Computer-Aided Approach for The Development and Characterisation of Bioplastics from Potato Peel Incorporated with Rice Husk

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DECLARATION

I hereby declare the work embodied in this report is the result of my own research except for the excerpt as cited in the references.

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Computer-Aided Approach for The Development and Characterisation of Bioplastics from Potato Peel Incorporated with Rice Husk

ABSTRACT

This research was conducted to develop a bioplastic with starch from sweet potato peel incorporated with silica from rice husk as reinforcement filler. Rice husk and sweet potato peel are agricultural waste that has a high potential and economic interest. Therefore, the utilization of these materials will provide substantial improvement towards waste reduction. A total of 18 formulations were generated by Design Expert Software using central composite design as a response surface methodology to determine the best formulation to develop the bioplastic. The optimum formulation was based on ratio of silica, volume of glycerol and volume poured into petri dish to obtain optimum thickness, density, and moisture content of bioplastic. The optimum formulation that was selected using numerical optimization exhibit a combined value of desirability (73.72 %). The value of data means for thickness was 1.96466 while density and moisture content were 0.22217 and 31.0667 respectively. Furthermore, thermo gravimetric analysis was conducted to examine the thermal properties and stability of the optimum silica in starch-based bioplastic. The findings from the studies showed that the optimum formulation of bioplastic was succesfully obtained and the incorporation of silica from RHA as reinforcing filler successfully has improved the thermal resistance. The starch/silica bioplastic degraded completely at 340 ^{o}C showed signifcant different between starch bioplastic without fillers that degrades at 330 ^{o}C. Higher content of silica gave a better thermal stability towards the bioplastic.

Keywords: silica, RHA, potato peel, thermogravimetric, response surface methodology

Pendekatan Berbantukan Komputer untuk Pembangunan dan Pencirian Bioplastik daripada Kulit Ubi yang Digabungkan dengan Sekam Padi

ABSTRAK

Tujuan penyelidikan ini adalah untuk menghasilkan bioplastik dengan kanji dari kulit ubi keledek dan digabungkan dengan silika dari sekam padi sebagai pengisi struktur bioplastik. Sekam padi dan kulit ubi keledek adalah salah satu dari sisa pertanian yang mempunyai potensi besar dan kepentingan ekonomi. Penggunaan bahan – bahan ini akan memberi impak yang positif terhadap pengurangan sisa. Sebanyak 18 formulasi yang dicipta oleh perisian Design Expert menggunakan "central composite design" sebagai "response surface methodology" untuk mencari formula terbaik untuk mencipta bioplastik. Formula optimum dicipta berdasarkan faktor nisbah silika, isipadu gliserol, isipadu yang dituang ke dalam cawan petri untuk mencari ketebalan, ketumpatan dan kandungan lembapan yang optimum. Formula optimum yang dipilih menggunakan pengoptimuman berangka mempamerkan nilai gabungan kebolehinginan ialah 73.72%. Nilai data purata untuk ketebalan adalah 1.96466, ketumpatan dan kandungan lembapan adalah 0.22217 dan 31.0667. Tambahan pula, analisis termogravimetri telah dijalankan untuk mengkaji sifat terma dan kestabilan silika dalam bioplastik berasaskan kanji. Dapatan daripada kajian telah menunjukkan bahawa rumusan optimum bioplastik telah diperolehi dan penggabungan silika daripada RHA sebagai pengisi pengukuhan berjaya meningkatkan rintangan haba. Bioplastik kanji/silika terdegradasi sepenuhnya pada 340 ^{o}C menunjukkan perbezaan ketara antara bioplastik kanja tanpa pengisi yang terdegradasi pada 330 ^{o}C Kandungan silika yang lebih tinggi akan memberikan kestabilan haba yang lebih baik terhadap bioplastik.

Kata kunci: silika, RHA, kulit ubi keledek, termogravimetri, 'response surface methodology'

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LIST OF ABBREVIATIONS AND SYMBOLS

RHA	Rice Husk Ash
RH	Rice Husk
SSB	Silica/Starch Bioplastic
g	Grams
mL	Millilitre
cm^3	Centimetre cubic
h	Hour
min	Minutes
%	Percent
^oC	Degree Celsius
T_g	Glass transition temperature
kg	Kilograms
cap	capita
tons	tonnes
T_m	Melting temperature
Tmin	Minimum temperature
Tcc	Crystallisation temperature
TPS	Thermoplastic starch
MFI	Melt flow index
LOI	Loss on ignition
C-O-H	Carbon-Oxygen-Hydrogen
$C_6H_{10}O_5$	Starch

CHAPTER 1

INTRODUCTION

1.1 Research Background

The advantages of plastics over other materials are the factor of why plastics are commonly used for packaging and other applications. Plastics, for example, are low-cost, lightweight, and chemically inert. Furthermore, they can be heat-sealed, are simple to print on, and can be crafted into range of forms. The depletion of already scarce natural resources resulting in plastics as number one material of choice in numerous applications. Plastics has vastly replaced many materials such as jute, paper, wood, glass and metal. Later, the Earth is facing crisis. Conventional plastics are made with petrochemical basis making them non-biodegradable and non-renewable. These significant downsides of plastics are resulting in serious substantial urban waste and critical environmental degradation.

Every year, 998 million tons of agricultural waste is produced internationally. India's consumption of plastics is 2 kg per person per year. In comparison to the rest of the world, this amount is considered insignificant. In America, an average person consumes 80 kg to 90 kg of plastics per year. Other developed countries stated that the consumption of plastics is 60 kg per year per capita and 15 kg per year of world average (Kalia et al., 2000). In tandem with, Malaysia domestic waste generation is influence by region and economic class with a range of 0.85 kg to 1.5 kg per person per day.

It is vital to mention that Malaysia produce more domestic waste than other developing countries like Indonesian and Philippines with 0.22 kg and 0.4 kg per person per day correspondingly (Chen et al., 2021). As a result, the majority of consumers are under growing pressure to eliminate non-biodegradable waste and turn to biodegradable products. Figure 1.1 display the percentage increase of plastic waste in Malaysia from 1975 to 2010.

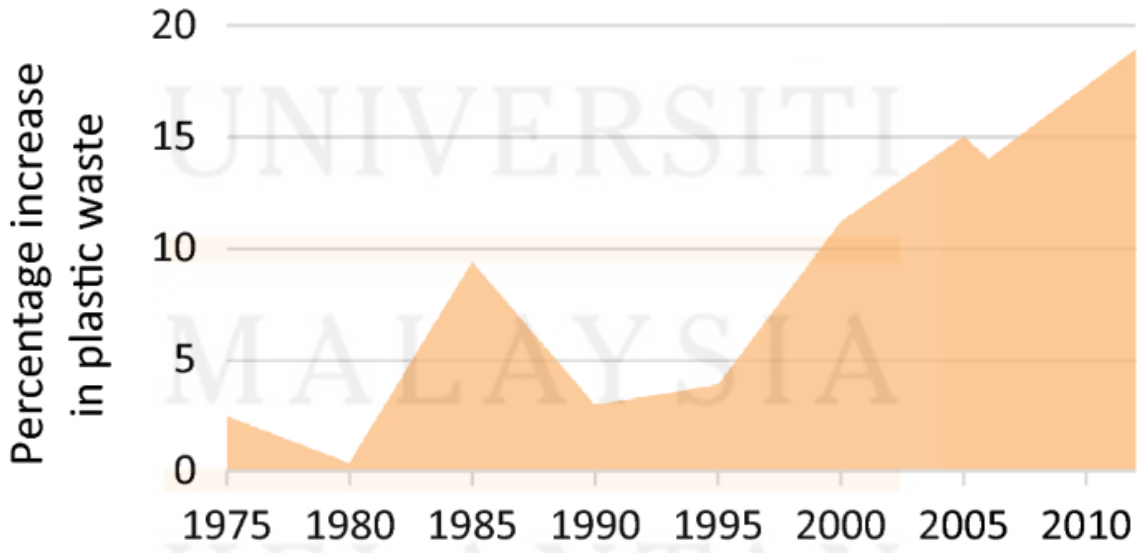


Figure 1.1: Generational plastic waste in Malaysia (Chen et al., 2021)

Despite this strain, no biodegradable plastics have been manufactured that merge all of the characteristics, functions, and economics-wise. In addition, agro-industrial waste, such as sugarcane bagasse, cereal straw and other canes are also the significant sources of biomass in areas where forestry supplies or residues are limited. Lignocellulosic are used to make pulp fibres, nano fibres, lignin, and biopolymers, and they have a wide variety of industrial application. Some of the applications are paper products, bio composites, rheology modifiers, food additives, biofuel and bio-energy generators. In addition to this topic, bioplastics have received wide acceptance as a possible substitute for traditional fossil-based plastics. Bioplastics are developed in distinction to recycled materials such as corn polylactic acid (PLA), sugarcane (Bio-polyethylene, Bio PE), as well as wastage from fats and oil like second generation Bio PE. Application of chemical and biotechnology pathway often associated with the production of bioplastics. For instance, bacteria can produce polyhydrohyalkanoates (PHAs) from sugar sources (Jiang et al., 2016).

Natural polymers are not a novel concept. In the interim of Roman and Middle Ages, amber, shellac, and gutta percha were the organic resins used. Long before European contact, the methods for creating ladles and spoons originated from animal horns were made by the Native Americans. Ford Motor Co. also began testing out soybeans to develop plastics to reinforce the idea of sustainability in the 1920s (Ashter, 2016). Polyhydrohyalkanoates (PHA) on the other hand is categorized as bio-based and biodegradable as a result of the chemical network within. This indicate that structure plays vital role in determining the biodegradability in preference of source.

It is vital to comprehend that biodegradable does not apply to all bio-based materials. It is only considered as biodegradable if it can degrade with the assist of microbes under desired environment. The microbes then will consume degrade materials as a food source. It converts into compost when the fragmented food source undergoes total microbial integration in a proper environment within 180 days (Brodin et al., 2017).

Based on Department of Statistics Malaysia, agricultural sector generated about 8.1 % or RM 89.5 billion to the Gross Domestic Product (GDP) in 2018. Nevertheless, every single year, without exception Malaysia discarded 12 million tons of agricultural waste into landfills every single year. Approximately, 15% of the annual waste in Asia originated from agricultural waste. It is recorded that in 2009, Malaysia estimate produced agricultural waste of 0.122 kg per cap per day. By 2025, prediction indicate the capacity of agricultural waste generated will reach 0.210 kg per cap per day (Ali, 2020). In conjunction, it has also been documented that approximately 110 million tons of rice husk and 16 to 22 million tons of rice husk ash (RHA) are generated worldwide (Tambichik et al., 2018). Consequently, the rate of commercialization for rice husk is relatively small for its abundant source. Therefore, the researcher from Malaysia and all part of the world are studying extensively on application of RHA on other substance. Utilization of this waste would contribute to reduction of environmental problem (Tambichik et al., 2018).

1.2 Problem Statement

This research is vital to understand the use of rice husk and potato waste that can be utilized in other form. The properties of bioplastics such as thermal resistance, tensile strength, durability, and permeability can be improved by incorporating silica from RHA into starch-based bioplastic. Potato peel is usually discarded in food industry and lead to a mass of food waste. It is also sensible to note that one of the main agriculture wastes in Malaysia is rice husk. It is a residual product from agriculture sector throughout the process of rice refining. It had identified that these valuable resourced has a potential applicability to develop a quality bioplastic. Although it is currently being utilized in other departments, potato peel and rice husk is still considered as abundant waste matter excreted from agriculture industry. Therefore, with the usage of potato peel and rice husk as bioplastic will be a great improvement to agriculture industry and help to utilize and minimize waste in Malaysia.

1.3 Significance of the Study

The development of starch/silica bioplastic (SSB) will definitely result in significant waste reduction in agriculture industry. Bioplastic made from starch and silica will be able to degrade easily compared to conventional plastic and participate in reduction of litter. This will lead to improvement in environmental pollution crisis as less plastic waste is generated. Material such as starch and silica are environmentally friendly and therefore will not harm the ecosystem in a long term. Biodegradable plastic is able to provide lesser carbon footprint and contribute to global sustainability.

1.4 Objectives

The key objective of this study is to develop a starch bioplastic from sweet potato peel incorporated with silica from rice husk.

Along with the main objective, there are several specific objectives including:

a. To investigate the relationship between ratio of silica, volume of glycerol and volume poured into petri dish with thickness, density and moisture content of SSB.
b. To find the optimal formulation for SSB.
c. To investigate thermal properties of SSB.

CHAPTER 2

LITERATURE REVIEW

2.1 Composition of Potato Peel

Polyphenols and phenolic acids are present in potato peels, which contribute to their antioxidant properties. Potato peel also consist of fatty acids and lipids that contribute to antibacterial properties. Potato peel is 25 % starch, 30 % non-starch polysaccharide, 18 % protein, 20 % acid-soluble and acid-insoluble lignin, 1 % lipids, and 6 % ash on a dry matter. The carbohydrate content of potato peel is 52 % dry extract. In table 2.1, the chemical composition of a potato peel, per 100 g is tabulated (Javed et al., 2019).

Table 2.1: Chemical composition of raw potato peel, g per 100 g (Source: Javed et al., 2019)

Compound	Minimum and maximum values
Water	83.3 – 85.1
Protein	1.2 – 2.3
Total lipids	0.1 – 0.4
Total carbohydrate	8.7 – 12.4

Starch	7.8
Total dietary fibre	2.5
Ash	0.9 – 1.6
Total phenolic content	1.02 – 2.92
Total flavonoids	1.51 – 0.96

2.2 Waste in Food and Agriculture Industry

2.2.1 Potato Peel

Following by wheat, rice and maize, food industry considers potatoes as one of the most valuable agricultural crops for human consumption. In 2004, 336 mega tons of potatoes were produced around the world continuously rising to 274 mega tons produced hugely from Europe and Asia (Majeed et al., 2017). Normally, before consumption potato were peeled off and the peel waste may range from 15 % to 40 % losses in production depending on the peeling method. A massive amount of potato peel waste outgrowth the potato remains in the food industry annually. This leads to excessive waste and is growing into a concern for waste management industry. Figure 2.1 shows the global potato production during 2004 until 2013 by FAO in 2016 (Food, 2016).

