



Faculty of Resource Science and Technology

SYNTHESIS AND CHARACTERIZATION OF STARCH AEROGEL

Lee Siaw Chien (36641)

Bachelor of Science with Honours
(Resource Chemistry)
2015

Acknowledgement

First and foremost, I wish to thank my research supervisor, Associate Professor Dr. Chin Suk Fun for her patient, guidance and encouragement throughout this final year project. Besides that, I also feel very grateful to have Mr. Shafri especially on the technical data particularly SEM micrographs presented in this thesis.

In addition, I would like to thank some of the postgraduate student: Miss Voon, Miss Ainn and Miss Lim for giving me enlightening discussion and useful resources during my laboratory work.

Last but not least, I would like to thank my family for their understanding and continuous support throughout the final year project. I am greatly indebted for their unconditionally love which encourage me to the completion of this course

Declaration

I hereby declare that no portion of this dissertation has been submitted in support of an application for another degree of qualification of this or any other university or institution of higher learning.

.....

(LEE SIAW CHIEN)

Department of Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

Table of Contents

Acknowledgement	I
Declaration.....	II
Table of Contents	III
List of Abbreviations.....	V
List of Tables.....	VI
List of Figures.....	VII
Abstract.....	VIII
1.0 Introduction.....	1
2.0 Literature Review	3
2.1 Aerogels.....	3
2.2 Hydrophilic and Hydrophobic Aerogels.....	3
2.3 Characteristics of Aerogels.....	4
2.4 Factors Affect the Drug Release Capacity of Starch Aerogels.....	4
2.5 Applications of Aerogels	5
2.5.1 Aerogels for Aerospace Engineering.....	5
2.5.2 Aerogels as Sensors	6
2.5.3 Aerogels as Adsorbents	6
2.5.4 Aerogels as Catalysts.....	7
2.6 Factors Affecting the Porous Network of Starch Aerogels	7
3.0 Materials and Methods	8

3.1	Materials	8
3.2	Synthesis of Starch Aerogel.....	8
3.2.1	Solvent Exchange Method 1.....	10
3.2.2	Solvent Exchange Method 2.....	10
3.2.3	Solvent Exchange Method 3.....	11
3.2.4	Critical Point Drying Method.....	11
3.2.5	Freeze Drying Method.....	12
3.3	Characterization of Starch Aerogels	12
3.3.1	Scanning Electron Microscope (SEM).....	12
3.3.2	Swelling Studies	12
4.0	Results and Discussion	14
5.0	Conclusion	25
6.0	References.....	27

List of Abbreviations

nm	Nanometer
M	Molar
pH	Power of hydrogen
NASA	<i>National Aeronautics and Space Administration</i>
APXS	Alpha Particle X-Ray Spectrometer
ATP5O	Adenasine triphosphate synthase subunit O
w/v %	Percent of weight of solution in the total volume of solution
UV-Visible	Ultraviolet-visible
SEM	Scanning Electron Microscope
mL	Milliliter
FD	Freeze Drying
CPD	Critical Point Drying
CO ₂	Carbon Dioxide

List of Tables

Table	Title	Page
1	Parameters involved in the synthesis of starch aerogel	10
2	Effects of starch solution concentration on the mean pore size of starch aerogels	19
3	The swelling ratio of starch aerogel for different starch solution concentration	22
4	The swelling ratio of 15.0 w/v % of starch aerogel prepared by critical point drying and freeze drying method	23

List of Figures

Figure	Title	Page
1	Basic processing method to synthesize starch aerogel	8
2	SEM micrographs of starch aerogels improved through various parameters: (a) without manipulation of parameter (b) time (c) temperature (d) solvent exchange method (e) types of solvent for solvent exchange (f) ratio of starch gel to solvent for solvent exchange	14
3	SEM micrographs of starch aerogels prepared with different concentration of starch solution: (a) 10.0 w/v % (b) 12.5 w/v % (c) 15.0 w/v % (d) 17.5 w/v % (e) 20.0 w/v %	18
4	Effects of starch solution concentration on mean pore size of starch aerogels	19
5	SEM micrographs of 15.0 w/v % starch aerogel prepared with different drying method: (a) Critical point drying (b) Freeze drying	20
6	Effects of starch solution concentration on the swelling ratio of starch aerogels	22

Synthesis and Characterization of Starch Aerogel

Lee Siaw Chien

Department of Chemistry

Faculty of Resource Science and Technology

Universiti Malaysia Sarawak

Abstract

Aerogel is a material that has wide variety of applications throughout the world. It has the properties of large surface area, low density, high refractive index, low thermal conductivity, and low velocity of sound. Aerogel made from native sago starch are biodegradable and biocompatible which it can be used for the medical science applications. However, researches that had been done on the starch aerogels are still lacking. In this study, starch aerogels of different morphology were synthesized by varying the time, temperature, solvent exchange method, solvent exchange ratio, drying method and native sago starch to water ratio. The swelling studies and characterization of starch aerogel by using SEM were also studied. The increase in the duration of processing time and temperature helped in improving the pore structure of the starch aerogels. Besides, the increase in native sago starch to water ratio caused the decrease in the pore size of starch aerogel. In addition, the swelling behavior of the starch aerogels depends on both of the pore size and the gel network of starch aerogel.

