Effects of Cellulose, Bentonite and Hybrid Cellulose/Bentonite Fillers on Morphology, Ambient and Low Temperature Tensile Properties of Thermoplastic Starch Composites for Refrigerated Food Packaging Application

by

Ahmed Moh. T. L. Ashafee

(1631622003)

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School of MaterialsEngineering

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LIST OF ABBREVIATIONS

TPS	Thermoplastic starch
OH	Hydroxide
SEM	Scanning Electron Microscopy
FESEM	Field Emission Electron Microscopy
FTIR	Fourier Transform Infrared
XRD	X-ray Diffraction
DSC	Differential Scanning Calorimetric
PET	Polyethylene terephthalate
PLA	Polylactic acid
SiO_4	Silicates
Ca	Calcium
Mg	Magnesium
MMT	Montmorillonite
Tg	Glass Transition Temperature
CNF	Cellulose nanofibers
BC	Bacterial nanocellulose
Bent	Bentonite

LIST OF SYMBOLS

%	Percentage
wt%	Weight percentage
°C	Degree Celsius
g	Gram
J	Joule
Kg	Kilogram
m^3	Cubic Metre
mm	Milimetre
min	Minimum
mg	Miligram
ml	Milimetre
cm^3	Cubic centimetre
ΔH_f	Enthalpy of fusion

Kesan – kesan Pengisi Selulosa / Bentonit dan Selulosa / Bentonit Hibrid ke atas Morfologi , Sifat – sifat Tegangan Ambien dan Suhu Rendah Komposit Kanji Termoplastik

ABSTRAK

Kanji termoplastik (TPS) ialah satu plastik berasaskan bio yang boleh terbiodegradasi dan diperbaharui yang mempunyai potensi yang basar untuk fabrikasi filem yang boleh dimakan dan mesra alam untuk aplikasi pembungkusan makanan simpanan peti sejuk. Di dalam kajian ini, penambahbaikan di dalam sifat-sifat tegangan di bawah suhu ambien dan rendah disasarkan dengan penambahan pengisi-pengisi hibrid. Komposit TPS yang mengandungi 5 % berat pengisi hibrid bentonit / selulosa (Bent/Selulosa) di dalam nisbah berlainan (100:0, 80:20, 60:40, 40:60, 20:80 dan 0:100) disediakan melalui proses penuangan filem. Proses ultra-sonik telah dilakukan untuk menambahaik penyebaran pengisi di dalam matrik TPS dan meningkatkan interaksi pengisi-matrik. Morfologi pengisi di dalam keadaan asal dan terultrasonikasi dicirikan manakala sifat-sifat mekanikal dan termal TPS tanpa pengisi dan komposit-komposit TPS masing-masing dinilai dan dibandingkan dengan ujian tegangan dan analisis DSC.

Keputusan menunjukkan bahawa bentonit terultrasonikasi mempunyai bentuk yang lebih berplat dengan platelet-platelet yang lebih bercerai dan seragam jika dibandingkan dengan bentonit asal. Sebaliknya, selulosa menunjukkan pengurangan di dalam saiz gentian (diameter dan panjang) setelah proses ultrasonikasi. Perubahan-perubahan di dalam morfologi kedua-dua bentonit dan selulosa menghasilkan penyebaran dan interaksi pengisi yang lebih baik dengan rantaian molekul TPS disebabkan luas permukaan pengisi yang lebih besar. Sifat-sifat tegangan TPS dan komposit-komposit TPS dinilaikan setelah sampel-sampel di pra-kondisi pada keadaan ambien dan 2°C. Pengisi-pengisi terultrasonikasi menyebabkan peningkatan yang lebih baik di dalam sifat-sifat tegangan apabila sampel-sampel dipra-kondisi pada keadaan ambien dan 2°C. TPS telah mencapai kekuatan tegangan dan pemanjangan pada takat putus yang tertinggi (ambien dan 2°C) apabila bent/selulosa hibrid terultrasonikasi di dalam nisbah 80:20 ditambah ke dalam strukturnya. Apa yang mengejutkan, komposit TPS tersebut juga menunjukkan kekuatan tegangan dan pemanjangan takat putus yang lebih tinggi apabila dipra-kondisi pada 2°C. Ini boleh jadi disebabkan kesan interaksi-interaksi suhu rendah di antara kanji, pemplastik (gliserol dan air) dan pengisi-pengisi hibrid. Analisis DSC membuktikan perubahan di dalam penghabluran dan ciri-ciri dinamik rantaian molekul TPS yang menyumbang di dalam meningkatkan pemanjangan takat putus dan keliatan biopolimer tersebut, walau disimpan di dalam keadaan sejuk/dipetisejukkan. Adalah boleh dikonklusikan bahawa komposit TPS dengan bentonite/selulosa hibrid bernisbah 80:20 mempunyai potensi untuk dibangunkan dalam aplikasi pembungkusan makanan simpanan peti sejuk. Oleh itu, penyelidikan lanjut ke atas sistem TPS komposit ini perlu diteruskan di masa hadapan.