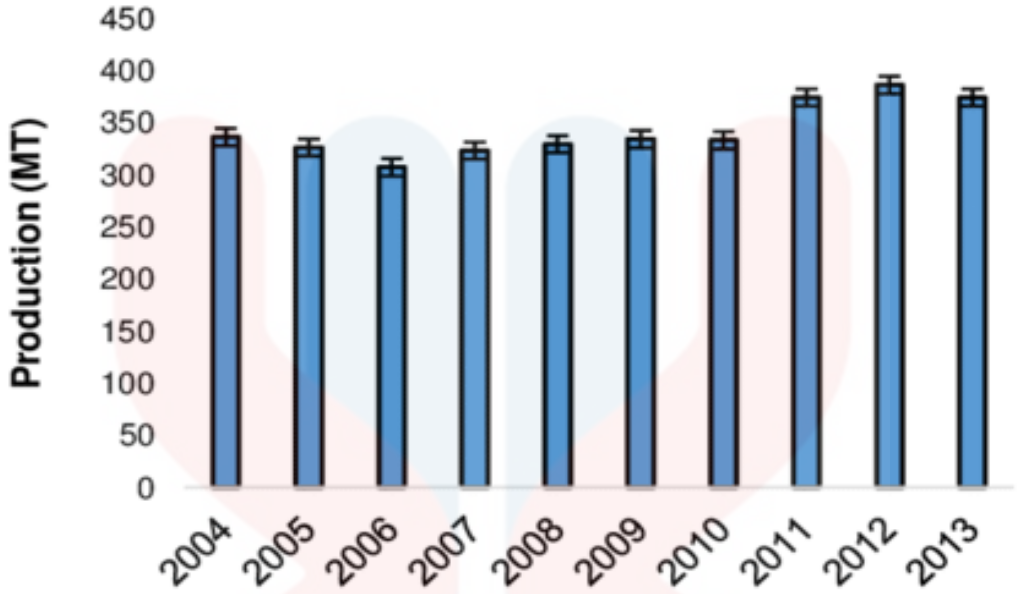


Figure 2.1: 2004 – 2013 International production of potato (Source: Food, 2016)

Usually, potato peel waste is classified as zero value in food manufacturing. In 2013, the waste emitted are more than 100 million tons leading to problem arising. The moisture content of potato peel is high, and it is susceptible to microbial infection. Therefore, it is often rejected and only utilized as food supply for husbandry. This undermines a valuable resource of strong economic interest and chemical value in regard to its antioxidant, antibacterial, apoptotic, anti-carcinogenic, and anti-inflammatory activities. Nevertheless, hemicellulose, lignin, starch and fermentable sugar shift potato peel as a potential residue that can be converted into valuable goods are being put into serious considerations for future applications (Dos Santos et al., 2016).

2.2.2 Rice Husk

Presently, approximately 20 % of rice husk is utilized for utilitarian reasons. For instance, rice straw is known to be converted into biodiesel, sheets, organic compost, and silages. The rest is often being burnt on wasteland, absorbed into soil or applied as compost for the subsequent harvest. Notwithstanding this, incorporation of rice husk in farmland decomposes poorly and cause rice diseases. Open burning also is intolerable by public as it leads to air pollution. This also encompasses of greenhouse emissions and smoke (Goodman, 2020). A study from India also stated that the fibrous content in rice husk might be dangerous to cattle feeding (Gidde & M.R. Jivani, 2007). In defiance of the potential of rice husk, it is only being recycled for low-value applications contrast to its increasing amount of production worldwide. The low-value applications are not in systematic manner, and this may carry a disadvantage to the future. Therefore, various studies are done to apply rice husk into a polymeric material as a filler and convert this waste into a valuable application and safe for the environment at the same time.

2.3 Starch Based Bioplastic

In the early stages, manufacturer and research collaborated to develop photodegradable plastic, but in time, the plastic is time-limited due to its degradability property can only be done in a presence of sunlight. Plastic with long-term biodegradability is desired for composters and urban landfills. Plastic processing is then transferred to natural materials, with microorganisms and plants synthesising many bio-based plastics.

The main benefits of bio-based plastics are low carbon emissions, low production in labour costs, and reduced contamination due to increased compost ability. Amongst others, polyhydroxlalkanoate is a microbial produced polymer, and polylactic acid (PLA) is a chemically synthesised polymer made from monomers extracted from agri-resources. Nevertheless, the cost of manufacturing plastic by microbial fermentation is costly with the addition of strictly monitoring of the bioreactor (Ismail et al., 2016). With that being said, most researchers and manufacturers see potential in starch as a viable option to develop a sustainable bioplastic. This is due to the properties of starch as a plant-based material that has a high level of biodegradability and renewability. Starch is also low cost and have a stable chemical compound for handling (Ismail et al., 2016). Usually, the source of starch used by researchers are from banana peel, potato, cassava, corn, yam and rice. These sources are abundant; thus, they are being utilized to make a bioplastic. However, due to the disadvantages of starch characteristics which are hydrophilic, undesirable mechanical and thermal properties, high fragility and high moisture absorption, the addition of plasticizer such as glycerol is able to increase shelf-life and elasticity of the bioplastics, it can also reduce the formation of crystallinity and resulted in more functional properties as it is incorporated with a different kind of polymeric materials for different applications (Abdullah et al., 2019).

2.3.1 Crystallinity of Starch Bioplastic

The structure of starch is damaged when it is stored at high relative humidity or high amount of plasticizer leading to recrystallisation. In this condition, starch is in a rubbery state and therefore able to develop crystallinity by increasing macromolecular mobility. Four factors that could affect the formation of different type of crystallinity are the

amylose content of starch, the starch origin, the process used and the additives. Usually, water or glycerol will be used as a plasticizer in mixture of starch bioplastics.

However, Roos & Jouppila (2003) stated that degree of crystallinity and kinetics of crystallisation increase as more water placed in the mixture acting as the plasticizer while glycerol portrayed lower crystallinity kinetics as more of it is used in the mixture. This shows that glycerol is able to regulate amylopectin through the creation of complex interactions as well as the reduction of local macromolecular mobility, which is needed for the formation of crystallites. Regardless of the original form or geometry, the recrystallisation of rubbery starch-based materials which is starch is critical to their longevity. It also has a direct impact on mechanical properties as predicted. Crystallites is assumed to act as physical crosslinking points, hence an internal stresses is developed and damage the starch based materials (Delville et al., 2003). The number of crystals produced is mostly determined by the complexity of the polymer chain: the simpler it is to "fold" the chain into crystalline platelets, the more crystals are produced.

2.3.2 Thermal Properties of Starch Bioplastic

The plasticizer such as glycerol or water commonly will transform starch to thermoplastic starch (TPS) at high temperature about 90 ^{o}C to 180 ^{o}C allowing it to be extruded, poured, moulded, and rolled. Starch is classified as crystalline substance because it is made up of linear amylose and highly branched amylopectin. Limited quantities of starch and water with the force of heat and water will cause unpremeditated damaged. A thermoplastic starch (TPS) is a homogenous melt that consist of thermoplastic characteristics. The

polymer chain arrangement is linear or branched and does not become cross-linked. TPS is difficult to undergoes evaporation during processing as it is subjected to thermal forces (Alrefai et al., 2020).

There are many transformation temperatures based on this semicrystalline configuration that contributes to the polymer's structure as well as its heat resistance. The glass transition temperature (T_g) transit amorphous portion in the structure of the polymer into mobile, allowing side groups to slide and rotate slightly. Second, a polymer's melt temperature (T_m) is the point at which the ordered crystal structure transforms into a viscous liquid. To allow manufacturing, T_m of a semicrystalline substance should be higher than the highest temperature where the final package can be used, but far below the melting temperatures.

Third, when cooling a polymer from a melt, the crystallisation temperature (T_{cc}) is the temperature at which crystalline regions tend to develop as the polymer starts to cool. T_{cc} indicates the solidification of a semicrystalline polymer that should be equal as minimum temperature (T_{min}) in theory. T_{cc} usually generate lower value in operation since a certain amount of super-cooling is required to induce crystalline nucleation. Ultimately, the last factor will be rare complete of the crystallisation once polymer has been processed and cooled. As a result, another transition of temperature is vital. The post crystallisation upon re-heating the polymer solid is important until further crystallization is formed, and maximum potential is reached.

2.3.3 Mechanical Properties of Starch Bioplastic

Research stated that when the amount of glycerol is higher than the content of the starch, the property of the function is altered as the glycerol lower the intermolecular interaction and increases polymer chain's mobility. This shows that higher concentration of glycerol generated lower tensile strength but improved the flexibility and extensibility significant (Abdullah et al., 2019). The movement of glycerol from starch matrix also affect the reduction of elongation as the movement restrict the mobility of starch chains and increase the reduction of elongation. As glycerol quantity is added, the mobility of starch chains is accomplished and the elongation is increased again (Battegazzore et al., 2016). According to another research, the corporation of glycerol also decrease the interactions between the bonds resulting in fading proximity between starch chains.

Although the mobility is assisted by glycerol, it still reduces the bioplastic's tensile strength. The rate of elongation is impacted by the concentration of starch. Nevertheless, the elongation increases when starch concentration is added up to 5 % but elongation breaks when starch is added to 6 %. Focusing on glycerol, the elongation of the bioplastics become higher as the concentration of glycerol become lower. In the film stiffness context, it is also stated that higher content of starch and low content of glycerol as plasticizer will contribute to higher stiffness of the bioplastic's materials (Santana et al., 2018).

2.4 Composition of Rice Husk Ash (RHA)

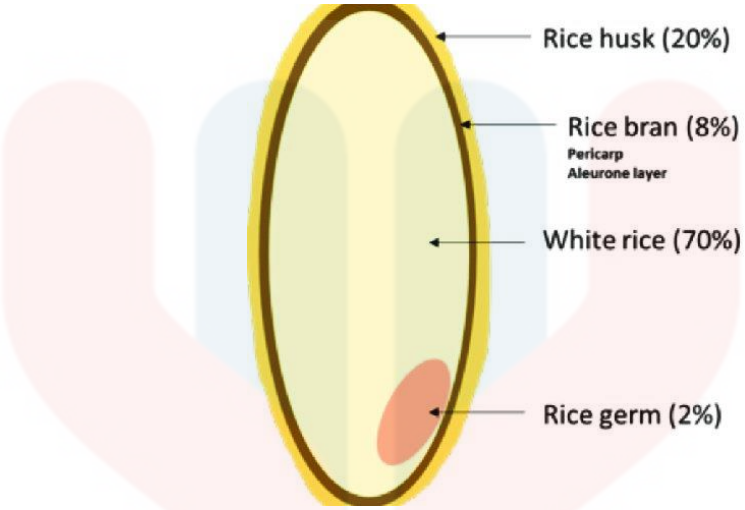


Figure 2.2: Layout of rice husk (Source: Shafie & Esa, 2017)

When paddy is harvested, the key residues during the rice milling process are rice husk (RH) which is the very outer layer as shown in Figure 2.2. Rice husk incineration led to ash from rice husk (RHA). Owing to its high silica content and the ample availability of RHA, RHA has stimulated considerable research interests, at lower costs. Rice husks which has been removed during paddy milling process consist of 75 % organic volatile matter and 25 % of the RH weight is incinerated into RHA (Prasad et al., 2001). Therefore, RH is about 20 % by the weight of rice paddy. For instance, in every 1 ton of paddy milled, around 200 kg of RH will be obtained. After incinerating in furnace, around 50 kg of RHA will be gained. Researchers that employ RHA as a raw material for their respective study are certainly needed to understand the composition of the RHA utilized the research. In general, RHA needs to contain approximately 87 % to 97 % amorphous silica and some negligible quantities of alkalis and some remainder components (Prasad et al., 2001). Dissimilar of RHA constituents influenced by geological conditions, soil chemistry, yielding year, approach to analysis and preparations for experiments.

Table 2.2 Composition of RHA from different countries (Source: Prasad et al., 2001)

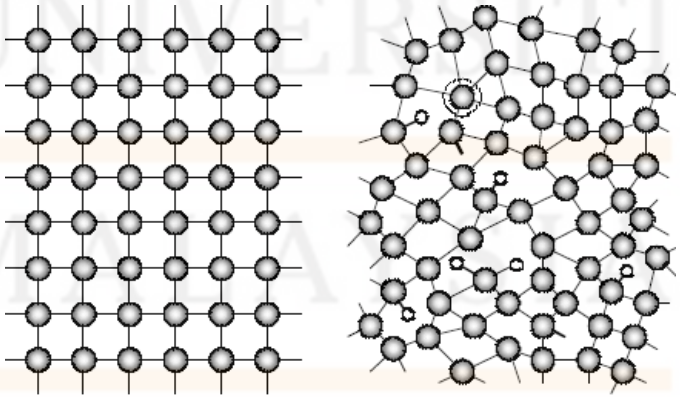
	Malaysia	**Brazil**	**Netherlands**	**India**	**Iraq**	**USA**	**Canada**
SiO_2	93.10	92.90	86.90	90.70	86.70	94.50	87.2
AI_2O_3	0.21	0.18	0.84	0.40	0.40	Trace	0.15
Fe_2O_3	0.21	0.43	0.73	0.40	0.19	Trace	0.16
CaO	0.41	1.03	1.40	0.40	1.40	0.25	0.55
K_20	2.31	0.72	2.46	2.20	3.84	1.10	3.68
MgO	1.59	0.35	0.57	0.50	0.37	0.23	0.35
Na_2O	*	0.02	0.11	0.10	1.15	0.78	1.12
SO_3	*	0.10	*	0.10	1.54	1.13	0.24
Loss on ignition	2.36	*	5.14	4.80	3.30	*	8.55

It is apparent from these results obtained that RHA obtained from burning of RH comprises an excessive percentage of silica (SiO_2) together with other trivial constituents considered as impurities. Potassium oxide, calcium oxide, magnesium oxide, iron (III) oxide, aluminium oxide and sodium oxide and others as the most common trace elements present in RHA (Obuasi & Ibemesi, 2011). The fairly wide range of the loss of ignition (LOI), which is indicative of the amounts of unburned components, suggest that the efficiency of the combustion process, which depends on the combustion temperature and time, affects the LOI value, and consequently, the silica content particularly. This is because the higher the LOI value resulting from incomplete combustion, the lower the silicon oxide content and vice versa.