Keywords: Starch aerogels, pore size, surface morphology

Asbtrak

Aerogel merupakan sejenis bahan yang mempunyai pelbagai aplikasi di seluruh dunia. Ia mempunyai ciri-ciri seperti kawasan permukaan yang luas, ketumpatan yang rendah, indeks biasan yang tinggi, kekonduksian terma yang rendah, dan halaju bunyi yang rendah. Aerogel diperbuat daripada kanji sagu asli adalah bio-terurai dan bio-serasi dimana ia boleh aplikasikan dalam sains perubatan. Walau bagaimanapun, kajian semasa yang telah dilakukan ke atas aerogels kanji masih belum mencukupi. Dalam kajian ini, aerogels kanji yang mempunyai morfologi yang berbeza telah disintesis dengan mengubah masa, suhu, kaedah pertukaran pelarut, nisbah pertukaran pelarut, kaedah pengeringan dan nisbah kanji sagu asli kepada air. Kajian bengkak dan pencirian kanji aerogel dengan menggunakan SEM juga telah dikaji. Dengan meningkatkan tempoh masa dan suhu untuk pemprosesan, ia boleh membantu dalam penambahbaikan struktur liang bagi aerogel kanji. Selain itu, penambahan dalam nisbah kanji sagu asli kepada air menyebabkan berkurangan dalam saiz liang kanji aerogel. Di samping itu, tindakan bengkak aerogels kanji bergantung kepada kedua-dua situasi, iaitu saiz liang dan rangkaian gel.

Kata kunci: Kanji aerogel, saiz liang, morfologi permukaan

1.0 Introduction

Aerogels is an important material that had been studied since a long time ago. Samuel Kistler was the first researcher who synthesized it in the year of 1931 (Kistler, 1931). Aerogel is a material that has the properties of large surface area, low density, high refractive index, low thermal conductivity, and low velocity of sound (Pajonk *et al.*, 1997).

Starch is a type of organic polysaccharide that can be used to synthesize aerogel. It is a cheap material and it presents in great quantity. Starch exists in the form of granules and can be found easily in many plants (Doane, 1992; Duarte *et al.*, 2009; Dumitriu, 2005; Wing *et al.*, 1991). The used of organic aerogel in medical applications were proposed around 60 years after Kistler's discovery. They are used as artificial tissues, diagnostic agents and for drug delivery systems (Berg *et al.*, 1995). Large internal surface area, high surface to volume ratios, large and consistent pore sizes are the essential criteria for drug delivery (Sher *et al.*, 2007; Ahuja and Pathak, 2009; Arruebo, 2012).

Aerogels have wide variety of applications because of their unique properties. Nowadays, aerogels can be used as absorbents, composites, template, thermal insulator, catalysts, storage media, sensors and materials with low-dielectric constant. Besides, they can also being used in space, in clothing, apparel, blankets as well as in housing, refrigerators, skylights and windows (Gurav *et al.*, 2010a).

The properties of aerogels are easily influenced by the synthesis parameters. The type of antisolvent being used for regeneration process is one of the factors that affect the shrinking of cellulose aerogels. Varying the concentration of cellulose to higher weight

percent can minimize the shrinking action of the aerogels (Schimper *et al.*, 2011). Next, the porosity of silica aerogels can be affected by varying the washing temperature and the protic solvent. Hydrophobicity of the aerogels is also affected when they are dried by using different temperature (Bangi *et al.*, 2010).

There are several ways to prepare the aerogels for drug delivery system. For example, aerogels can be prepared by loading the drugs before gelation, during the aging process, bathing the pure aerogels in the drug solution after the process of supercritical drying, or loading the drugs during supercritical drying process (Liu *et al.*, 2010; Aegerter *et al.*, 2011).

There are many researches being done on different types of organic and inorganic aerogels. However, the understanding towards starch aerogels is still yet to be improved. The purpose of this study is to synthesize and characterize starch aerogels. In this study, numerous starch aerogels of different morphology were synthesized by varying the time, temperature, solvent exchange method, solvent exchange ratio, drying method and native sago starch to water ratio. The swelling studies on starch aerogels were determined. In addition, they were also being characterized by using Scanning Electron Microscope (SEM).

2.0 Literature Review

2.1 Aerogels

Aerogels are the materials that gain a lot of scientists' attention from all over the world due to its wide range of applications in different fields (Pajonk *et al.*, 1997). Nowadays, there are many types of aerogels had been synthesized. According to García-González *et al.* (2011), starch aerogels is one of the promising organic aerogels used for the applications of drug delivery. It can be synthesized by using the same method as inorganic silica aerogels. The synthesizing of starch aerogels need to go through the step of formation of hydrogels, followed by aging or solvent exchange step and finally the step of supercritical drying. Starch aerogels have sufficient surface area for the applications of drug delivery although they are smaller compared to silica aerogels.