Effects of Cellulose, Bentonite and Hybrid Cellulose/Bentonite Fillers on Morphology, Ambient and Low Temperature Tensile Properties of Thermoplastic Starch Composites for Refrigerated Food Packaging Application.

ABSTRACT

Thermoplastic starch (TPS) is a biodegradable and renewable bio-based plastic which has great potential for the fabrication of edible and biodegradable film for refrigerated food packaging application. In this study, improvement in the TPS ambient and low temperature tensile properties was aimed by the incorporation of hybrid fillers. TPS composites incorporating 5wt% bentonite / cellulose (Bent/Cellulose) hybrid fillers in different ratios (100:0, 80:20, 60:40, 40:60, 20:80 and 0:100) were prepared by film casting process. Ultra-sonication process was done to improve the filler dispersion in the TPS matrix and enhance the filler-matrix molecular interactions.The morphology of the pristine and ultra-sonicated fillers was characterized while the mechanical and thermal properties of the neat TPS and TPS composites were evaluated and compared by tensile test and DSC analysis, respectively.Results indicated that the ultra-sonicated bentonite possesses more plate-like shape with delaminated and more uniform platelets as compared to the pristine bentonite.On the other hand, cellulose exhibits reduction in the fiber size (diameter and length) upon the ultra-sonication process.Changes in the morphology of both bentonite and cellulose resulted in greater filler dispersion and interactions with the TPS molecular chains due to the obtained higher filler surface area.Tensile properties of the neat TPS and TPS composites were evaluated after the samples pre-conditioned at ambient and 2°C. Ultra-sonicated fillers resulted in greater improvement in the tensile properties when the samples pre-conditioned at both ambient and 2°C.The TPS has achieved its highest tensile strength and elongation at break (ambient and 2°C) when the ultra-sonicated hybrid bent/cellulose in 80:20 ratio was added into its structure.Surprisingly, the TPS composites also show higher tensile strength and elongation at break when pre-conditioned at 2°C. This could be due to the effect of low temperature interactions between the starch, plasticizers (glycerol and water) and the hybrid fillers. DSC analysis proved the changes in the crystallinity and dynamic characteristic of the TPS molecular chains which benefit in enhancing the biopolymer elongation at break and toughness, even when stored at cold/refrigerated condition. It can be concluded that the TPS composite with the hybrid bent/cellulose ratio of 80:20 has potential to be further developed for refrigerated food packaging application. Therefore, further investigation on this TPS composite system should be continued in the future.

CHAPTER 1

INTRODUCTION

1.1 Research Background

The advancement of science and technology, as experienced in modern times, is responsible for the synthesis of petrochemical-based plastics for wide variety of applications, including for food packaging. Although, these synthetic plastics have high mechanical and barrier properties, they are non-biodegradable bringing high potential for major threats to both humans and the environment(Babu, O'Connor & Seeram, 2013). These plastics will take millions of years to degrade under natural atmosphere and weathering. During combustion, it can produce toxic byproducts which pollute the atmosphere. Due to these ecological concerns and concomitant depletion of petrochemical resources, replacing the synthetic polymers with biopolymers as biodegradable renewable resources is therefore, mandatory(Babu, O'Connor & Seeram, 2013; Mohammadi, Moradpour, Saeidi, & Alias, 2013; Van Soest, Hulleman, De Wit & Vliegenthart, 1996; Xie et al., 2014).Notably, the most useful biopolymer is 'starch' since it can be easily processed and accessible as renewable material. Also, starch has good ability for thermal processing. Maize, potato, rice, wheat and tapioca are the commonly used starches and they are produced in a global form of sphere granules, within a size of 1 μm and 100 μm. The species of the starch plant determine the composition, size and the obtainable amount of granules (Perez, Baldwin, & Gallant, 2009).

