Synthesis and Characterization of Starch/Titania Nanocomposite from Native Sago and Potato Starches

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DECLARATION

No portion of the work referred to this dissertation has been submitted in support of an application for another degree of qualification of this or any other university of institutions of higher learning.

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Table of Content

List of Tables

List of Figures

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ABSTRACT

Sago and potatoes starches are common food sources for people in Sarawak. It can be found either in the wild or being cultivated especially in Sarawak. The aim of this study is to enhance utilization of these locally available agriculture products for the non-food application industries. Generally, in this study starch sponges were prepared from both types of the starches and then characterized using established characterization techniques. These starch sponges were mixed with titanium dioxide nanoparticles to form starch/titania nanocomposite. These nanocomposites were further heated under controlled conditions to form carbon/titania nanocomposite or nanostructured titania xerogels. The physical and chemical properties of these nanocomposites and xerogels were characterized by standard characterization techniques.

Keywords: sago starch, titanium dioxide, starch/titania nanocomposites, titania xerogels

ABSTRAK

Kanji dari sagu dan ubi kentang merupakan salah satu sumber makanan utama terutamanya bagi masyarakat Sarawak. Ia boleh diperolehi dari sumber semulajadi atau pun melalui teknik pengkulturan. Tujuan utama kajian ini dijalankan adalah untuk memperkembangkan lagi penggunaannya untuk tujuan industri selain penggunaannya yang sedia ada dalam industri makanan. Metodologi yang digunakan dalam kajian ini merangkumi penyediaan span kanji dari kedua-dua jenis kanji tersebut dan sifat fizikal dan kimianya ditentukan menggunakan teknik penentuan yang sedia ada. Seterusnya span-span kanji ini dicampurkan dengan nanopartikel titanium dioksida yang akan membentuk bahan nanokomposit kanji/titanium. Bahan nanokomposit ini kemudiannya dibakar dalam keadaan terkawal dan membentuk nanokomposit karbon/titanium dan titanium xerogel dengan struktur nano. Nanokomposit dan xerogel yang terhasil ini juga ditentukan sifat-sifat fizikal dan kimianya.

Kata kunci: kanji sagu, titanium dioksida, nanokomposit kanji/titanium, xerogel titanium

CHAPTER 1

1. Introduction

Native sago and potato starches can be considered as valuable agriculture products that not only can be used as food sources but also have huge potential for the production of starch based metal-oxide composite materials. Starch is also widely used in food industries and in other industry such as in pharmaceutical. Both materials are abundant and can be easily obtained from the agriculture industrial sector or at the local store and can be used to make more useful materials for human consumption and utilization.

The objectives of this study are to prepare starch based metal-oxide nanocomposites from both native sago and potatoes starches and to characterize them chemically and physically. Such nanocomposites can be further introduced to the industrial sector in Malaysia so that they can be produced in a larger scale for various non-food applications. Using sago and potatoes as raw materials is really a new innovative way to replace plastics or any other non biodegradable materials in making composite materials. Other than their biodegradable and eco-friendly characteristics, these starches are also cheap. Developing composites with these materials will involve only low cost materials but its quality will be comparable or even better than composite materials nowadays. This will benefit us as a consumer because it is our right to have good quality products with a reasonable price.

Growing concern about the environmental consciousness also help lead to the development of biopolymer materials in the widely acceptable products. As stated by Kolybaba *et al* (2004), productions of plastics at the global scale consume approximately 270 million metric tons of fossil fuel as a source of feedstock and energy each year. Production of bio-based product using the natural raw material such as starches is a promising alternative in reducing the dependence on the fossil fuels. Additionally, non-degradable conventional plastics such as polyethylene and polypropylene consuming too much land space when it comes to the disposal process. Many countries are facing this very same problem because of the limited space for waste disposal. Using biodegradable product may be the solution for this problem in fact that wastes from this type of product can be dispose naturally.

Recycling of plastic and other non-biodegradable materials is a very positive effort to help reduce the environmental pollution but attempts at expanding this effort have been less than effective. Statistically, less than 10% of plastic products are recycled after being used in the United State (Kolybaba *et al.*, 2003). It is obvious that the use of plastics based on renewable feedstock which are biodegradable is a more reasonable option than recycling the conventional plastics.