2.5 Amorphous and Crystalline Form of RHA Silica

The silica in RHA undergoes structural transformation from amorphous to crystalline form is dependent on the incineration RH temperature and period. The dissimilar temperature result in a different form of RHA which has different properties. Thus, a proper selection of RHA form is crucial for certain application due to this reason. Amorphous denotes the shape is not defined or regular. Amorphous silica displays atom arrangement to be more scattered on the microscopic level, they do not form a well-arrange structure and do not have any particular order. A large surface area for reaction to occur has caused the amorphous silica to be more reactive.

On the other hand, the crystalline silica resulted from higher temperature, it was constructed by replication of many simple units. Inversely, the silica tetrahedron of this form is regular and has oriented 3-dimensional structure that create crystalline domains, which means that the presence of crystals can be observed on the microscopic level. The shape is basically linked by two silicon atoms connected to oxygen and each oxygen apex is linked in every apex as shown in Figure 2.3.



a) Crystalline silica b) Amorphous silica

Figure 2.3: The structure of crystalline and amorphous silica (Source: Dey et al., 2019)

2.6 Thermal Properties of RHA

The incorporation of the RHA into the polymer composites could improve the thermal stability of a material. In one research done from University Malaysia Sabah, the thermal treatment gives positive impact on the mechanical properties of tapioca starch material. These properties are inter-related and different variables provide different result. The thermal treatment given on the starch also upgrade the tensile properties (Norsyafina et al., 2017). Various other research also has been carried out to test the thermal resistance properties of bioplastics polymer using cost-effective and environmentally friendly fillers with the goal of expanding the applications of these materials in wider industrial scale.

As the amount of RHA increases, the composite component of RHA received and absorbed more heat. Therefore, higher temperature is required to supply threshold energy for the start of the material's degradation process, thus accounting for the material's thermal stability. For certain thermoset nanocomposite thermoplastic materials, materials properties such as different in cationic power, high surface broad, and wide aspect ratio are important to improve thermal stability and thermal properties as well as the amount of silica filler in a moderate and measured quantity (Ginting et al., 2014).

2. 6. 1 Thermal Properties of Silica Particles

Technically, the measurement of silica nanoparticles often associated within the movement of the particles. However, the measured values (also known as effective thermal conductivities) may include multiple factors from solid-state conduction, gas conduction, and thermal radiation, and therefore might not accurately reflect the

nanoparticles' inherent thermal conductivity. It is worth noting that the thermal conductivity of silica nanoparticles declines as the size of the particles becomes higher. The shrinkage on the heat conductivity of silica nanoparticles, on the other hand, is not substantial. It is also said that the predicted heat performance drops as surface roughness increases revealing that surface scattering have a significant impact on the heat transmission of amorphous silica particles. An extremely small contact area is generated when two individual silica particles aggregate together, which normally has a very high thermal resistance. As a result, as it passes through the limited contact region, solid-state heat conduction will be effectively reduced (Gao & Jelle, 2019).

2.7 Mechanical Properties of RHA

In general, the addition of RHA into bioplastics resulted in improvement of tensile modulus and lower the tensile strength and elongation at break in comparison of bioplastics without fillers. However, this statement was disagreed by some as the variables are also affected by poor filler-polymer compatibility in RHA composites. Furthermore, the difference of rice husk at such of white and black, resulted in a different result as well. Both type of rice husk generated an improvement on flexibility of modulus at the cost of tensile strength as the amount of rice husk is added. Nevertheless, the flexibility of modulus on black rice husk is higher than white rice husk on polypropylene composites.

Over and above, another factor affecting the polymer-RHA composites is the measurement of melt flow. Melt flow index (MFI) degrades as the amount of filler increase. This is due to the transportability of polymer being inhibited when filler is added into the polymer. This can also be observed in the tensile modulus. A low MFI indicates that increment in melt viscosity and stiffness is aided to escalated reinforcing grade (N. Cardona Uribe, et al., 2018). Another research proposed that usage of RHA as a filler showed the increment in tensile modulus and hardness with addition of the filler. However, the elongation and tensile strength decreases with increment of the filler. It was also noteworthy that properties such as water absorption, specific gravity and flame resistance increase along with increment of RHA (Okpara et al., 2016).

2.8 Silica-based Bioplastic

In the bioplastic making, silica is often used as additional materials or filler to as a reinforcement to the bioplastic matrix. Silica is most often derived from bamboo leaves, sugarcane waste ash, green leaves, rice husk or synthetically made. Silica naturally is a hydrophobic material that repels moisture. The addition of silica into starch-based bioplastic will create a desirable quality. The particle size of silica also plays major role in determining the behaviour of the matrix. Different particle size reacts differently on the structure of the starch-silica composite. Based on research, particle size of 23 µm, 20 nm and 200 nm of silica is similar to starch particles which is round structure and layering network. However, 200 nm particle size of silica was described as the perfect dispersion size for starch matrix and 20 nm easily formed a precipitation. (Liu et al., 2021).

2.9 Bioplastic Testing

2.9.1 Thickness

Thickness is an important aspect in determining a good property for bioplastics. It is vital in order to yield a desired mechanical and physical property such as flexibility, transparency, tensile and brittleness. These factors are correlated with thickness. Thickness is also important as it requires a standard amount of strength to withstand weight for packaging. Based on European Plastic Converters, the minimum required thickness for bioplastic bag is 16 microns (Izzaty et al., 1967). A study done by taking fifteen measurements at different spots on the bioplastic using a Vernier calliper. Then the average value is used. The data obtained was 0.28 mm – 0.32 mm (Oluwasina et al., 2021). Another report shows a lower value 0.087 mm – 0.091 mm by Zhang et al., (2018) where micrometre was used and measurement was taken at 10 different spots.

2.9.2 Density

Density especially, is a vital key in bioplastic characteristic due to the trading issue. Bioplastic bag is usually traded for cost per pound basis. The specific gravity and density of the bioplastic decides the cost of it. More materials are used per pound or part weight if the bioplastic has small amount of density. Many factors that could contribute to density such as crystallinity, loss of plasticizers and porosity.

Density is also important as it can indicate the type of material used, the average density of bulk masses and value of strength weight and cost-weight ratios (Bag et al., 2003). A range of 1.2 g/cm^3 to 1.3 g/cm^3 is said to be good and light bioplastic (Dawam Abdu et

al., 2018). In one report calculate density by dividing mass with area multiply by thickness. The data reported 1.62 g/cm^3 to 1.69 g/cm^3 is high compared to desired. This may due to different amount of plasticizer (Oluwasina et al., 2021). In comparison, another report measure density by dividing mass with volume. The data presented were between 0.75 g/cm^3 to 2.35 g/cm^3 with different amount of plasticizer used. Plasticizer with 20 % have the most desired value of density (Maulida et al., 2016).

2.9.3 Moisture Content

Moisture content is also a vital parameter to develop a good quality bioplastic that can be manufactured and use daily lives. Bioplastic which is usually made with compostable materials are susceptible to degradation by microorganisms which grow in high moisture. Therefore, a good bioplastic needs to acquire a low moisture content in order to maintain its grade for other future processing. Analysis of moisture content was calculated by finding the different between initial and last weight, divided with the initial weight multiply by 100 to obtain the percentage. The final weight data was recorded after placing the sample in an oven for 3 h at 105 ^{o}C. The data obtained was in a range of 14.26 % to 11.24 % which is high, however the percentage drops as the amount of silica added (Oluwasina et al., 2021). Another report measured the moisture content by placing the sample in desiccator for 2 days at room temperature. The value recorded was in between 10.25 % and 12.45 %.

2.10 Optimization of Bioplastic

Response surface methodology (RSM) is a group of statistical and mathematical pathways that can be applied in order to create, improve or optimization. It can also be used to create a new design, to develop and to formulate new products or processes. Usually, RSM is used when there is more than one variable that is desired as a characteristic of a product. It is labelled as response. In this technique, results are often laid by using graphical and contour plot. Optimization by RSM in bioplastic were done by several researchers. One report mentioned that, the starch bioplastic made from jackfruit seed and corncob obtained a desirability of 72.50 % with zinc oxide as filler with residual, water resistance and heat resistance as responses (Widhiantari & De Side, 2021). Another report also mentioned that bioplastic made from banana peel have a desirability of 95.1 %. This study accounted residence time, elongation at break, tensile strength, water absorption and biodegradability as responses (Aster, 2017). One more researcher carry out the study by using starch from cassava peel flour. This study found that the optimization of the bioplastic has a desirability of 57.79 % with tensile strength, elongation, swelling and biodegradability as responses (Pulungan et al., 2020).

CHAPTER 3

METHODOLOGY

3.1 Chemicals

The chemicals used for this research were glycerol and sulphuric acid.

3.2 Apparatus

The apparatus used for this research were 50 mL, 10 mL and 5 mL measuring cylinder, glass rod, 1000 mL, 500 mL and 100 mL beakers, aluminium foil, crucible dishes, petri dishes, 100 mL conical flasks, glass funnel, magnetic stirrer, Whatman paper No. 41, muslin cloth, Spurtar Vernier-Calliper 1505555 with 0.02 mm precision, spatula, magnetic stirrer, storage containers, sieve with size range of 0.002 cm to 12.5 cm, 50 mL Falcon tubes and zip lock bags.

3.3 Preparation of Material

3.3.1 Collection of Sweet Potato Peel and Rice Husk

The sweet potato peel was collected from local stall near UMK Jeli Campus. The potato peel was selected according to the condition of the peel such as colour, texture and freshness. The chosen potato peel was stored in a container before undergoes further processing. Rice husk was purchased from e-commercial platform, Shopee and kept in a container before undergoes further processing as well. Figures 3.1 and 3.2 show raw sweet potato peel and rice husk.

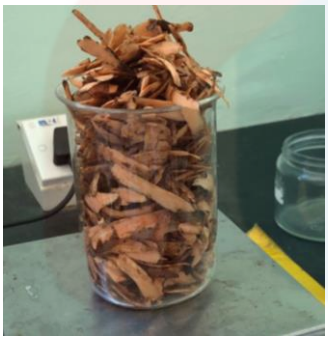


Figure 3.1: Sweet potato peel

Figure 3.2: Rice husk

3.4 Instruments

The instruments used for this research were Philips's HR 2056/00 electrical blender, Eppendorf Centrifuge 5810R 50 mL, Stuart US152D hot plate, Sartorius BSA4202S - CW weighing balance with precision of 0.01 g, Sartorius BSA224S-CW weighing balance with precision of 0.0001 g, Memmert UF110 universal drying oven, Protherm ECO Series furnace and Mettler Toledo TGA/DSC 2 GmbH Star System.

3.5 Method

3.5.1 Extraction of Starch from Sweet Potato Peel

The process of starch extraction is summarized in figure 3.3 and further elaborated below.

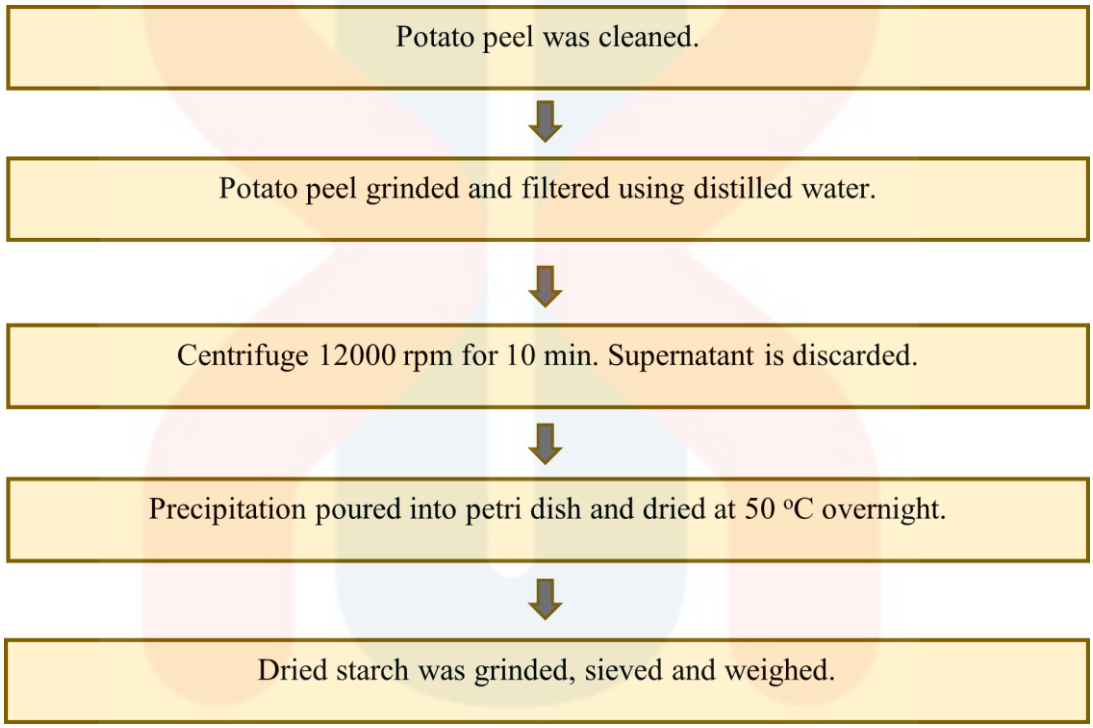


Figure 3.3: Flowchart of starch extraction

The procedure started with cleaning process of potato peel. An amount of 650 g of potato peel was cleaned with distilled water and rinsed a few times to make sure dirt is removed. Then, it was grinded by using Philips's HR 2056/00 electrical blender. It was filtered using muslin cloth. The filtration underwent centrifugation at 12000 rpm using Eppendorf Centrifuge 5810R for 10 mins. A 50 mL of Falcon tube was used in this procedure. After centrifugation finished, supernatant was discarded. The precipitation was poured into petri dish and was dried at 50 ^{o}C for overnight in Memmert UF110 universal drying oven. After that, dried starch is grinded by using the electrical blender. It was sieved using a sieve with size range of 0.002 cm to 12.5 cm. The weight was obtained with Sartorius BSA4202S - CW weighing balance with precision of 0.01 g. It is kept in a zip-lock bag until further usage (Bezirhan & Bilgen, 2019). A total of 25 g of dried starch was obtained as shown in figure 3.4.