Through industrial process, homogenous amorphous thermoplastic material, i.e. the thermoplastic starch (TPS), are derived from starch through the plasticization process. The plasticization process is the de-structuration of the semi crystalline granular structure by a plasticiser. This is done under thermo-mechanical processes like extrusion, internal mixing and injection molding (Mohammadi, Moradpour, Saeidi, & Alias, 2013; Van Soest, Hulleman, De Wit & Vliegenthart, 1996; Xie*et al*., 2014). According to some literatures (Perez, Baldwin, & Gallant, 2009, Xie*et al*., 2014), plasticised starch is referred to as thermomechanoplastic, other than being thermoplastic. The conventional methods of extrusion, internal mixing, injection molding, blow molding, film blowing, foaming and thermoforming can be used in processing TPS (Mohanty, Misra & Hinrichsen, 2000; Tharanathan, 2003; Vaidya & Bhattacharya, 1994). However, low mechanical properties of TPS have been identified as a possible factor for its non-suitability in some applications. It is on this basis that various types of fillers and nano fillers are suggested to be added into the TPS structure for improving the biopolymer's mechanical properties. Layered silicates such as montmorillonite, bentonite, hectorite and fluoromica are common clay based nano filler used to reinforce the TPS. Other types of filler/nano filler being used are starch nanocrystals, carbon nanotubes, metal oxide nanoparticles and cellulosic fibers(Dufresne& Vignon, 1998; Luduena, Alvarez & Vazquez, 2007).

Bentonite is a naturally-occurring material with clay mineral smectite as its predominant composition. They occur in layers between other types of rocks, and are formed by altering volcanic ash in a marine environment. The most widely available bentonite is the dioctahedral smectite in its mineral montmorillonite, with possible occasional experience of other forms of smectite. The needed properties in bentonites are influenced by the presence of smectite, with the nature of the exchangeable cations

in the interlayer as possible factor that can also influence the properties (Averous, 2004).

Cellulose is a polymer made from repeated end-to-end glucose molecules which can be up to hundreds and 10,000 glucose units in length. It is an organic compound with the formula n, a polysaccharide consisting of a linear chain of several hundred to many thousands of β linked D-glucose units. It is of similar structure with starch and glycogen which are also complex carbohydrates. Other products from multiple subunits of glucose are polysaccharides. However, the linkage pattern of the glucose molecules is the core difference between cellulose and other complex carbohydrate molecules. Also, cellulose differs from starch, which is a coiled molecule, because it is a straight chain polymer of long and rod-like shape molecules. Due to this structural difference, cellulose cannot be broken down into glucose subunits by any enzyme of animal origin.

It is observable that more stringent material property requirements are requisite in choosing suitable candidate materials for certain applications. Therefore, the use of hybrid fillers (more than one type of filler) in biopolymer-based composites has started to increase (Criado, Caputo, Roberts, Castro, & Barneix, 2009). The benefits can be obtained from the synergistic effects that the hybrid fillers can provide from the combination of both fillers properties. With regard to this matter, this study has proposedthe use of hybrid fillers from bentonite and cellulose fiber to reinforce TPS composites. The use of inorganic (bentonite) and organic (cellulose fiber) was postulated to provide durable and compatible fillers in reinforcing the TPS. The mechanical and barrier properties can be improved by the addition of the inorganic clay fillers, in which it can also reduce the cost of material production through replacement of some portion of the starch composition. On the other hand, the use of natural fiber as co-filler was due to its compatibility with TPS as both are organic, bio based materials.

Therefore, it was expected that good fiber-matrix interactions would improve the mechanical properties of the host TPS. It was hypothesized that the combination of bentonite and cellulose fiber as hybrid fillers can enhance both ambient and low temperature tensile properties of the TPS host material. Studies on morphology and properties of TPS biocomposites incorporating hybrid fillers were performedto understand the structure-performance relationship of the materials and their viability for refrigerated food packaging application.