Starch nanoparticles are biocompatible, biodegradable, and nontoxic, so it can be use as biocompatible implant materials and drug carriers. The chemically modified forms of starch are used in drug delivery system. .For example, epichlorohydrin cross-linked high amylase starch was used as a matrix for the controlled release of contramid. Besides, starch has also been used as a carrier for phenethylamines, acetylsalicylic acid, and estrone (Chakraborty *et al*. 2005).

CHAPTER 2

2. Literature Review

2.1 Background of Starch

Starch $(C_6H_{10}O_5)n$ can be defined as an odorless, tasteless carbohydrate which is obtained mainly from cereals and potatoes and is important part of human diet. Starch belongs in polysaccharide group along with glycogen and cellulose. This type of carbohydrate is build up by long chains of monomer molecules of glucose. There are two types of polysaccharide which are homopolysaccharide and heteropolysaccharide (Garret & Grisham, 2005). As the name suggest, homopolysaccharide consist of only one same type of monomer. On the other hand, heteropolysaccharide consist of two or more different types of monomer.

Starch is the common storage polysaccharide in plant that exists in two forms; α-amylose and amylopectin. Most forms of starch in nature are 10% to 30% α-amylose and 70% to 90% amylopectin (Garret & Grisham, 2005). Starch can be widely found in plants especially being stored in roots, tubers, seeds and fruits. Amylopectin is a highly branched chain of glucose unit where the branch linkages are $\alpha(1\rightarrow6)$. In contrast, amylose is composed of linear chains of glucose in a $\alpha(1\rightarrow4)$ linkages (Garret & Grisham,2005). Figure 17 and 18 (Corn Refiners Association, 2006) in Appendix show the structure and linkage of amylopectin and amylose respectively.

Plant stores starch in granulated form in the stroma of plastids, one of the plant cell organelles in two types of plastids. First one is in chloroplast which where the photosynthesis process take place. The second one is in amyloplasts, plastids that are specifically use for accumulating starch. When the starch is being digested, it will yield glucose by the process known as starch phosphorylase (Garret & Grisham, 2005). This process involved breaking down the starch into its monosaccharide components which is the glucose molecules.

Glucose then will be used by the consumer's cells as energy. Starch granules are insoluble in cold water. But it will disrupt when heated and will produce a colloidal suspension or gelatinous solution (Solomons & Fryhle, 2004).

2.2 Application of Starch

Of the two components of starch, amylose has the most useful functions as a hydrocolloid. Its extended conformation causes the high viscosity of water-soluble starch and varies relatively little with temperature. The extended loosely helical chains possess a relatively hydrophobic inner surface that is not able to hold water well and more hydrophobic molecules such as lipids and aroma compounds can easily replace this. Amylose forms useful gels and films. Its association and crystallization (retrogradation) on cooling and storage decreases storage stability causing shrinkage and the release of water (syneresis) (Bertoft, 2004). Increasing amylose concentration decreases gel stickiness but increases gel firmness.

Amylopectin interferes with the interaction between amylose chains (and retrogradation) and its solution can lead to an initial loss in viscosity and followed by a more slimy consistency. Mixing with κ-carrageenan, alginate, xanthan gum and low molecular weight sugars can also reduce retro gradation (Smith, 2005). At high concentrations, starch gels are both pseudo plastic and thixotropic with greater storage stability. Their water binding ability (high but relatively weak) can provide body and texture to foodstuffs and is encouraging its use as a fat replacement (Taggart, 2004).

Starch is often combined with non-starch hydrocolloids in order to control viscosity, stability and other properties of foods. The interaction between starch and non-starch hydrocolloids had been studied widely. The admixture of non-hydrocolloids to starch dispersions gave significant increase in viscosity.

This effect is largely due to the accumulation of the non-starch in the continuous phase, that is to phase separation rather than to a true synergistic interaction between the polymeric components (Conde-Petit *et al*., 2001). Addition of non-starch hydrocolloids can also helps control the rheological properties of starch by influencing the extent of starch granule swelling and amylose leaching.