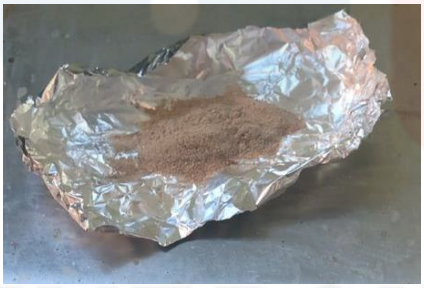


Figure 3.4: Starch powder

3.5.2 Extraction of Silica from Rice Husk

The silica was extracted from rice husk. This process is summarized in a figure 3.5 and further elaborated below.

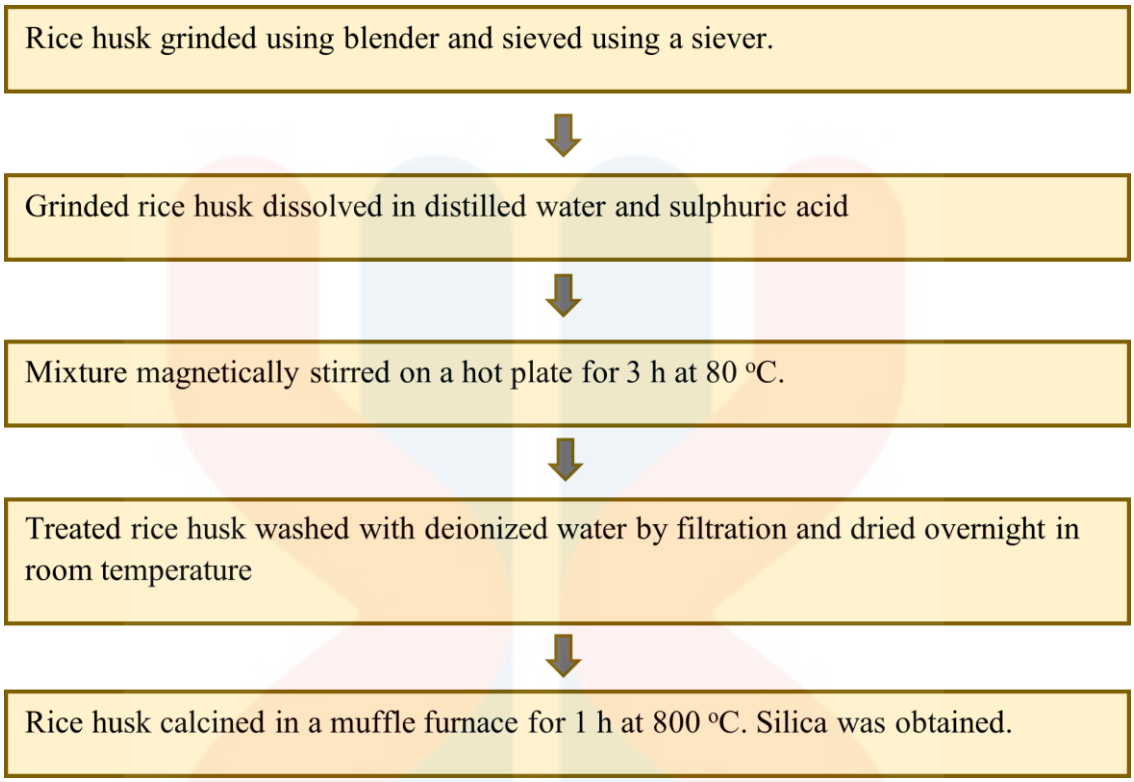


Figure 3.5: Silica extraction from rice husk

A total of 40 g of rice husk was grinded using Philips's HR 2056/00 electrical blender and sieved using a sieve to obtain uniform size. The grinded rice husk was placed in a beaker containing 386 g of distilled water and 7.65 mL of sulphuric acid under magnetic stirring for 3 h at 80 °C as an acid treatment to remove metallic impurities using Stuart US152D hot plate at power level two. After that, residue of treated rice husk was washed with deionized water by filtration with Whatman paper No. 41 and dried overnight in room temperature. Then, the dried rice husk was calcined in a Protherm ECO Series furnace at 800 °C for 1 h (Battegazzore et al., 2014). This method was repeated twice and approximately 10 g of silica was obtained. Silica was sieved using sieve with size range of 0.002 cm to 12.5 cm and weighed using Sartorius BSA4202S - CW weighing balance with precision of 0.01 g. Example of silica powder can be seen in figure 3.6.

Figure 3.6: Silica powder

3.5.3 The Making of Silica/Starch Bioplastic, SSB

The making of SSB was summarized in figure 3.7. This process is further elaborated below.

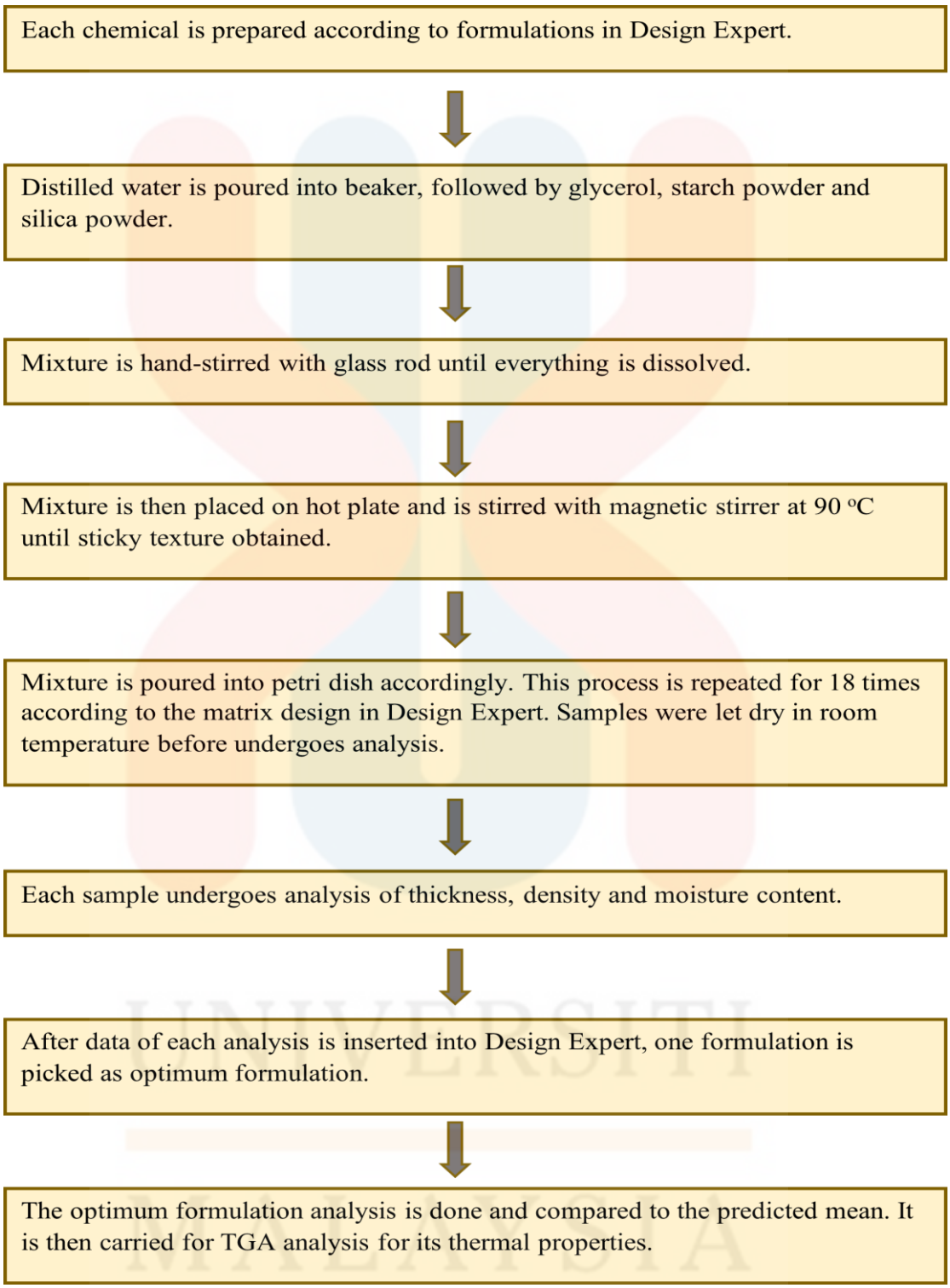


Figure 3.7: Flowchart of SSB

The mixture SSB were made using 17 mL of distilled water, 1 g of starch, 1 g of silica and 1 mL of glycerol with slight modification according to method (Norsyafina et al., 2017). The formulation was done using Design Expert Software version 13. The factors accounted for this formulation is ratio of silica, mass of glycerol and volume of mixture poured into petri dish. The formulations generated by Design Expert Software. There were 18 formulations in total. Table 3.1 is the matrix designated by Design Expert Software.

Table 3.1: Design matrix from Design Expert

Std	Run	Factor 1	Factor 2	Factor 3
		A: ratio	B: volume of glycerol	C: volume pour into petri dish
		%	mL	mL
10	1	5	6.7	8.5
16	2	5	2.5	8.5
9	3	13.4	2.5	8.5
11	4	5	2.5	4.3
2	5	10	0	6
18	6	5	2.5	8.5
6	7	10	0	11
12	8	5	2.5	12.7
15	9	5	2.5	8.5
4	10	10	5	6
14	11	5	2.5	8.5
5	12	0	0	11
7	13	0	5	11
1	14	0	0	6
8	15	10	5	11
17	16	5	2.5	8.5
3	17	0	5	6
13	18	5	2.5	8.5

3.6 Data Analysis using Design Expert

The data for all 18 formulations were analysed using Design Expert version 13 using Central Composite Design. This method was chosen as it can design a curvature thus give an optimal formulation for further analysis.

3.6.1 Thickness Response Analysis

The thickness of each bioplastic sample was measured by using a Spurtar Vernier-Calliper 1505555 with 0.02 mm precision. Each data was recorded in mm unit. The measurement was taken at five different places and average value was recorded using Equation 3.1 by (Oluwasina et al., 2019). Figure 3.8 shows the measurement of thickness using a vernier calliper.

$$\frac{\text{Sum of measured values}}{5} = \text{thickness (mm)} \tag{3.1}$$

Figure 3.8: Measurement of thickness

3.6.2 Density Response Analysis

The density of each bioplastic sample was measured by Equation 3.2. All weight is measured by Sartorius BSA4202S - CW weighing balance with precision of 0.01 g. Weight of petri dish for each sample was taken beforehand. All data was recorded using g/cm^3 unit. Method was done according to (Maulida et al., 2016) with some modifications. Figure 3.9 and figure 3.10 shows weighing of petri dish with sample and without sample to perform density calculation.

$$\frac{\text{Weight of petri dish+sample}-\text{weight of petri dish}}{\text{volume poured into petri dish}} = \text{density (g/cm}^3\text{)} \quad (3.2)$$

Figure 3.9: Weighing petri dish with sample

Figure 3.10: Weighing empty petri dish

3.6.3 Moisture Content Analysis

The moisture content of each bioplastic sample was measured by recording the initial weight of sample by using analytical weighing balance and placing in the drying oven at 90 ^{o}C overnight. The final weight is recorded after the sample was cooled down in room temperature. Then, the moisture content was calculated using Equation 3.3 as applied by (Venkatesh & Sutariya, 2019). Figure 3.11 shows all samples inside drying oven in order to analyse moisture content.

$$\frac{\text{Initial weight of sample} - \text{final weight of sample}}{\text{Initial weight of sample}} \text{ x } 100 = \text{moisture content } \% \quad (3.3)$$

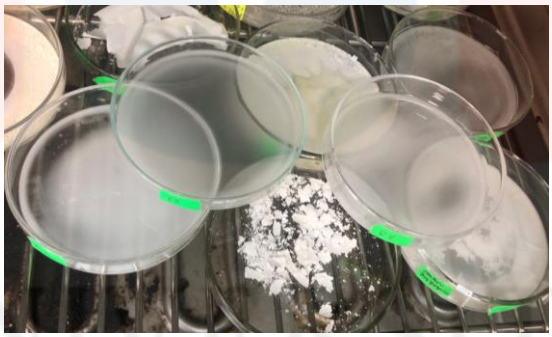


Figure 3.11: Analysis of moisture content

3.6.4 Optimization of Starch/Silica Bioplastic, SSB

The optimum formula was picked based on the best physical properties shown in each sample. One sample from the optimum formula was developed and underwent three analyses mentioned above. The data obtained was compared to the predicted mean in Design Expert. Afterward, the sample underwent TGA analysis using Mettler Toledo TGA/DSC 2 GmbH Star System. Figure 3.12 shows the SSB with optimum formulation.

Figure 3.12: SSB with optimum formulation

3.7 Thermogravimetric Analysis

The optimum formula is analysed for thermalgravimetric analysis (TGA) to determine the thermal resistance for the sample. This analysis was done by using the Mettler Toledo TGA/DSC 2 GmbH Star System. This equipment was provided by laboratory in UMK Jeli Campus. 5 mg of sample was weighed in a mini crucible dish Sartorius BSA224S-CW weighing balance with precision of 0.0001 g.

An empty mini crucible dish was used as control. Both crucibles were heated from 30 ^{o}C to 200 ^{o}C at heating rate of 10 ^{o}C/min. Then, the sample was heated at 40 ^{o}C – 500 ^{o}C with a heating rate of 10 K/min under inert atmosphere (N_2 flow 40 ml/min). This method was designed by (Abdullah et al., 2019). Figure 3.13 shows the TGA analysis running on the equipment.

Figure 3.13: Mettler Toledo TGA/DSC 2 GmbH Star System

CHAPTER 4

RESULT AND DISCUSSION

4.1 Analysis from Design Expert

Composite Central Design (CCD) was chosen from Response Surface Methodology (RSM) in Design Expert Software version 13 to obtain optimum formulation based on factors and responses desired. In this research, an optimum formulation for this SSB is obtained based on thickness, density and moisture content as responses. The formulations are 18 in total. Table 4.1 shows all data recorded for these three responses.