1.2 Problem Statement

In this current era, majority of the material consumed for food packaging are particularly non-biodegradable synthetic plastics. This is the reason why more plastic materials eventually buried in landfills than other types of materials and create a major issue of global environment(Piringer& Baner, 2008). Furthermore, recent survey on the industrial prospect claimed that the conventional synthetic plastics used for packaging will be much more expensive in the future due to significant increase in petroleum prices (Luijsterburg& Goossens, 2014; Olajire, 2014). Due to these concerns, bio-based resources are currently being used for the development of edible and biodegradable packaging films. The use of natural bio-based polymers is safer to human health and can reduceplastic wastages(Tharanathan, 2003). However, the usage of edible and biodegradable polymers are rare, reason being, the performance related problems (such as low mechanical properties, brittleness, poor gas and moisture barrier), processing (such as low heat distortion temperature), and cost. Thermoplastic starch, for example, has gained serious attention as biodegradable thermoplastic polymer. But, its poor performance causes severe issues of water sensitivity, limited mechanical properties

(Vaidya & Bhattacharya, 1994) andhigh fragility, over time(Dufresne & Vignon, 1998). Their low mechanical properties are major concern, especially when exposed to hydrolytic, oxidative and high temperature conditions. The organic nature of TPS, in terms of easy-aging and degradation during usage and storage, is also to be considered in food packaging applications because it may result in the reduction of quality and lower shelf life of the TPS-based products.

In view of this, improving the mechanical properties of the TPS plastic is urgently important in order to develop sustainable packaging material. Findings from previous studies revealed that layered silicate nanofillers such as bentonite and montmorillonite have the ability to improve mechanical and barrier propertiesof the TPS if dispersed homogenously in the matrix (Muller et al., 2012).The adoption of nanotechnology on this biopolymer has the potential to further improve the properties and lowered the production cost (Sorrentino, Gorrasi & Vittoria, 2007). For instance, exfoliation and dispersion of the clay particles into individual nano-size layers can more efficiently enhanced the mechanical and barrier properties of the TPS due to increased surface area for nanofiller-TPS interactions. In this study, bentonite clay was selected as filler material to reinforce the TPS. The main advantage of bentonite is that it is a naturally abundant material which composed of clay minerals formed from volcanic ash. In its pristinelayered silicate form, this filler can be easily dispersed in the host TPS because of its hydrophilic nature. This leads to stronger polar interactions, most importantly, in the hydrogen bonds formed between the silicate's –OH groups and the starch molecules.The use of cellulose fiber as co-filler with the bentonite was anticipated to provide greater toughness property to the TPS matrix. Cellulose and TPS can be combined together because both are organic based materials and chemically

compatible. The combination of both bentonite and cellulose as hybrid fillers can provide better reinforcement for TPS.

This study, therefore, investigates the ambient and low tensile properties of the produced TPS biocomposite films containing various ratios of cellulose/bentonite hybrid fillers. This is to determine the optimum cellulose/bentonite ratio to best improve the mechanical properties of the TPS.

1.3 Objectives of the Study

This project focusses on the morphology, tensile properties and crystalline behaviour of thermoplastic starch composite incorporating bentonite, cellulose and hybrid cellulose/bentonite fillers. The specific objectives of the study are:

i. To investigate the effect of ultra-sonication process on the morphology of cellulose, bentonite and cellulose/bentonite as hybrid fillers in the TPS matrix.
ii. To evaluate the ambient and low temperature tensile properties of TPS composites containing cellulose, bentonite and cellulose/bentonite hybrid fillers and the properties affected by changes in the crystalline behaviour of the materials.
iii. To identify the optimum cellulose/bentonite filler ratio for the production of TPS composites with improved ambient and low tensile properties.

1.4 Scope of the Study

Cellulose, bentonite and hybrid cellulose/bentonite were prepared as fillers for TPS matrixto form TPS composites using film casting technique. The cellulose and bentonite were dispersed using ultrasonic probe in a water medium before it is mixed and cast with the TPS matrix. Then, the non-pre-dispersed cellulose and bentonite fillerswere also prepared as fillers in the TPS matrix (as control samples) to compare the effectiveness of ultra-sonication process in dispersing the fillers in TPS and subsequently enhance the ambient and low tensile properties of the TPS.

Scanning electron microscopy (SEM), field emission electron microscopy (FESEM), Fourier Transform Infrared (FTIR)and X-ray diffraction (XRD) are techniques used in characterizing the structure and morphology of the fillers (before and after ultra-sonication) and the TPS composites. SEM and FESEM were used to analyze changes inparticle shape/size of the fillers upon ultra-sonication process. FTIR was performed toanalyze the functional groups of cellulose and bentonite fillers, the TPS and TPS composites. XRD was done to investigate dispersion level of the fillers upon ultra-sonication and after being incorporated into the TPS. Furthermore, it was used to characterize the crystallinity of the TPS and TPS composites.