2.3 Background of Titanium Dioxide

Titanium dioxide also known as titania is among the natural occurring oxide of titanium with chemical formula TiO_2. Basically, titanium dioxide exists in four forms (Euvananont *et al*., 2007). Titanium dioxide occurring in the needle-like crystals is called rutile. The second one is anatase or octahedrite, a tetragonal mineral of bipyramidal habit. Brookite is another form of titanium dioxide with an orthorhombic shape mineral. Both anatase and brookite is considered as rare minerals. The final form is known as titanium dioxide (B) with the monoclinic mineral which means that it has a crystals system with three unequal axes of which one is at right angles to the other two (Euvananont *et al*., 2007).

2.4 Application of Titanium Dioxide

Many studies have been published on the use of TiO_2 as a photocatalyst for the composition of organic material. TiO_2 particularly in the anatase form is a good photocatalyst under ultraviolet light. Photocatalytic activity (PCA) is the ability of a material to create an electron hole pair as a result of exposure to ultraviolet radiation. The resulting free-radicals are very efficient oxidizers of organic matter. Photocatalytic activity in TiO_2 has been extensively studied because of its potential use in sterilization, sanitation, and remediation applications (Euvananont *et al*., 2007).

The ability to control PCA is important in many other applications utilizing TiO_2 including paint pigments and cosmetics that require low PCA. Recently it has been found that titanium dioxide, when spiked with nitrogen ions, is also a photocatalyst under visible light. The strong oxidative potential of the positive holes oxidizes water to create hydroxyl radicals. It can also oxidize oxygen or organic materials directly. Titanium dioxide is thus added to paints, cements, windows, tiles, or other products for sterilizing, deodorizing and anti-fouling properties and is also used as a hydrolysis catalyst. It is also used in the Graetzel cell, a type of chemical solar cell.

2.5 Studies on Starch

Starch also has been widely studied recently especially in making composite materials because it is a renewable and biodegradable materials. Besides, it is cheap and also abundant make it easily available. Zhang *et al*, 2001 had made a study using starch as material. The aim of the study was to produce zeolite materials using silicalite nanoparticles and starch gel template. Zeolite material is any of a large group of minerals consisting of hydrated alluminosilicates, used as a cation exchanger and molecular sieves.

Two methods were used in the study. The macroporous block consisting of microporous silicalite were prepared by mixing 50nm sized zeolite nanoparticles into freshly prepared viscous starch gels, and then followed by air-drying and calcinations. The size of the pores ranges from 0.5 to 50µm. Varying the amount of starch and the weight ratio between starch to silicalite will make sure that pores prepared fall in that ranges.

Starch sponges having high microporosities were prepared by freezing and thawing of starch gels. Then these sponges will be filled up by colloidal suspensions of silicalite nanoparticles and air-dried to produce silicalite-starch foams with pores up to 100µm across.

The zeolite nanoparticles will be obtained by removing the starch template by calcinations without any significant damage to the silicalite structure.

2.6 Starch Properties and Cellular Structure

Various aspects of the combined characteristics of cellular structure and starch properties related to culinary qualities of potato varieties. According to Salunkhe *et al*. (1991), larger tissue cells and larger average starch granules are associated mealiness. Smaller cells and starch granules characterize the less mealy and waxy varieties. Within a variety, proportionately larger numbers of large starch granules are associated with tubers of high specific gravity, and smaller granules with low specific gravity. The percent of small starch granules is reduced markedly during storage of tubers. The microscopic examination of starch grains from various parts of a potato tuber indicated variations in distinctness of the lamellae. The lamellae of starch grains of Russet Rural tubers were more distinct than those of Kennebec.

Differences in the size of the starch granules are associated with differences in amylose and amylopectin (Salunkhe *et al*., 1991). Small granules contain less amylose and gel at higher temperatures than the larger starch granules. The amylose content of potatoes is strongly influenced by the variety. The varietals differences in the amylose content reflect fundamental differences in the properties of starch gels formed when different varieties of potatoes are cooked. The starches within the different tissue zones of individual tubers also vary significantly. Similarly, cell size varies characteristically within different tuber regions.

2.7 Quality of Raw Potatoes

Several factors such as shape and size of the tuber, depth of the eyes, color of the flesh and skin, extent of surface blemishes due to disease and pest and superficial damage or internal damage determine the final tuber quality and the acceptability of the product to the consumer (Salunkhe *et al*., 1991). Plant density or population per unit area influences the size of the potato tubers significantly. Plant density directly affects the tuber size by altering the number of the tuber by each plant, which depends upon stem density, spacial arrangement, variety and season. The tuber size also affects the dry matter content of the tuber. Potato processing involving peeling and slicing operations has an important bearing on the shape of the tubers. The tuber shape is also partly controlled by the prevailing climate during growth, especially the temperature. Temperatures in the range of 12 to 20^{o}C have been reported to produce tubers of more even shape than temperatures above or below this range. Four distinct shapes, viz., round, oval, pointed oval and kidney shape have been recognized.