Table 4.1 Responses from Design Expert

Std	Run	Response 1 thickness mm	Response 2 Density g/mL	Response 3 moisture content %
10	1	1.5	0.44	37.92
16	2	3	0.38	46.27
9	3	3	0.3	19.38
11	4	2	0.25	52.78
2	5	1	0.082	51.96
18	6	3	0.38	46.27
6	7	0.5	0.1	1.76
12	8	1	0.34	48.49
15	9	3	0.38	46.27
4	10	3	0.61	46.17
14	11	3	0.38	46.27
5	12	1	0.1	3.57
7	13	3	0.45	49.29
1	14	0.5	0.09	3.7
8	15	4	0.42	35.7
17	16	3	0.38	46.27
3	17	3	0.82	36.99
13	18	3	0.38	46.27

4.1.1 Thickness Response Analysis

In table 4.2, the model summary statistics compared which model is suitable to obtain optimum formulation. In this response, quadratic model is suggested. R^2 value from this model is 0.8946 and adjusted R^2 is 0.7761 which is deemed acceptable. However, the predicted R^2 is - 0.7726 indicating the model is overfitting. Cubic model is not suggested as it is aliased.

Table 4.2 Model summary statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	0.3505	0.3981	0.2692	-0.0564	3.02	
2FI	0.3919	0.4088	0.0864	-1.3718	6.78	
Quadratic	**0.1940**	**0.8946**	**0.7761**	**-0.7226**	**4.92**	**Suggested**
Cubic	0.0000	1.0000	1.0000		*	Aliased

The model F-value of 7.55 implies the model is significant. There is only a 0.46% chance that an F-value this large could occur due to noise. P-values less than 0.05 indicate model terms are significant. In this case B, B^2, C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. This means that the ratio of silica, volume poured into petri dish, interaction between ratio of silica and volume of glycerol (AB), ratio of silica and volume poured into petri dish (AC), volume of glycerol and volume poured into petri dish (BC), and interaction between ratio of silica on each other (A^2) are insignificant terms. This data is recorded in table 4.3.

Table 4.3: ANOVA for Thickness Response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	2.56	9	0.2840	7.55	0.0046	significant
A-ratio of silica	0.0001	1	0.0001	0.0024	0.9618	
B-volume of glycerol	1.66	1	1.66	44.12	0.0002	
C-volume pour into petri dish	0.0135	1	0.0135	0.3576	0.5664	
AB	0.0090	1	0.0090	0.2385	0.6384	
AC	0.0126	1	0.0126	0.3356	0.5783	
BC	0.0090	1	0.0090	0.2385	0.6384	
A^2	0.0321	1	0.0321	0.8544	0.3823	
B^2	1.06	1	1.06	28.04	0.0007	
C^2	0.3117	1	0.3117	8.28	0.0206	
Residual	0.3010	8	0.0376			
Lack of Fit	0.3010	3	0.1003			
Pure Error	0.0000	5	0.0000			
Cor Total	2.86	17				

Based on the perturbation graph, it displays how the response changes according to each factor from chosen reference point. This reference point is generated by Design Expert Software. In the plot, factor A which is the ratio of silica displays a small effect as it changes from reference point. Therefore, it is acceptable to use factor B as X1 - axis, volume of glycerol and factor C X2 - axis, volume poured into petri dish and slice on factor A in figure 4.1.

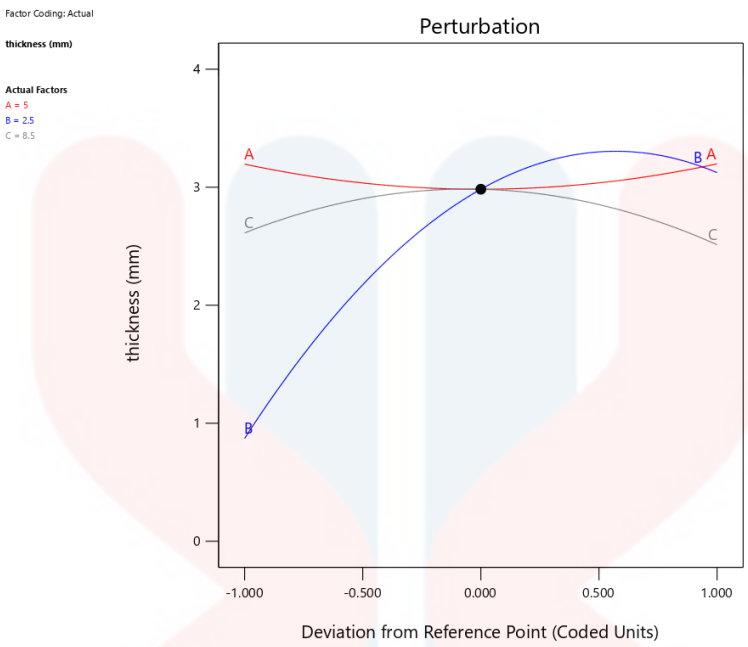


Figure 4.1: Perturbation plot for thickness response

In contour and 3D surface plot, the response characteristics for this analysis is in a form of maximum response. The correlation between two variables is that the higher volume of glycerol added, the higher the thickness. The lower the volume pour into petri dish, the lower the thickness. This is due to the function of glycerol as plasticizer. It disrupts and restructured the intermolecular polymer chain networks and increase thickness of bioplastic by converting all free volumes (Tarique et al., 2021). This was similar to study found by Nordin et al., (2020) where increase in volume of mixture bioplastic used, will simultaneously increase the thickness of bioplastic film. The maximum response indicate that silica content is high. This also proves that incorporation of silica adds more thickness to the bioplastic. This finding correlates with study done by Oluwasina et al., (2021) where a silica from bamboo leaves was used. If volume poured into petri dish is 7.95 mL and volume of glycerol is 4.05 mL, then the thickness response will be 3.8 mm at maximum. This can be analysed in figure 4.2 and 4.3.

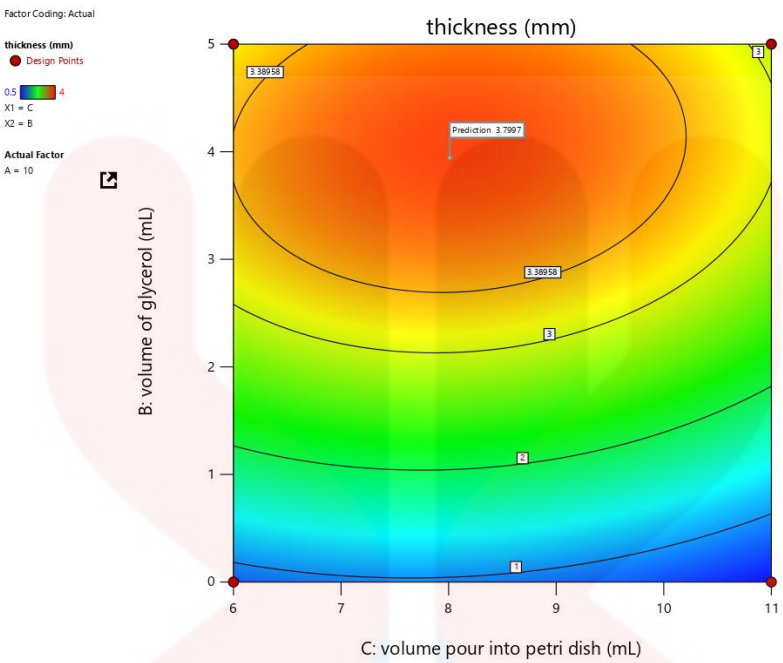


Figure 4.2: Contour Plot for thickness response

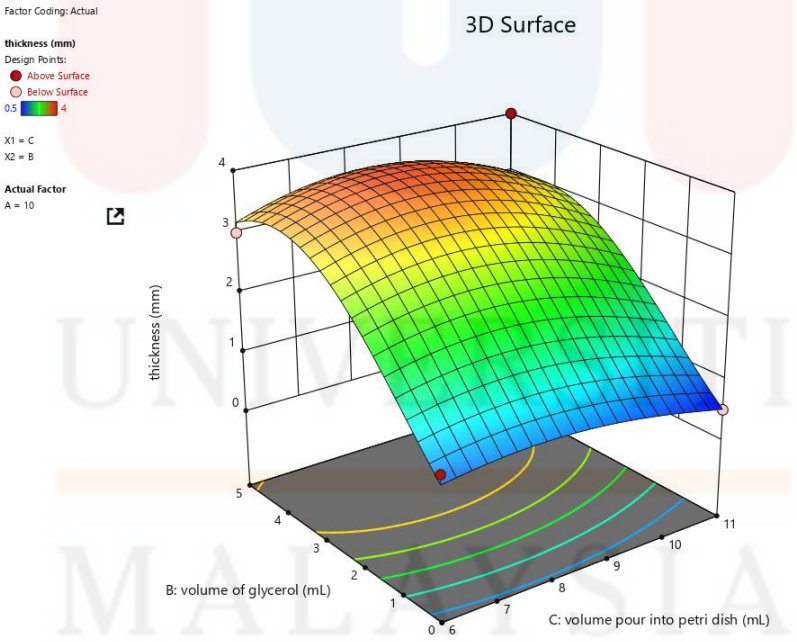


Figure 4.3: 3D Surface Plot for thickness response

4.1.2 Density Response Analysis

In table 4.4, the comparison between models highlighted those linear and quadratic models are suggested for this response. However, quadratic model will be chosen as the value of R^2 is 0.9516 which is near to 1.0000 than linear model value. The R^2 value of quadratic model is 0.9516 which is higher than adjusted R^2. Therefore, it is acceptable. The value of predicted R^2 is 0.2784 indicating that the model is overfitting. The data is recorded in table 4.4.

Table 4.4: Model summary statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	**0.0934**	**0.7468**	**0.6926**	**0.5225**	**0.2305**	**Suggested**
2FI	0.0939	0.7992	0.6897	0.1579	0.4064	
Quadratic	**0.0540**	**0.9516**	**0.8972**	**0.2784**	**0.3483**	**Suggested**
Cubic	0.0000	1.0000	1.0000		*	Aliased

The model F-value of 17.48 implies the model is significant. There is only a 0.02% chance that an F-value this large could occur due to noise. P-values less than 0.05 indicate model terms are significant. In this case B, BC, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. This signify that ratio of silica, volume poured into petri dish, interaction between ratio of silica and volume of glycerol (AB), ratio of silica and volume poured into petri dish (AC), ratio of silica square (A^2) and volume poured into petri dish squared (C^2) are insignificant terms. This data is presented in table 4.5.

Table 4.5: ANOVA for density response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	0.4593	9	0.0510	17.48	0.0002	significant
A-ratio of silica	0.0076	1	0.0076	2.61	0.1451	
B-volume of glycerol	0.3997	1	0.3997	136.87	< 0.0001	
C-volume pour into petri dish	0.0024	1	0.0024	0.8290	0.3892	
AB	0.0022	1	0.0022	0.7643	0.4075	
AC	0.0017	1	0.0017	0.5702	0.4718	
BC	0.0214	1	0.0214	7.33	0.0268	
A^2	0.0007	1	0.0007	0.2331	0.6422	
B^2	0.0668	1	0.0668	22.87	0.0014	
C^2	0.0044	1	0.0044	1.50	0.2558	
Residual	0.0234	8	0.0029			
Lack of Fit	0.0234	3	0.0078			
Pure Error	0.0000	5	0.0000			
Cor Total	0.4826	17				

In perturbation graph in figure 4.4, the graph shows that factor A, ratio of silica shows the least significant changes after passing through the reference point. Therefore, it is suggested that factor B, volume of glycerol as X1 – axis and factor C, volume poured into petri dish as X2- axis and slice on factor A.

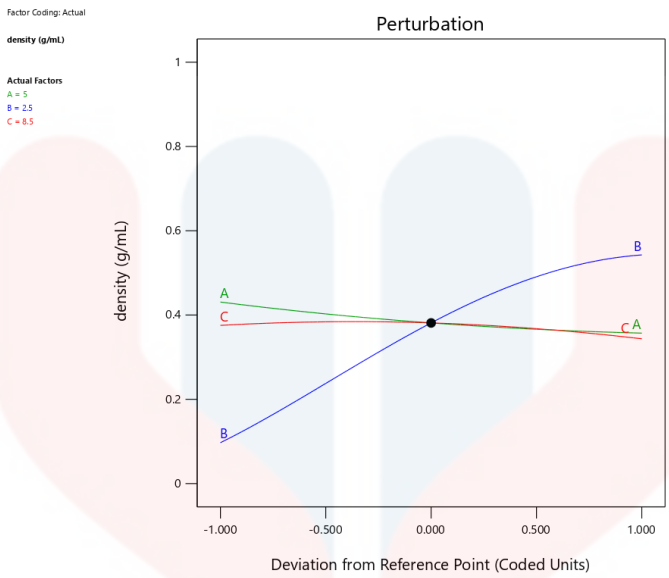


Figure 4.4: Perturbation plot for density response

Based on contour and 3D surface graph, this displays the data in a form of maximum response. The correlation between two variables can be determined when volume of glycerol added increases, the density of bioplastic sample increases as well. This is because plasticizer expands the starch network structure and increase in network density. This correlated with a study using cassava peel and sorbitol as plasticizer (Maulida et al., 2016). This statement is also further proven by Dawam Abdu et al., (2018) that used sweet potato with glycerol. The research stated that the density is strongly correlated with thickness. Therefore, the increase in bioplastic thickness will increase the density as well. Furthermore, the study also explains where large particle such as silica may contribute to increment in density. Besides that, glycerol was also in charge of interfering the intermolecular bonding within polymer chains and resulting in a more compact arrangement of polymer structure. This decrease the volume of starch and increase density of bioplastics (Razavi et al., 2015). Nonetheless, volume poured into petri dish only give little effect on the density value. The density decreases slightly when less volume is poured. This further enhance the relationship of density with thickness as

mentioned above. The highest prediction value for density response is 0.53 g/mL when 4.94 mL volume of glycerol added as X1 – axis and 6.05 mL volume poured into petri dish as X2 – axis. This data is displayed in figure 4.5 and 4.6.

