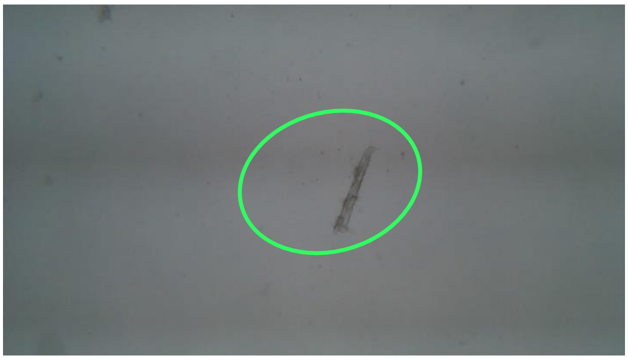


Figure 35. Microscope image of 10% ethanol solution after 15 minutes.

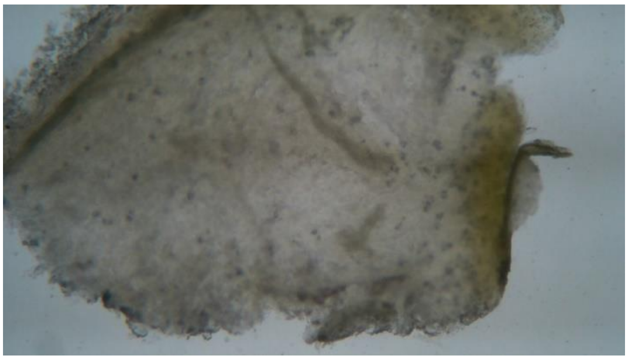


Figure 36. Microscope image of 10% ethanol solution after 15 minutes (2).

- 10% ethanol after 30 minutes

Garlic fibers and particles from the coating are recognized in the images after 30 minutes in 10% ethanol (figures 37 and 38).

Figure 37. Microscope image of 10% ethanol solution after 30 minutes.

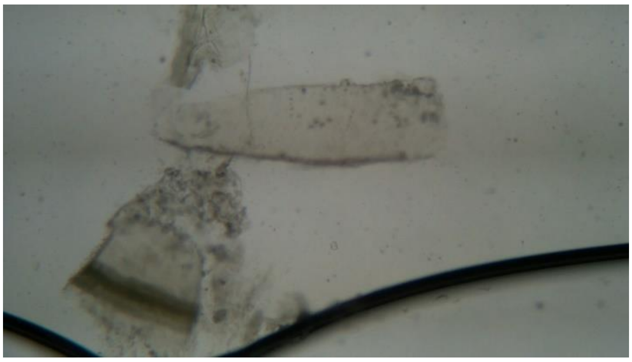


Figure 38. Microscope image of 10% ethanol solution after 30 minutes (2).

- 10% ethanol after 60 minutes

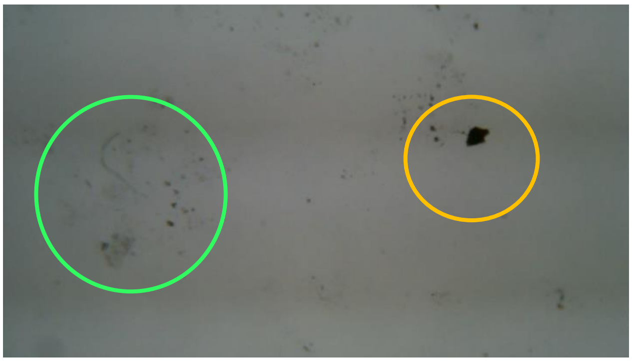


Figure 39. Microscope image of 10% ethanol solution after 60 minutes.

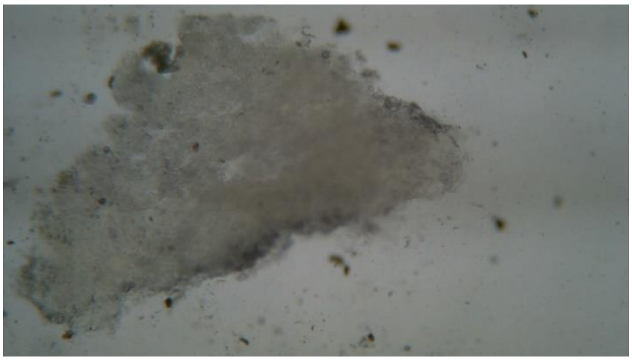


Figure 40. Microscope image of 10% ethanol solution after 60 minutes (2).