Depth of the eyes is largely a genetically controlled characteristic. It is related to the color and appearance of the skin. Depth and appearance of the skin may be important in determining susceptibility to scuffing damage in netted, skinned varieties such as Netted Gem. The thickness of the periderm is usually a varietal feature, but it can markedly influenced by cultural factors (Gotlieb & Capelle, 2005). The flesh color of potatoes is either white or yellow. The presence of anthocyanins dissolved in the cell sap of the periderm or peripheral cortical cells forms the basis of the skin pigmentation. A dozen different types of carotenoids were identified in potato tubers which were shown to have a close relationship with flesh color. Six anthocyanins has been reported occurring either as the 5-glucoside, 3-rhamnoslyglucoside acetylated with p-coumaric acid, or as 3-rhamnoslyglucoside were found in cultivated potatoes (Salunkhe *et al*., 1991).

CHAPTER 3

3. Materials and Methodology

3.1 Sample Collection:

Both of the sago and the potato starches were purchased at the local market in the form of flour.

3.2 Preparation of Starch Sponges:

The preparation of starch sponges was based on the method reported by Zhang *et al*, (2001). 5.0g of starch were added to 50.0ml of deionised water in a beaker with stirring. Then the starch slurry (semi solid mixture) was placed on a paraffin oil bath preheated to 95^{o}C and manually stirred until gelatinization occurs. The gelatinized starch paste was kept at this temperature for additional 10min without stirring. Then it was transferred into petri dishes and was frozen in a freezer for 15 hours at -20^{o}C. After that, it was left to age at room temperature for another 15 hours. Steps involved in the preparation of starch sponges are as shown in Figure 1.

3.3 Preparation of Titanium Dioxide (TiO_2) Sol:

The preparation of TiO_2 sol was based on method reported by Mansor and Ismail, (2003). The sol was prepared by adding 5ml of tetraisopropyl-orthotitanate (TIP) to a 50ml beaker containing a mixture of glacial acetic acid and ethanol that have been mixed for 5min. The chemical composition of the starting alkoxide solution was $Ti(O\text{-}i\text{-}C_3H_7)_4$: C_2H_5OH: CH_3COOH = 1: 45: 0.3 in molar ratio. It was vigorously stirred by using the magnetic stirrer during the addition and for another 6min after the addition of the precursor at the room temperature. The solution was then stirred at room temperature for at least two hours. Steps involved in the preparation of TiO_2 sol are as shown in Figure 2.