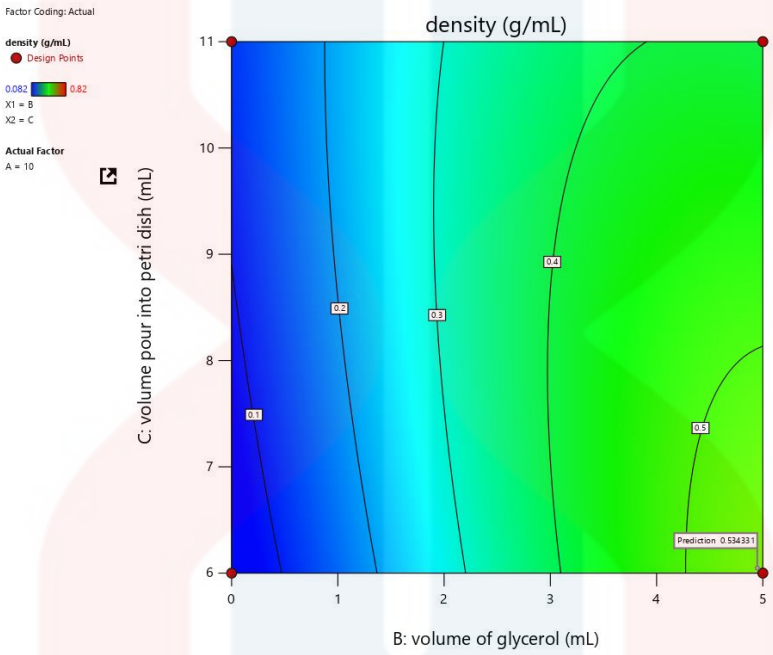


Figure 4.5: Contour plot for density response

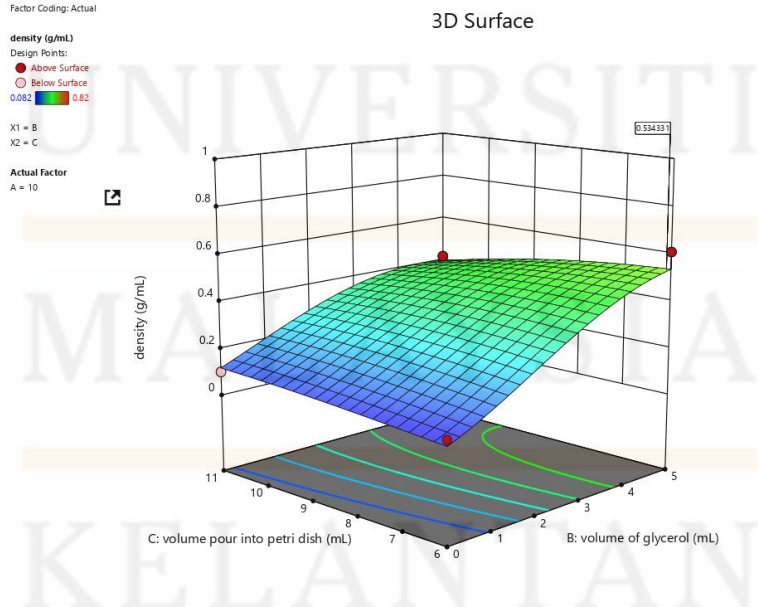


Figure 4.6: 3D surface plot for density response

4.1.3 Moisture Content Response Analysis

In table 4.6, the model summary statistics for moisture content response suggested quadratic model. The value for R^2 is 0.9600 and adjusted R^2 is 0.9150 which is deemed acceptable. The predicted R^2 is 0.2589 which is low indicating that the model is overfitting. Cubic model is not suggested as it is labelled aliased.

Table 4.6: Model summary statistics

Source	Std. Dev.	R^2	Adjusted R^2	Predicted R^2	PRESS	
Linear	16.44	0.2637	0.1059	-0.4470	7432.90	
2FI	14.94	0.5219	0.2612	-1.3353	11995.88	
Quadratic	**5.07**	**0.9600**	**0.9150**	**0.2589**	**3806.88**	**Suggested**
Cubic	0.0000	1.0000	1.0000		*	Aliased

The model F-value of 21.33 implies the model is significant. There is only a 0.01% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. This signifies that only volume poured into petri dish squared (C^2) is insignificant terms. All data is recorded in table 4.7.

Table 4.7: ANOVA for moisture content response

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	4931.35	9	547.93	21.33	0.0001	significant
A-ratio of silica	187.78	1	187.78	7.31	0.0269	
B-mass of glycerol	1425.68	1	1425.68	55.50	< 0.0001	
C-volume pour into petri dish	227.30	1	227.30	8.85	0.0177	
AB	323.34	1	323.34	12.59	0.0075	
AC	663.21	1	663.21	25.82	0.0010	
BC	340.08	1	340.08	13.24	0.0066	
A^2	939.98	1	939.98	36.59	0.0003	
B^2	674.07	1	674.07	26.24	0.0009	
C^2	58.36	1	58.36	2.27	0.1702	
Residual	205.50	8	25.69			
Lack of Fit	205.50	3	68.50			
Pure Error	0.0000	5	0.0000			
Cor Total	5136.85	17				

In perturbation plot, factor C volume poured into petri dish shows the least significant changes when passing the reference point. Therefore, factor A ratio of silica as X1 - axis and factor B volume of glycerol as X2 - axis will be used and slice on factor C in figure 4.7.

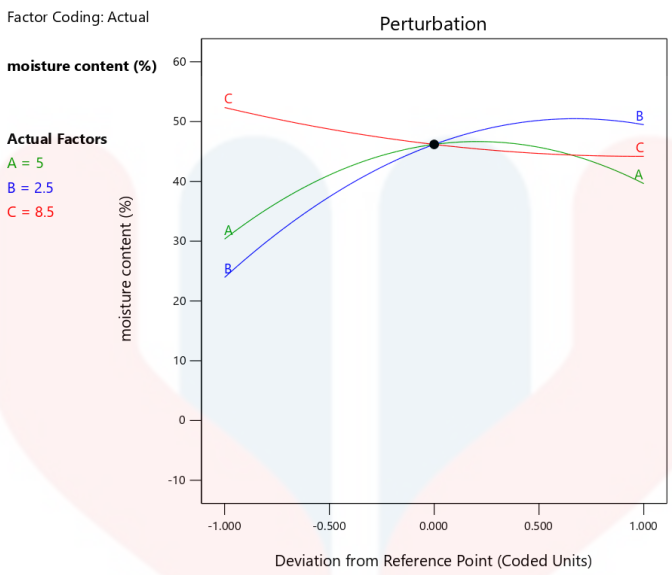


Figure 4.7: Perturbation plot for moisture content response

In contour and 3D surface graph, this data is presented in a maximum form of response. The correlation between the factor is that the higher the amount of ratio silica added, the moisture content becomes lower. This is due to the interaction between glycerol within starch – silica matrix that decreases the availability of hydroxyl group to form a bond with water. Then, this allow the matrix to form in a less hygroscopic state, Nafchi et al., (2013) done this study by using starch from potato and commercial silica. Comparing this result with study done by Oluwasina et al., (2021), the study that used silica from bamboo leaves identified that the chemical state of silica may be a contribution when incorporated with starch matrix that leads to less moisture. Higher hydrogen bonds are formed between silica – starch matrix and prevent free movement of water molecules interaction. The incorporation of silica replace empty sites on starch matrix that is usually filled with water (Torabi & Mohammadi Nafchi, 2013) that also uses potato peel and commercial silica. However, by increasing the volume of glycerol, the moisture content increases as well. This is due to the strong attraction of water molecules from hydroxyl groups in glycerol

that allows the bioplastic to retain water and develop hydrogen bonds in the structure (Tarique et al., 2021).

The prediction value for maximum moisture content response is 50.49% with ratio of silica added as X1 - axis is 4.98% and volume of glycerol added as X2 - axis is 4.97 mL This is presented in figure 4.8 and 4.9.

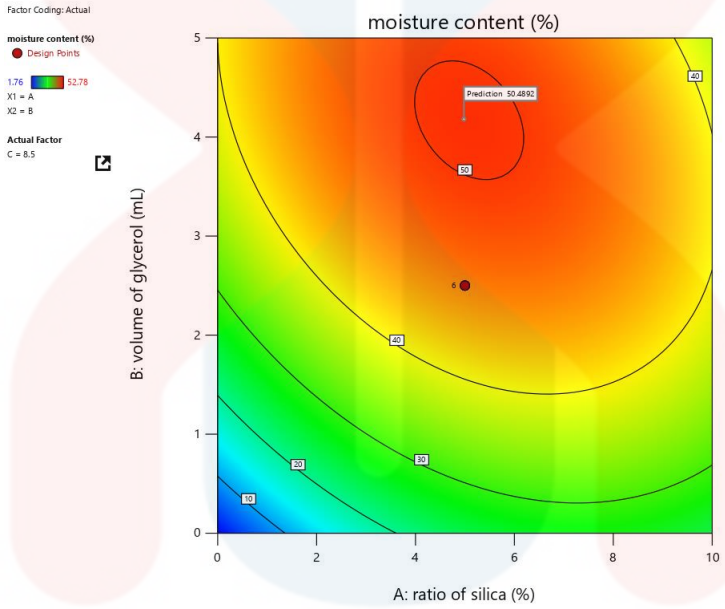


Figure 4.8: Contour plot for moisture content response

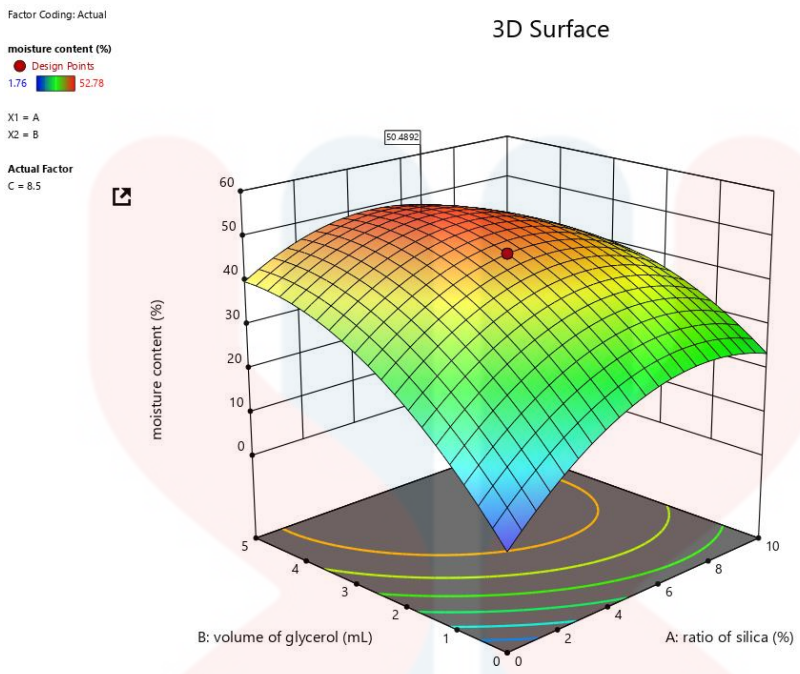


Figure 4.9: 3D surface plot for moisture content response

4.2 Optimization of Starch/Silica Bioplastic, SSB

A numerical response optimization technique is used to obtain the optimum formulation for starch bioplastic incorporated with silica. The main goal for constrained optimization were in target for ratio of silica, minimize volume of glycerol added and in target for volume poured into petri dish (Mosisa & Vighneswara, 2021). These factors are keeping thickness and density in target and minimize moisture content percentage as much as possible. The value is presented in table 4.8.

Table 4.8: Constraints for optimization

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
A: ratio of silica	is target = 10	0	10	1	1	3
B: volume of glycerol	minimize	0	5	1	1	3
C: volume pour into petri dish	is target = 8.5	6	11	1	1	3
thickness	is target = 1.83211	0.5	4	1	1	3
density	is target = 0.355153	0.082	0.82	1	1	3
moisture content	minimize	1.76	52.78	1	1	3

After the parameters and constraints were selected, a total of 22 solutions were generated. In order to analyse an optimum formulation, the average value from the 22 solutions was chosen for further analysis. The average values for the three factors were ratio of silica (10%), volume of glycerol (0.962 mL) and volume poured into petri dish (8.627 mL) that will result a thickness of 1.870 mm, density of 0.196 g/mL and moisture content of 31.224 % as an optimum response. Table 4.9 presents the numerical optimization solutions. Solution one was chosen as the optimum formula.

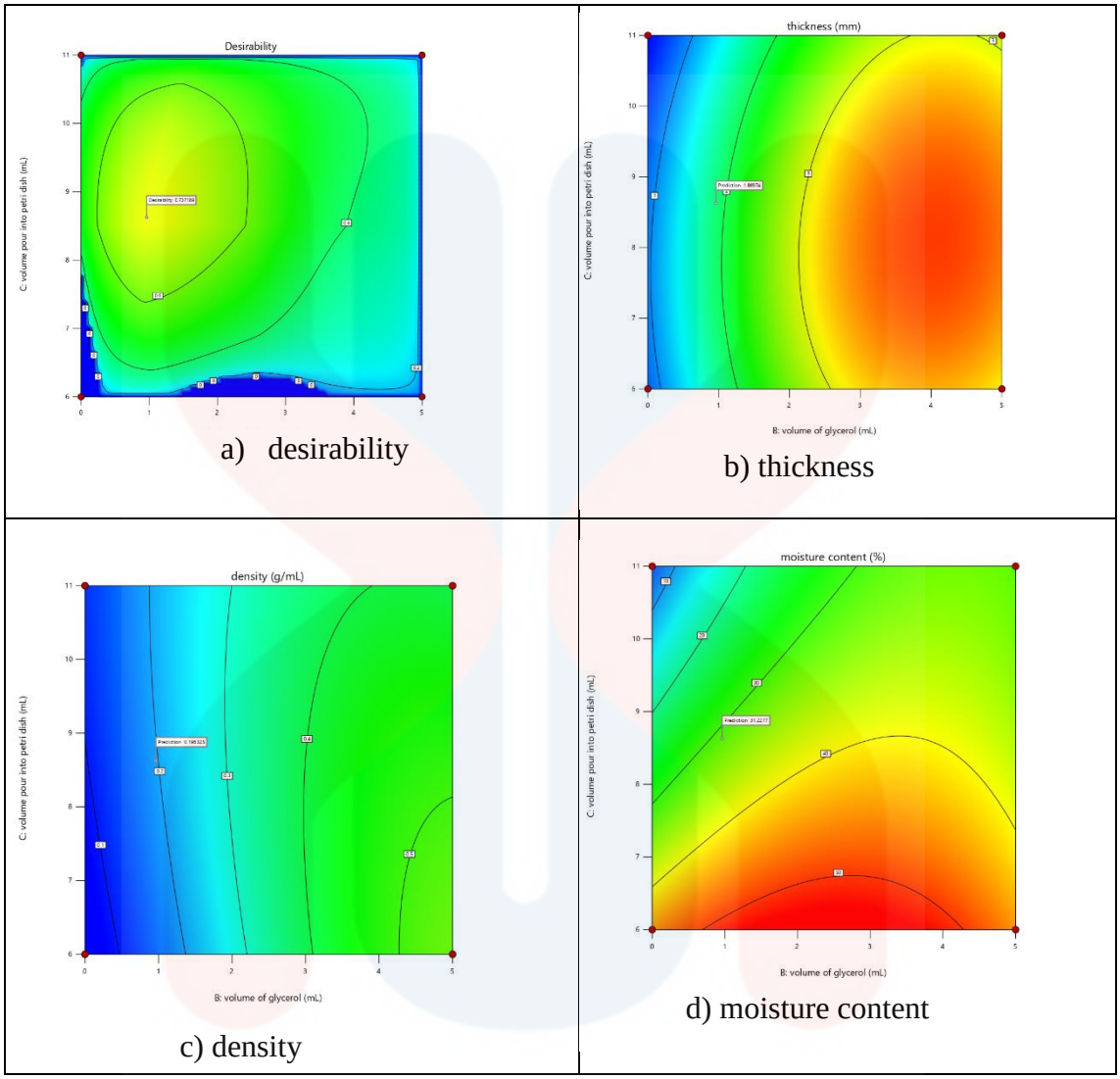
Table 4.9: Numerical optimization solutions