Citrus and garlic fibers, as well as particles from the coating are identified as migrants in 10% ethanol after 60 minutes (figures 39 and 40).

Table 10 summarizes the migration behavior of the coated material at room temperature with (+) as indication of a positive presence of the migrant in the food simulant, and a (-) for the absence of the specific migrant in the food simulant media.

Table 10. Table summarizing the sorption and migration behavior of the coated material at room temperature.

Food simulant	***Immersion duration (min)***	***Average Sorption %***	***Starch***	***Glycerol and D-sorbitol***	***Coating***	***Agar***	***Garlic fibers***	***Powdered citrus fibers***
Water	1	1						
	3	1						
	5	2						
	7	5						
	10	11	-	-	+	-	+	+
	15	20	-	-	+	-	-	-
	30	32	-	-	+	-	+	-
	60	47	-	-	+	-	+	-
Oil	1	0						
	3	0						
	5	0						
	7	1						
	10	1	-	-	-	-	+	-
	15	1	-	-	-	-	+	-
	30	1	-	-	-	-	-	-
	60	1	-	-	-	-	+	+
10% ethanol	1	0						
	3	0						
	5	1						
	7	1						
	10	6	-	-	-	-	+	+
	15	7	-	-	+	-	+	-
	30	19	-	-	+	-	+	-
	60	28	-	-	+	-	+	+

CHAPTER VII

OPPORTUNITIES AND CHALLENGES

A. Comparison with traditional materials

To conclude potential applications for the developed material, comparing its properties with the properties of typical materials is essential for a better understanding of its possible uses. Accordingly, its density, mechanical, and thermal properties were compared with traditional materials.

According to figure 41, the density of the biomaterial developed in this study, which is equal to 1019.7 Kg /m3, is similar to the density ranges of woods and wood products, polymers and rubbers. Consequently, and from a density point a view, the developed material has the potential to be used in applications that are currently compatible with woods and wood products, polymers and rubbers.

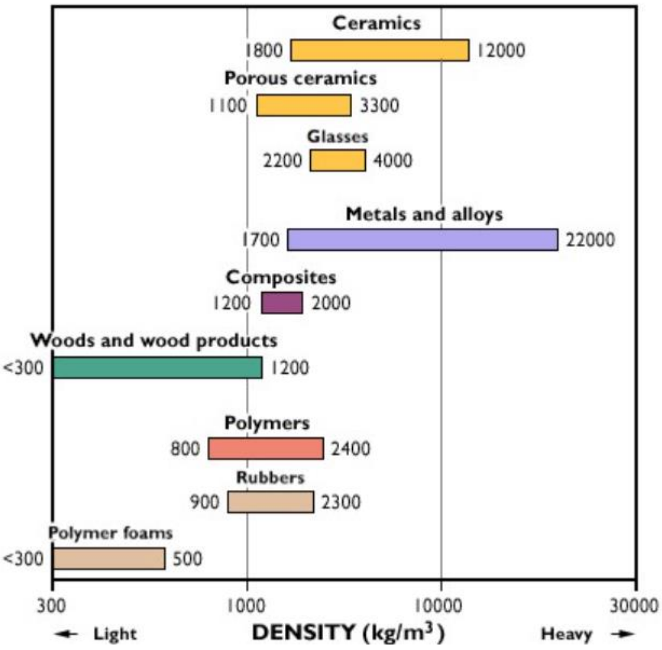
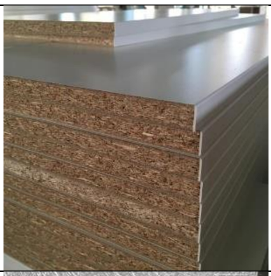


Figure 41. Representation of different materials and their respective densities (Property Information, Density, n.d.).