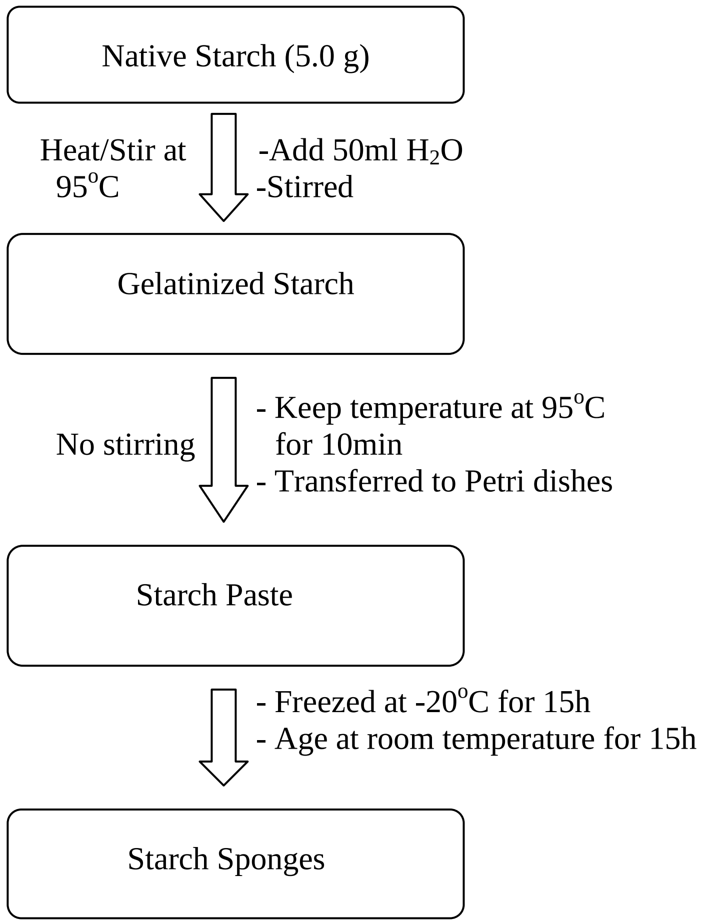

Figure 1: The Flow Chart for the Preparation of Starch Sponges

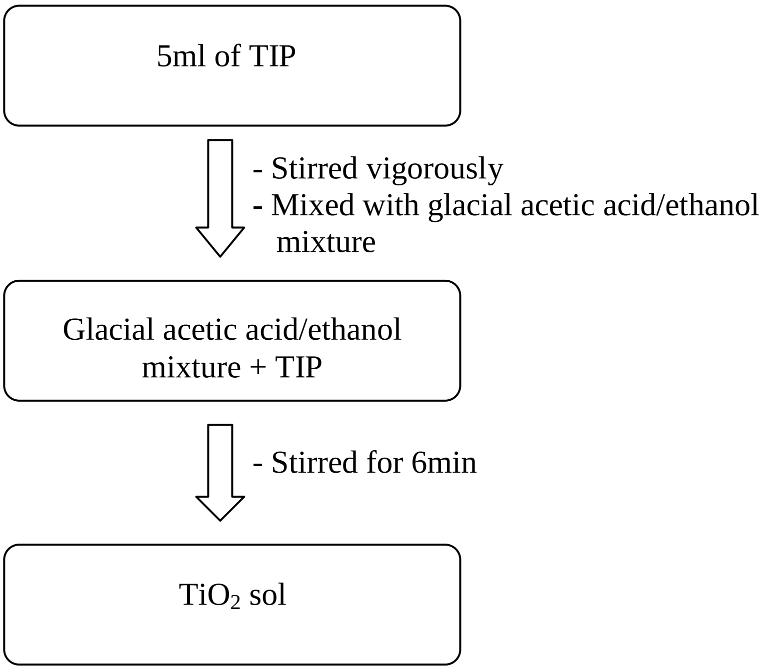

Figure 2: The Flow Chart for the Preparation of TiO_2 Sol

3.4 Preparation of Starch/Titanium Dioxide Nanocomposites:

The preformed starch sponges were sliced into thin slices (5mm) and immersed into the colloidal dispersions of titanium dioxide sol with gentle stirring for 12h. They were then removed from the TiO_2 sol and washed with deionized water and left to air-dried. The starch/TiO_2 nanonocomposites were calcinated at 600^{o}C in nitrogen gas for two hours, or at 600^{o}C in air for six hours.

3.5 Physical and Chemical Characterization:

This research was conducted in the Physical Chemistry Laboratory at UNIMAS. Characterizations of starch sponges, nanocomposites and xerogels were made by using four main instruments which included the Optical Microscope (OM), Scanning Electron Microscope (SEM), Fourier Transformed Infrared Spectroscopy (FTIR), and CHN Elemental Analyzer. Optical micrographs were obtained using the optical microscope in the OM Laboratory at UNIMAS and using optical microscope at Timber Research Center (TRC), Sarawak. SEM at both UNIMAS and TRC were used to characterize the surface morphology, size and shape of starch sponges and nanocomposites. SEM can resolve objects as small as 20nm, at a magnification up to approximately 50000X. Preparing a specimen for the SEM involves coating it with a thin layer of gold or palladium (Black, 2005).

FTIR was used to confirm the composition of starch samples prepared under various synthesis conditions. Infrared spectra were recorded as KBr discs using Perkin Elmer Spectrum GX Fourier-Transform Spectrometer (4000–370 cm^{-1}) at UNIMAS. CHN Elemental Analyzer was used to determine the total carbon, hydrogen and nitrogen content in the starch sponges, nanacomposites and xerogels that were prepared under various synthesis conditions. The CHN analyses were recorded with CHN Elemental Analyzer FlashEA 1112 Series at UNIMAS.