The tensile test was used in determining the ambient and low temperature tensile properties of the neat TPS and TPS composites using the Instron machine. Differential scanning calorimetry (DSC) was performed to investigate thermal properties and crystallinity changes in the neat TPS and TPS composites after conditioned at low temperature (~2°C). Finally, the structure-property relationships of these materials werediscussedin chapter 4.

CHAPTER 2

LITERATURE REVIEW

2.1 Bio-plastic for Food Packaging Application

The world summit on food security in 2009 reported that by 2050, the need for food production would have increased by 70 % in order to feed the anticipated 9 billion people (Khan, *et al*. 2010). Although, improving crop yield is one aspect of meeting this increased food supply needs, the packaging, shipping and transportation are also important, especially with the record of substantial food loss to spoilage during storage and packaging (Sgolastra, Petrucci, Severino, Gatto & Monaco, 2015). In this context, food demands align with its packaging need, where million tons of food packaging made from plastics is produced each years (Piringer& Baner, 2008). Thin films, containers and coatings are used to cover processed foods and farm produces to extend their shelf life. However, majority of food industries still use petroleum-based plastics for the purpose of foodpackaging (Luijsterburg & Goossens, 2014; Piringer& Baner, 2008). Polyethylene terephthalate (PET), polyethylene and polypropylene are utilized to make a variety of films and containers for food, confectionary and beverage products.As these synthetic plastics are non-biodegradable in nature, waste disposal of foods' packaging plastics is causing increase in environmental issues to the global community every year (Gaelle, 2015). Therefore, many environmental analysts believe that environmentally deployable plastic has a bright future in replacing the conventional plastics for the food packaging industry (Gaelle, 2015; Olajire, 2014). The growing environmental awareness among the people, the rising of the pre-packaged

disposable meal and the anti-pollution legislation have driven the development of bio-based plastics that could be derived from natural and renewable resources, such as plant-based starch (Gaelle, 2015).

However, several concerns must be addressed prior to commercial use of bio-based food packaging materials. The degradation rates of the bio-plastic under various conditions, potential for microbial growth, changes in mechanical properties during storage and release of harmful compound into the packaged food are among the factors to be critically analysed. The packaging material must be composted completely in less than 200 days and leaving no toxic residue behind (Marcin, Agnieszka& Leszek 2009). Furthermore, the chemical structure, molecular weights, crystallinity and processing conditions of the bio-plastics must be investigated because these factors can affect the physical and mechanical properties of the packaging material as final product. The physical and mechanical properties required in packaging are generally dependent on the items to be packed and the conditions (or environments) in which the packages are be stored (Hottle, Bilec & Landis, 2013). Fundamental knowledge on the raw materials used for the development of the packaging material is therefore, crucial. The following subsections will discuss the fundamental aspects of starch-based bioplastic, as primary material in the process of food packaging together with its associated additive materials.

2.2 Starch

Starch mainly contains different type and structure of granuleswhile thegranules have their cell walls which separate them from each other. These separating cells are based on crystal bundles from inside and are scattered with formless starch lipids and

waxes. Additionally, these cells contain individual crystalline region. The schematic starch morphology and chemical structure is shown in figure 2.1. Basically, starch comprises of amylase and amylopectin at the stage of molecular level in the helical coils (Mohammadi, Moradpour, Saeidi&Alias, 2013). The former is a linear glucose molecule whereas the latter is a highly branched molecule with anhydroglucose units linked. One of the most important features of starch is its semi-crystalline structure. The degree of crystallinity of starch granules ranges from 15%-50% depending on their moisture content and source. The behaviour of starch is highly dependent on the composition of starch, specifically the amylose and amylopectin content(Perez, Baldwin & Gallant, 2009).

Starch can be found in all plant but when it comes to commercial production it is produced at a very limited scale especially in corn which is considered as the major starch source (Crosbie, 1991). Corn is the most significant and commercially available source of starch, among the great variety of crops, which typically comprise of about 25% amylose and 75% amylopectin. It is possible to determine a quantitative measure and property of starch by separating them in individual constituents by different ways from the reaction that leads to formation or division of the weight of molecule in various components (Wunderlich, 2011).