Number	Ratio of silica	Volume of glycerol	Volume poured into petri dish	thickness	density	moisture content	Desirability	
1	**10.000**	**0.962**	**8.627**	**1.870**	**0.196**	**31.224**	**0.737**	**Selected**
2	10.000	0.960	8.609	1.870	0.196	31.332	0.737	
3	10.000	0.965	8.648	1.870	0.197	31.101	0.737	
4	10.000	0.967	8.666	1.870	0.197	30.992	0.737	
5	10.000	0.958	8.588	1.870	0.195	31.457	0.737	
6	10.000	0.971	8.698	1.870	0.198	30.804	0.737	

7	10.000	0.954	8.551	1.870	0.195	31.679	0.737
8	10.000	0.975	8.732	1.870	0.199	30.611	0.737
9	10.000	0.950	8.513	1.870	0.194	31.915	0.737
10	10.000	0.978	8.756	1.870	0.199	30.471	0.737
11	10.000	0.989	8.833	1.870	0.201	30.039	0.736
12	9.932	0.969	8.651	1.870	0.197	31.305	0.735
13	10.000	1.003	8.928	1.870	0.204	29.522	0.735
14	10.000	1.010	8.971	1.870	0.205	29.293	0.735
15	10.000	1.014	8.571	1.928	0.201	31.979	0.734
16	9.889	0.981	8.728	1.870	0.199	30.997	0.734
17	10.000	1.066	8.923	1.933	0.211	30.024	0.732
18	10.000	1.100	9.085	1.940	0.216	29.232	0.729
19	10.000	1.059	9.246	1.870	0.212	27.910	0.728
20	10.000	1.176	9.413	1.949	0.226	27.770	0.718
21	10.000	1.477	8.500	2.392	0.252	35.414	0.701
22	10.000	0.736	9.174	1.561	0.177	25.733	0.697

The desirability for numerical optimization is 73.72 % for overall responses to create the obtain best criteria for SSB. The optimum values which is relatively closer to desirability (100 %) is 73.72 %. This means that the formulation is easy to achieve and yield the availability of better output. This optimization meets best desired criteria out of the 22 solutions.

The purpose of analysing for optimum formulation is to identify best value in all factors to provide better responses. The X1 – axis is factor C volume poured into petri dish and X2 – axis is factor B volume of glycerol. The ratio of silica is constant which is 10 % according to solution one. This data can be analysed on contour and 3D Surface plot presented in figure 4.10 and 4.11 that shows a) desirability b) thickness c) density and d) moisture content.



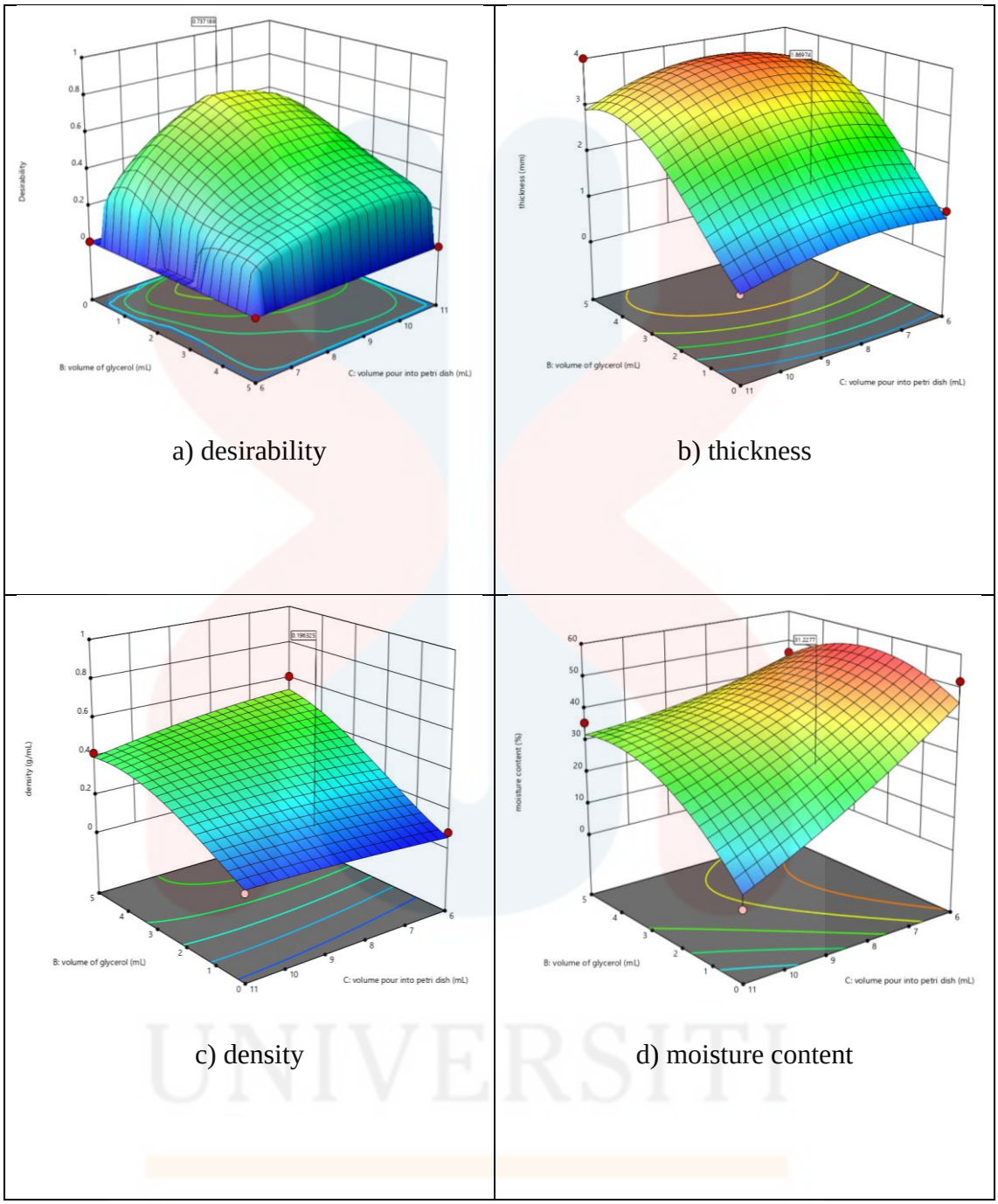
a) desirability

b) thickness

c) density

d) moisture content

Figure 4.10: Contour plot for optimization; a) desirability b) thickness c) density d) moisture content



a) desirability

b) thickness

c) density

d) moisture content

Figure 4.11: 3D Surface plot for optimization; a) desirability b) thickness c) density d) moisture content

In order to generate response prediction, solution one is chosen as the optimum formula. The confirmation is done by running solution one formula for three times to obtain the average value. Ratio of silica use is 10 %, the volume of glycerol is 0.962 mL and volume

poured into petri dish is 8.627 mL. The responses value obtained for three times were also recorded in the table. The data is presented in table 4.10.

Table 4.10: Response prediction and confirmation

Ratio of silica	Volume of glycerol	Volume poured into petri dish
10	0.962248	8.62648

Responses

thickness	density	moisture content
2	0.2	31.75
1.8	0.27	30.15
2.1	0.2	31.3

Based on the table 4.9, the optimum value obtained for all three responses are in between range given. The data mean for thickness response is 1.96466, density is 0.22217 and moisture content is 31.0667. Therefore, the model for optimum formulation is confirmed in table 4.11.

Table 4.11: Confirmation prediction

Solution 1 of 22 Response	Predicted Mean	Predicted Median*	Std Dev	n	SE Pred	95% PI low	Data Mean†	95% PI high
thickness	1.86974	1.83211	0.52780	3	N/A	1.01367	1.96466	2.89102
density	0.19633	0.19340	0.04770	3	N/A	0.11777	0.22217	0.28769
moisture content	31.2277	31.2277	5.06828	3	3.92881	22.1678	31.0667	40.2876

4.3 Chemical Reaction in Bioplastic

All green plants produce starch, which is a white, particle organic substance. Starch is a distasteful, soft white powder that is immiscible with water, alcohol, and other liquids. The starch molecule with the chemical formula $(C_6H_{10}O_5)$ n.is a polysaccharide made up of 1,4 connections between glucose monomers. The linear polymer amylose is the most basic type of starch, while amylopectin is the branched form (Pérez-Pacheco et al., 2016). Silica or silicon dioxide is formation of silicon and oxygen. Silica is often similar in formation but have configurations change. The two main type of silica are crystalline and amorphous silica. Silica can also form other atoms when it reacts with other compounds (Lunevich, 2019).

In figure 4.12, the dispersion of starch is difficult as the amount of starch used is high. The particles and crystalline structures are complicated thus took longer time to disperse as the gelatinization temperature increases. The small amount of plasticizer used allow the volume of starch macromolecules to roam freely decreases, thus forming a stronger interaction between polymer chain and increases the strength and stiffness of the bioplastic. The reduction of glycerol strengthens the hydrogen bond in the starch molecules and with glycerol as well. The crystallinity in starch also increases after gelatinization where the bonding of C-O-H is at the highest. This result allow increment in mechanical properties (Abdullah et al., 2019). When silica is introduced to the starch matrix, the intermolecular reaction occurred between the two compounds. Silica particles demolished the crystalline network of starch to reduce crystallinity. The smaller the particles of silica increase the dispersion rate in the starch matrix and interrupts the network structure, thereby forming less crystallinity (Zhang et al., 2018).

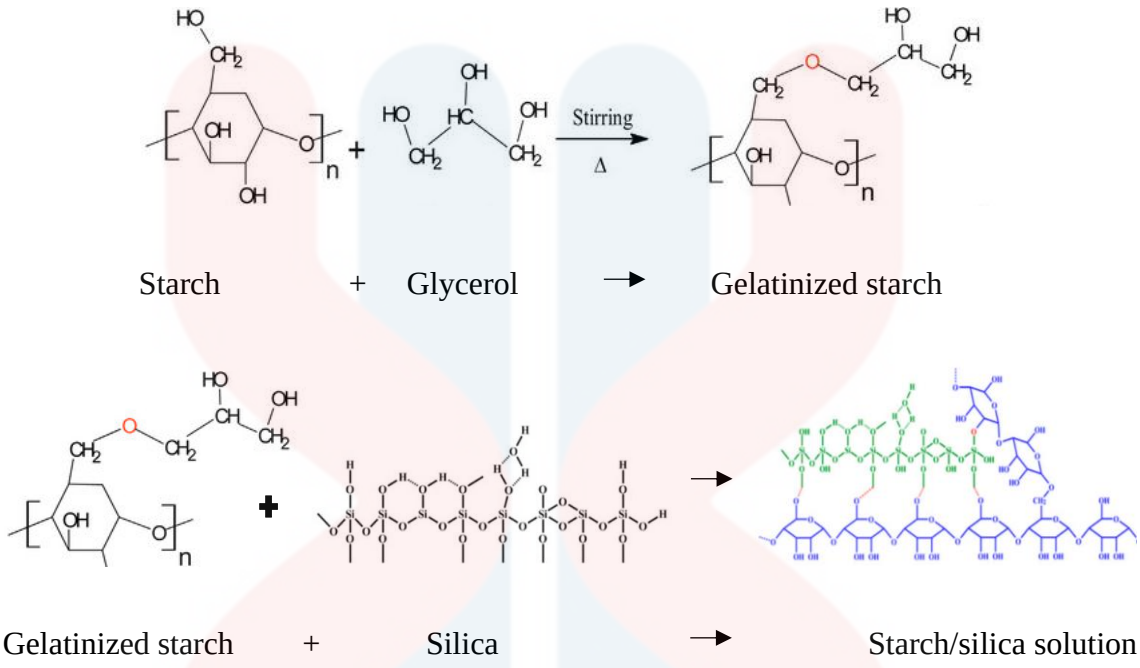


Figure 4.12: Chemical interaction in the bioplastic

4.4 Sensory Evaluation

Table 4.12 displays the sensory evaluation for each bioplastic formulation including texture, opacity and colour. Based on the observation, the texture, opacity and colour are different according to different formulation. In texture properties, formula that exhibit high moisture and sticky is due to the volume of glycerol added. Higher amount of glycerol resulting in poor homogenization between glycerol and other compounds. Increasing amount of glycerol increases the water content in starch – silica matrix (Basiak et al., 2018). In this condition, the hydrophilic polymeric chain expands, and alter the structure. The monolayer water content for each bioplastic sample is higher as amount of

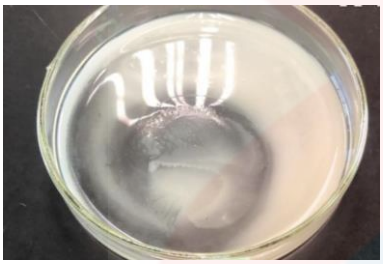
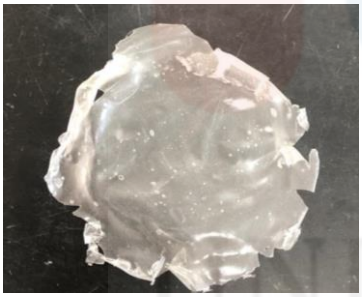
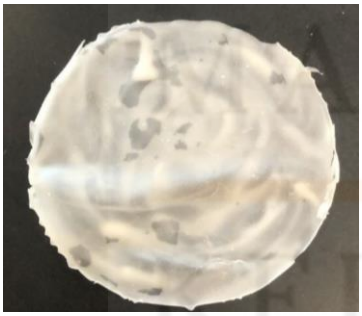
glycerol added increases. This factor is due to the characteristic of hygroscopicity of glycerol proven by study (Tavares et al., 2020).