Furthermore, the thermal conductivity of the material was compared to typical building materials and insulators. Table 11 shows that not only does the material compete with the density of typical building materials such as high density particle boards, it also offers a low thermal conductivity (λ= 0.350 W/m.K) that can compete with some insulators.

Table 11. Comparison of the thermal properties of the developed biomaterial with typical building and insulating materials (J.M. Lasance, 2002; Wilson, 2008).

	Photography	**Density (Kg/m^3)**	**Thermal conductivity (W/m.K)**
	Building materials		
Hardwoods (oak)		720	0.16
Softwoods (pine)		510	0.12
Acoustic tile		290	0.06
Particle board (low density)		590	0.08

Particle board (high density)		1,000	0.17
Fiberglass		150	0.04
Thermal insulators			
Cork		150	0.043
Balsawood		130	0.05
Rubber foam		100	0.042
Achieved biomaterial		***1019.7***	***0.350***

Besides, according to the Mechanical Engineer's Data Handbook, the achieved material appears to have a thermal conductivity close to plastics, especially low density polyethylene (λ= 0.33W/m.K). In addition, its thermal conductivity is comparable with lightweight concrete (λ= 0.1-0.3) which is traditionally used as a flooring and building material because of its low thermal conductivity and high heat resistance (Carvill, 1993).

Concerning the ultimate tensile and yield strength represented in table 12, the achieved biomaterial is relatively weak compared to traditional materials including rubber, HDPE, and wood (pine). Fortunately, the potential applications considered for this biomaterial such as tiles, boards, coasters and placemats, as well as disposable tableware items, do not demand high tensile strength during their use.

Table 12. Typical tensile and yield strengths of some materials (Monroe Engineering, n.d.).

Material	**Yield strength (MPa)**	**Ultimate tensile strength UTS (MPa)**
HDPE	26-33	37
Polypropylene	12-43	19.7-80
Polyester resin (unreinforced)	55	55
Brass	200+	500
Marble	N/A	15
Concrete	N/A	2-5
Wood (pine)	-	40
Rubber	-	16
Achieved biomaterial	0.935	1.052

Exploring the barrier properties of the accomplished biomaterial/ biocomposite prove that is should be properly coated with a waterproof natural coating with a relatively high melting point to be used for the various applications proposed in this project.

B. Areas of improvement

In this study, the preparation of the material was performed either manually for the tableware prototypes, or with the use of a dough sheeter for the preparation of the flat boards and coasters. For optimal and more standardized results, it is preferable to combine both the shaping, drying, and cooling steps under one process step, to decrease time and energy consumptions, and improve the standardization and quality of the products. Ideally, this is done with a compression-molding machine.

Another main area of improvement is the use of a more performant and efficient natural and waterproof coating that will have the following requirements: transparent, waterproof, biodegradable, food grade, has a high melting point and is cost efficient. One promising example for a potential biodegradable, compostable, and waterproof coating with a high melting point is Eco flex®.

During this study, coating the material with beeswax was done either by immersion or by painting with a brush. While this method was acceptable for the laboratory testing, another practice should be adopted for commercial and large-scale applications. Spray coating is a pertinent alternative for more standardized, uniform, and high quality products.

The introduction of a compression-molding machine in the process will also enable the possibility to eliminate some of the natural additives used in the current studied formula. There is a possibility to eliminate both D- sorbitol and agar, as the compression-molding machine will take care of shaping the product under pressure and temperature, without passing by a really plasticized and moldable material before shaping and drying it.

C. Next steps and proposed future work

Due to the external circumstances that have affected directly and indirectly the progress of this study, including the Covid-19 pandemic and the total lockdowns that were imposed on the country, the scope of the study had to be narrowed down for the moment.

To carry on the impact of this project, it is interesting to conduct additional testing procedures to further characterize the material, assess its behavior, optimize it and find the most appropriate application for it. Additional proposed studies are conducting a finite element analysis, water vapor permeability, creep experiment and studying the effect of temperature and humidity during storage on the mechanical properties. In addition, it could be interesting to measure the impact strength of the biomaterial. Moreover, quantitative migration studies could complement and validate the qualitative ones done in this study.