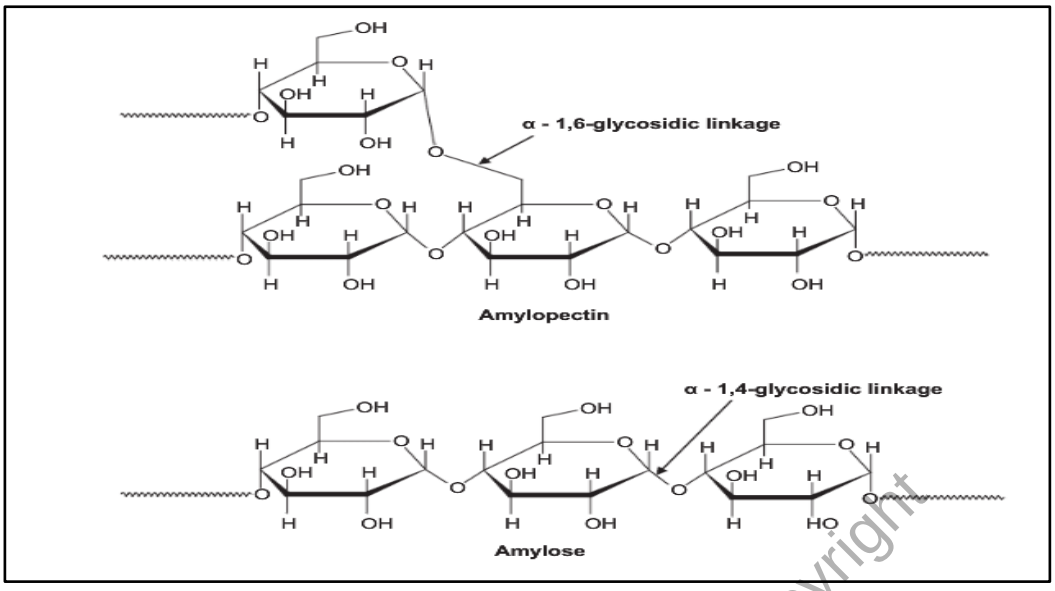

Figure2.1:Basic structure of starch

2.3 Thermoplastic Starch (TPS)

In modern life of human development and progress, a thermoplastic produced from biopolymer has been progressively developed to compete with the synthetic based thermoplastics. Starch is generally known in soil and water to be biodegradable. By producing biodegradable blends at low cost, starch equally utilized with a biodegradable synthetic plastic completely. Since starch is capable of remaining in a granular form in the plastic matrix, it therefore acts as filler. The limitation in processability of granular starch composites as a result of large particle sizes (5-100pm) is considered to be one of the critical issues. It is therefore clearly difficult to produce packing material from blown thin films of starch. Due to the above factor, incorporating poly-alcohols and/or water as plasticizers, thermoplastic can be made from starch called plasticized starch (PS) or thermo-plastic starch (TPS) by the application of thermal and mechanical energy through destructurization of molecules.

In the structure of the granules, the nature of crystalline and amorphous zones relies on the physical, processing and stability properties of TPSs. The process condition such as plasticizer content and temperature affects the change in granular starch. Glycerol and water are the most commonly utilized plasticizers. During various thermo-plastification processes, these plasticizers function as lubricant whereby the plasticizers enhance the movement of polymer chains and stabilize the retrogradation of TPS products (Mohammadi *et al*. 2013).

The thermoplastic starches have their own importance of providing various ranges of useful characteristics and relatively containconvenience of processing. However, inappropriately outdated and deep-rooted thermoplastics can create problems related to environment. These problems arise due toinstability and inability to degrade at applied rates even under optimal composting circumstances. Chemically, starch comprises many hydroxyl group (OH), which is commonly known as “hydrophilic group”. The thermoplastic starch has relatively high sensitivity for water in ambient state and it loses its characteristics as a mechanical property due to the drawbacks from the usage of TPS that becomes very limited in certain areas. At the same time, there are several ways through which water resistance of TPS can be reduced. These methods include selection of kind and content of plasticizers and mixing the same content with synthetic polymers. The alternative approach is to add reinforcing fillers. The addition of the filler may help in improving mechanical properties and also in resisting absorption of moisture by TPS (Babu, *et al*, 2013; Perez, *et al*, 2009). Such fillers are: cellulose fiber, clay, kaolin and pectin (Xie *et al*., 2014)