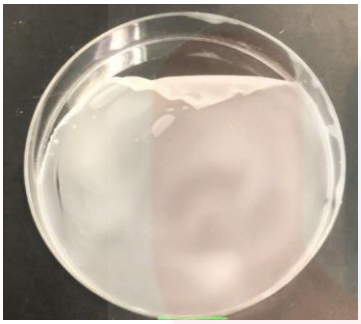
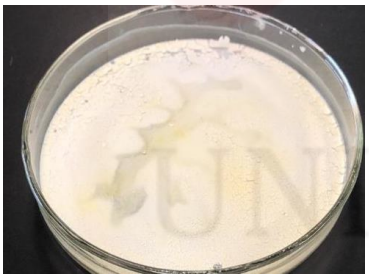
Furthermore, variance amount of glycerol will portray different effect on bioplastic sample. Increasing content of glycerol disrupt the hydrogen bonds that is responsible for balancing the structure of starch network thus reducing its cohesiveness (Basiak et al., 2018). However, in formulations R5, R7, R12, and R14, the bioplastic sample exhibit dry and brittle texture. These stated formulations were carried out with zero amount of glycerol. Absence of glycerol increases the brittleness and reduce flexibility of bioplastic sample (Lutfi et al., 2017). Therefore, the desired amount of glycerol added to these formulations is 2.5 mL as it can display good flexibility and lesser moisture on the bioplastic sample. This can be observed for formulation R2, R3, R4, R6, R8, R9, R11, R16 and R18.

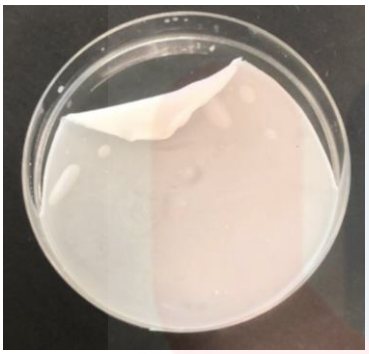
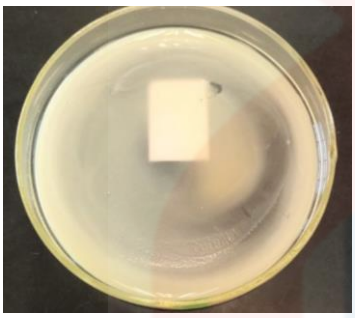
The observation for opacity and colour is vital as these attributes is accounted in packaging or films. Maximum transparency is desired in bioplastic attribute. In general, the opacity and colour of the bioplastic samples is influenced by different ratio of silica and volume of glycerol added. The transparency of bioplastic is at maximum when the amount of silica added is at 5% with 2.5 mL glycerol. However, transparency decreases when the ratio of silica added increases. Increasing ratio of silica will increase the opacity of the bioplastic sample, therefore turning the colour into more white (de Azêvedo et al., 2021). However, high volume of glycerol will increase transparency but failed to exhibit other desired quality such as desired tensile strength and elongation (Abdullah et al., 2019). This due to anti-plasticization behaviour exhibit by glycerol when volume of glycerol is beyond critical value (Abdullah et al., 2019). The opacity of the bioplastic also is influenced by the increasing amount of glycerol, as higher amount of glycerol added,

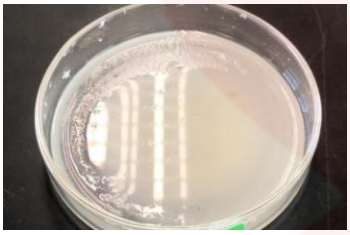
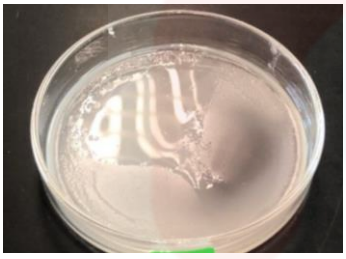
the opacity decreases (Nordin et al., 2020). Sensory evaluation data is presented in table 4.12.

Table 4.12 Sensory evaluation of SSB

Formulations	Observation		
	Texture	Opacity	Colour
R1 	• Very moist • Sticky	Transparent	No colour
R2, 6, 9, 11, 16, 18 	• No moist • Very flexible	Transparent	No colour
R3 	• Slight moist • Flexible	Translucent	Almost all white

R4 	• Slight moist • Brittle	Translucent	White
R5 	• Very dry • Brittle	Opaque	White
R7 	• Dry • Brittle	Opaque	White

R8	• Slight moist • Flexible	Opaque	White
			
R10	• Very moist • Sticky	Transparent	White
			
R12	• Very dry • Brittle	Opaque	White
			
R13	• Very moist • Sticky	Translucent	Almost all white
			

R14 	• Very dry • Brittle	Opaque	White
R15 	• Very moist • Sticky	Translucent	White
R17 	• Very moist • Sticky	Translucent	Almost white

4.5 Thermogravimetric Analysis of Optimal Starch/Silica Bioplastic, Optimal SSB

The purpose of investigating thermal analysis for silica/starch bioplastic is to determine the changes in weight with temperature serves as function. This analysis is done for the optimum formula obtained from Design Expert Software. The weight change in percentage and temperature with unit degree Celsius. The weight change profile is measured when the sample is exposed to heat in a controlled environment. In TGA, the conditions that influence the change of weight for sample are weight and volume of sample taken, physical form of sample, shape of sample holder, the atmosphere where the analysis is execute, interior chamber pressure and rate of heating or cooling (Loganathan et al., 2017). The application of dynamic thermogravimetric analysis is used in this study where the temperature will be increase continuously at a specific heating rate. The data implies that a total of 70. 9016 % of weight loss occurred during heating process. The residue left is 29.0928 % which may indicate any ash or external impurities left in the crucible. The initial weight loss started at 43.09 ^{o}C and ceased at 497.48 ^{o}C. The midpoint 312.78 ^{o}C lies in between starting and ending point of massive weight loss from the sample.

As presented in Figure 5.3, the initial weight loss signifying the evaporation of moisture content (Ashok & Rejeesh, 2018). This also correspond with the volatilization of glycerol as it contribute to the moisture content (Liu et al., 2021). A massive weight loss is recorded around 280 ^{o}C to 340 ^{o}C implying the decomposition of SSB. This also indicates that the bioplastic only consists of one glass transition temperature (T_g). Higher value of transition temperature leads to the higher barrier properties.

One glass transition temperature (T_g) indicates the silica compound is well blend within the starch matrix and consistent (Amin et al., 2019). The weight loss was constant afterwards until the temperature reach 500 ^oC, indicating the polymer was degraded completely. In comparison with the study done by Ashok & Rajeesh (2018), starch bioplastic without incorporation of silica has lower thermal resistance. The raw bioplastic degrades completely at 330 ^oC. In addition, study done by Oluwasina et al., (2019) using silica from bamboo leaves also recorded highest temperature at 300 ^oC implying starch-based bioplastics degrade faster without filler reinforcement. Another study also recorded weight loss between 300 ^oC and 360 ^oC with starch from potato and silica from sugarcane waste ash (de Azevedo et al., 2020). The study further proves that the incorporation of silica and starch bioplastic increases the thermal stability and resistance. Lower weight loss was also recorded and thermal degradation rate was significantly improved with incorporation of silica (Ashok & Rejeesh, 2018). The thermal decomposition rate is enhanced with the addition of silica to the starch matrix due to the ability of silica building a more stable network leading to more energy needed to demolish it (Liu et al., 2021). This statement is further supported by Kappert et al., (2014), the silica used was (TEOS) tetraethoxysilane-derived. It is recorded that highest weight loss for thermo gravimetric in silica is 375 ^oC due to dihydroxylation of silanol groups. This can be seen in figure 4.13.

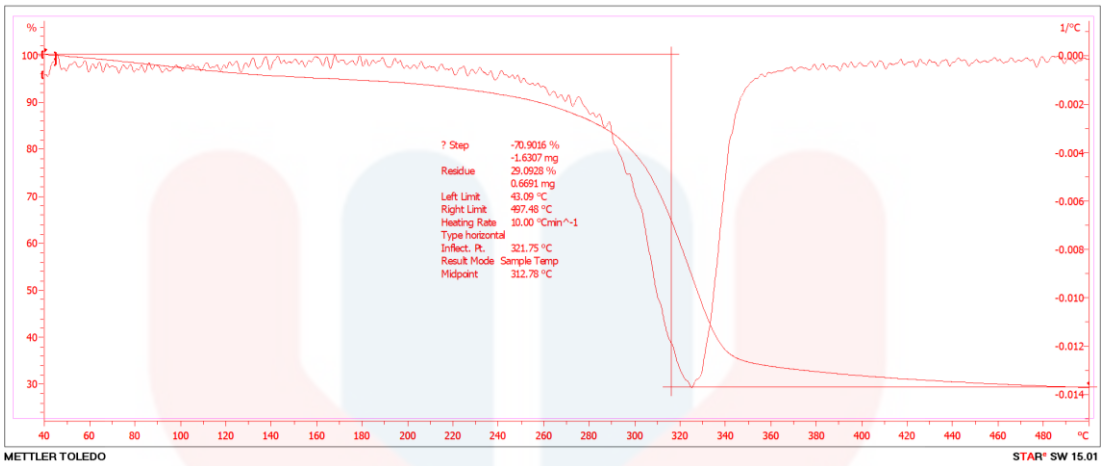


Figure 4.13: Thermal gravimetric analysis of optimum SSB

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a summary to this research, the relationship between three factors, ratio of silica, volume of glycerol and volume poured into petri dish with responses thickness, density and moisture content was obtained. Volume of glycerol and volume poured into petri dish exhibit notable affect towards the thickness and density. However, ratio of silica and volume of glycerol significantly affect the moisture content. The thickness increases as volume of glycerol and volume poured into petri dish increases. Furthermore, the density of SSB increases as volume of glycerol and volume poured into petri dish increases as well. This is also due to silica content in the bioplastic. Meanwhile for moisture content, it decreases as higher ratio of silica and increases when higher volume of glycerol added. Bioplastic from sweet potato peel starch incorporated with silica from rice husk was developed to find the optimum bioplastic by observing the thickness, density and moisture content properties. Based on the result produced by Design Expert Software version 13, it is acceptable to claim that the second objective of this study is achieved.

The quadratic model was chosen for all responses exhibit a statistically significant model for all factors that were developed to explain the relationship between thickness, density and moisture with the three factors. SSB formulation was optimized using central composite design in response surface methodology and statistical model display a good fit with R^2 data. The data for thickness $R^2 = 0.8946$, density $R^2 = 0.9516$ and moisture content $R^2 = 0.9600$ with low standard deviation respectively portray the significant effect on the conditions for the optimal formula. ANOVA results signifies the effect of each factor were significant and quadratic models were chosen to predict the responses.

The optimal formulation that was selected using numerical optimization exhibit a combined value of desirability (73.72 %). The value of data means for thickness (1.96466), density (0.22217) and moisture content (31.0667). The data mean for each response is aligned within the range of predicted mean. Therefore, the optimal formula is confirmed.

The third objective of this research was also achieved. Thermal gravimetric analysis was done subsequently after the starch/silica formulation was developed. The bioplastic that incorporated with silica display significant improvement in thermal stability within the heating rate. Massive drop of weight at 280 ^oC to 340 ^oC signify one glass transition temperature indicating good dispersion between silica – starch matrix in the bioplastic sample. In this study, it was found that silica can be a great reinforcement filler towards starch-based bioplastics. Silica was proven to improve thermal stability, reduce moisture content, improve density and thickness of the bioplastic as well. However, the addition of plasticizer such as glycerol and starch must be taken account. Costly fillers now can be replaced with silica from rice husk which is cheaper and greener.

5.2 Recommendation

It is recommended that further research develop more alternative methods to utilize sweet potato peel and rice husk in order to reduce agriculture waste and increase economic interest. This study also will label new value towards waste that usually were being discarded. Besides that, different plasticizer such as sorbitol or ethylene glycol can also be tested out to determine SSB with best mechanical and thermal properties. Last but not least, different ratio of silica can be applied towards starch-based bioplastics research to increase quality of the bioplastic. Thermal stability of this bioplastic can also be improved if more uniform size of silica is used leading to better dispersion rate. Higher dispersion rate will allow more hydrogen bond to react with silica and starch molecules and improve the overall thermal performance (Liu et al., 2021).

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APPENDIX

Figure A.1: Sweet potato peeling process

Figure A.2: Calcination of rice husk

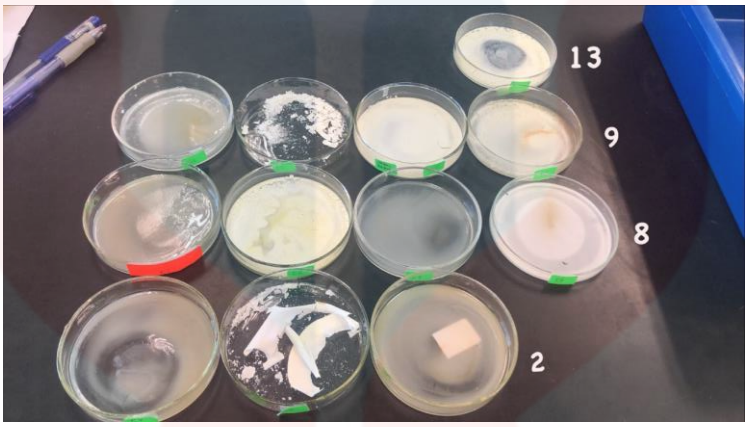

Figure A.3: SSB on first trials