CHAPTER 4

4. Results and Discussions

4.1 Gelatinization of Starch

Starch gelatinization is the disruption of molecular organization within the starch granules and this process is affected by starch-water interactions. Most starch processing involves heating in the presence of water and some other additives. For instance, sugar and salt were added to control gelatinization in the food industry or glycerols as a plasticizer for biodegradable plastics applications (Gotlieb & Capelle, 2005).

As stated by Smith (2005), starch gelatinization process involves six main steps which are; (i) the loss of crystallinity of the granule as measured by the loss of birefringence, (ii) an uptake of heat as the conformation of the starch is altered, (iii) hydration of the starch as accompanied by swelling of the granules, (iv) a decrease in the relaxation time of the water molecules, (v) loss of double helical order, and (vi) leaching of the linear molecules (amylose) from the ruptured granules.

Native starch granules basically are made up of amylose (linear) and amylopectin (branched) molecules. The addition of water will break up the crystallinity and disrupt helices. Heating and addition of more water will cause the granules to swell and amylose diffused out of the granule. The enrichment of amylose in the inter- and intragranular space is due to thermodynamics immiscibility of amylose and amylopectin. Granules containing amylopectin collapsed and being held in the matrix of amylose. Gelatinization of sago and potato starches produced cloudy and viscous starch slurry as a result of swelling and disruption of the starch granules.

4.2 Formation of Starch Sponges

Gel or sponge forms as temperature decreases and consists of the remaining wrapping of the starch granules enriched in amylopectin, following immersion in high amylose content. A rearrangement between starch chains occurs and a three-dimensional network is rapidly constituted (Lang & Vitopole, 2004). Hardness of the gel that formed depends on the amylose content in the starch. High amylose contents would produce harder gel. As starch chains rearrange, hydrogen bonds between chains reappear and a crystalline structure is created.

As reported by Zhang *et al*., (2001), starch sponges with high internal porosities were prepared by a method that involved the freezing and thawing of starch sponges. Thawing of the sponges at room temperature is necessary to ensure that the produced sponges have an intact macroporous starch structure. Sponges prepared without the room-temperature aging or thawing process did not show well-defined sponge structure (Zhang *et al*., 2001).

The starch sponges could be stored without loss of structure at room temperature when moist and were easy to handle and cut into desired shapes. Once dried, the sponges were tough and hard but not brittle or crispy.

4.3 Characterization of Starch Sponges Using the Optical Microscope

Optical microscope was used to observe the general surface morphology of the starch sponges' surfaces. Both potato and sago starch sponges were observed using the optical microscope. Based on the optical micrographs as shown in Figure 3, both types of sponges have rough and porous surfaces.

Sago sponge can be characterized with firm and stiff sponge while the potato sponge having stringy and slimy texture. Different rheological properties of both types of starch sponges were the results of differently oriented contribution of cations present by affecting the network of the amylopectin molecules in pasting and gel formation (Bergthaller, 1999). Other factors that may also cause the difference in the rheological properties between the starch sponges include the percentage of amylose content in the starch, rate of stirring and heating temperature (Bertoft, 2004).

Figure 4 shows the optical micrographs for treated potato and sago starch sponges with titanium dioxide (TiO_2) sol and were calcinated in nitrogen at 600^oC for two hours. The sponges have turned into black in colour as a result of carbonization.