Furthermore, after finding a more efficient waterproof coating that fits all the needed specifications, the sorption and migration properties of the material with the new coating should be tested again, as well as its melting point.

Finally, if a compression-molding machine is procured, and the material formulation optimized or amended, the mechanical properties of the updated material should be tested again to assess the changes and decide on the ideal material formulation in compatibility with the process of the compression-molding machine.

CHAPTER VIII

CONCLUSION

The world cannot withstand any more unsustainable resource exploitation, uses, and practices. Now is the time to explore and research new alternatives to replace non-renewable materials, especially across the agro food industry that is increasingly problematic.

This study explored the potential of recycling ligno-cellulosic components extracted from food processing wastes into a performant bio-based and biodegradable material. The concerned types of food processing wastes were citrus and garlic peels collected from citrus processing and garlic peeling industries. Citrus peels and garlic skins were chosen as they are challenging to the environment when disposed using traditional methods. Citrus peels are acidic, high in moisture and rich in oils, limiting their use as animal feed. In addition, they may be harmful to soil microorganisms and need longer composting times. As for the garlic stalks and skins, they are rich lignin, which is hard to digest by animals, and are toxic to plants. However, citrus and garlic processing wastes are very rich in fibers that are remarkably strong, and contain antimicrobial and antioxidant properties that will help in the durability of a potential biomaterial.

As a result, fibers were extracted from these two types of processing wastes and a formulation was developed to optimize their mechanical properties by complementing the fibers' properties with the ones of natural additives. The obtained biomaterial turned out to be very mechanically strong, customizable, and biodegradable.

To assess its potential applications, characterization tests were conducted to determine the mechanical, thermal, migration, and sorption properties of the material. The mechanical properties that were determined are the density of the material, its ultimate tensile strength, yield strength, modulus of elasticity, and 3- point bending. As for its thermal behavior, thermal gravimetric analysis (effect of temperature on percentage of mass change), measurement of the coating melting point, and testing of thermal conductivity and resistance were done. Finally, the sorption and migration behaviors were evaluated in the following three food simulant mediums: water, oil and 10% ethanol to mimic wet, oily, acidic, and low-alcoholic foods.

Specifically, sorption tests were carried out at room temperature and 40˚C on both coated and uncoated samples to assess the efficiency of the natural coating and its compatibility with the developed material. In addition to the sorption tests, qualitative migration studies were performed on the recuperated solutions from the sorption tests, to check if any of the ingredients present in the formulation or any of the coating particles, were migrating into the food.

Results of the thermal characterization showed that the material itself can sustain temperatures up to 210˚C without degrading, which is very promising and is more than enough in most of its possible applications. Yet, the melting point of the beeswax coating appeared to be low and inefficient for hot environments. This suggests the necessity of using another coating that would also be food grade, transparent, biodegradable, and waterproof, but with a higher melting point for direct contacts with hot foods or for use in hot environments.

Results from the sorption and migration studies showed that the uncoated material cannot be used with wet and/ or aqueous products. However, it absorbs very low percentages of food oil even without coating. When coated with a natural waterproof beeswax coating, the material absorbed a maximum 5% of its weight after 7 minutes of immersion in the three food simulants at room temperature. At 40˚C, it resisted for 5 minutes with a maximum 5% of its weight absorbed. As for migration at room temperature, there is evidence that the natural additives present in the material were not migrating into the food simulants even after 1 hour of immersion. Yet, some particles from the coating and some of the fibers were.

Comparing this new material with conventional ones showed that it is capable of competing with traditional building materials based on its low thermal conductivity (λ=0.350 W/m.K), high density (ρ=1019.7 Kg/m^3), and thermal resistance. It has a high bending strength that offers a competitive edge if used as disposable tableware items compared to plastic and paper that have the tendency to bend when used to carry heavy food products.

In conclusion, with a performant waterproof and biodegradable coating, this material has endless promising applications: from disposable tableware, to coasters, placemats, boards, tiles, building blocks, and furniture.

This project is an example of many recycling and repurposing opportunities for the food industry, proving the possibility of more sustainable and circular value chains, to alleviate the damage caused by current practices.

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