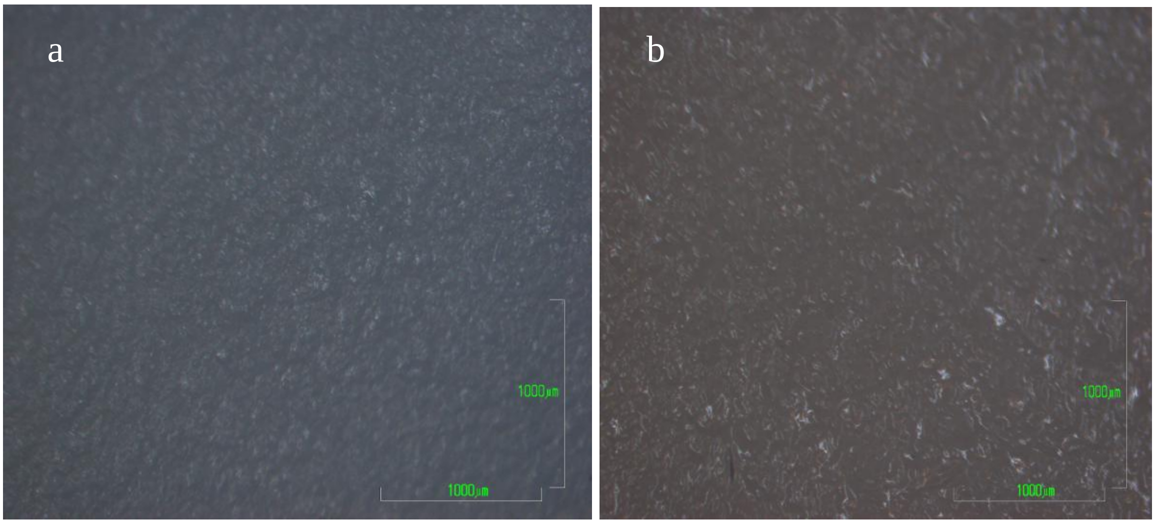

Figure 3: Optical micrographs of starch sponges prepared from native potato or sago starch; (a) potato starch sponge, and (b) sago starch sponge. Magnification 40x, scale bars = 1000 µm in both micrographs.

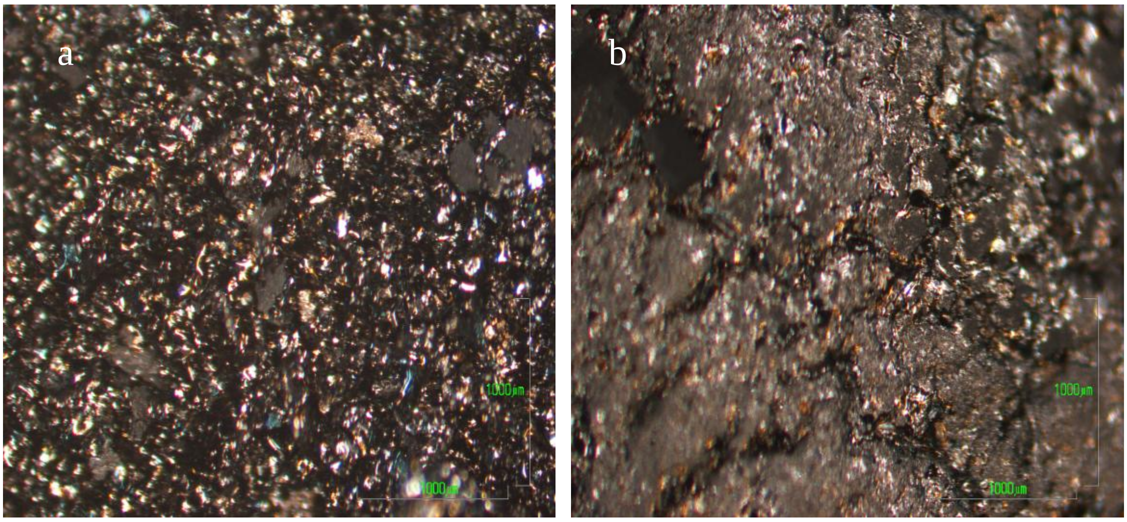

Figure 4: Optical micrographs of treated starch sponges with TiO_2 sol and calcinated in nitrogen; (a) potato/TiO_2 sponge, and (b) sago/TiO_2 sponge. Magnification 40x, scale bars = 1000 µm in both micrographs.

4.4 Characterization of Starch Sponges Using the Scanning Electron Microscope

Scanning electron microscope (SEM) was used to observe the internal structure of starch sponges that had been synthesized under various synthesis conditions. SEM micrographs show the starch sponge structures respectively. Figure 5 shows the internal structures for both potato and sago starch sponges. The sponges for both types of starches have intact structures with high porosity. As reported by Zhang *et al*., (2001), the sponges consisted of intact 3-D bicontinuous macroporous networks with pore sizes that were dependent on the starch concentration being used.

Potato and sago starch sponges were treated with titanium dioxide (TiO_2) sol for 12 hours with gentle stirring. Both treated sponges were observed using SEM under high magnification and the structures were as shown in Figure 6.