2.2 Hydrophilic and Hydrophobic Aerogels

Hydrophilic and hydrophobic aerogels react differently with water. Hydrophilic aerogels are more favour to water where the water can easily attach on the surface of the aerogels; however it is repelled by the hydrophobic aerogels. The hydrophobicity factors of the aerogels depend greatly to the functional groups on the aerogels' surface. Water will form bead on the hydrophobic surface of aerogels, whereas it easily wet the hydrophilic surface aerogels. In addition, the intermolecular forces such as hydrogen bonding, dipole-dipole interaction, acid base reaction and others will also affects the hydrophobicity of the aerogels (Anderson and Carroll, 2011).

2.3 Characteristics of Aerogels

Aerogels are materials that have the properties of large surface area, low in density, refractive index, thermal conductivity, and velocity of sound (Pajonk *et al.*, 1997). The characteristics of having large surface area, availability of the uniform pore sizes are the important components that need to be considered for the transportation of the drugs (Sher *et al.*, 2007, Ahuja *et al.*, 2009, Arruebo, 2012). The pores aerogels are usually categorizes according to the size. Micropores are pores that are smaller than 2 nm, whereas macropores are pores that are larger than 50 nm. For the pore size that are range between 2 nm to 50 nm, they are categorizes as mesopores. The shape, volume and size of the pores are the important factors for the effectiveness of various applications (Davis, 2002).

Therefore, the number of thesis studies and research articles on the study of drug delivery by using aerogels are gaining more and more attention from the researchers (Smirnova *et al.*, 2002; Suttiruengwong, 2005; Aegerter *et al.*, 2011; Alnaief, 2011).

2.4 Factors Affect the Drug Release Capacity of Starch Aerogels

According to Smirnova *et al.* (2004), the loading of drug in hydrophilic aerogels will have the effect of very fast drugs release compared to the nanocrystals. According to the research done by Yunos *et al.* (2010), they found that piperine loaded in silica matrices in both 0.1M HCl, pH \approx 1 and phosphate buffer saline, pH \approx 7 conditions are more soluble and resolve are more quickly compared to the crystalline piperine.

Starch granules are hydrophilic in nature. Therefore, the aerogels synthesized by using the starch granules have hydrophilic properties (Wootton and Bamunuarachchi, 1979). According to Suttiruengwong (2005), the release of drugs can be enhanced by contacting the hydrophilic aerogels with a dissolution medium. The aerogels collapsed spontaneously when drugs are adsorbed. This results in the expected fast release rates of drugs.

Li *et al.* (2002), mentioned that the speed of paddle and stir significantly affect the percentage release of acetaminophen. The percent of release of acetaminophen increased when the speed of stir was speeded up. Likewise, the acceleration of the paddle speed can also increase the percent release of acetaminophen. Higher rotational speed can contribute to larger turbulence in the dissolution medium. Thus, the percent of drug release increased. Khougaz *et al.* (2000) also mentioned that the accelerating of stirring speeds increased the percent of drug release for a short run intervals. By comparing the rate of drug released for stir speed and paddle speed, the stir speed contributes significant effect on drug released rate (Li *et al.*, 2002).

2.5 Applications of Aerogels

2.5.1 Aerogels for Aerospace Engineering

Aerogels have been used to capture hypervelocity particles in space. The Stardust Mission which was launched in year 1999 at Kennedy Space Center was one of the most successful projects that provide a lot of scientific information to the world. In that mission,

their goals were to capture coma samples and interstellar dusts which after that brought back to be analyzed (Brownlee *et al.*, 1996; Brownlee *et al.*, 2003; Ishii *et al.*, 2008).

Next, aerogels has also been used for thermal insulation in space engineering. By having the characteristic of very low conductivity, many researches were performed by *National Aeronautics and Space Administration* (NASA) towards the field of thermal insulation. In the year of 1997, silica aerogels was the first insulator aerogels being used. The function of the aerogels was to protect the primary battery pack of Alpha Particle X-Ray Spectrometer (APXS) from very low temperature (Eisen *et al.*, 1998)

2.5.2 Aerogels as Sensors

Aerogels are suitable to use as a sensor due to the characteristics of having high surface area, high porosity and good pore availability. Aerogels are found that they can be used as a biosensor. They are synthesis by using sol-gel polymerization in the presence of ionic liquid at room temperature. An immobilized oligonucleotide probe located on the surface of the aerogels successfully recognized a short human gene ATP5O (Li *et al.*, 2010).

2.5.3 Aerogels as Adsorbents

Aerogels are materials with high surface area and this causes them to be the good absorbent. According to Fisher (2008), heavy metals found in the water at polluted industrial places can be cleared by using aerogels. For the places that are polluted with oil, silica aerogels can be used to absorb them (Gurav *et al.*, 2010b). Next, carbon nanotube

aerogel is one of the effective materials for oil absorption because it has the ability to absorb oil up to 80 - 100 times of its own weight (Gui *et al.*, 2010).

2.5.4 Aerogels as Catalysts

There are many type of catalysts have been synthesized by using aerogels and they have wide variety of application. The aerogel catalyst synthesize by Kearby *et al.* (1938) have the ability to convert alcohols to amines. According to the research done by Guilminot *et al.* (2007), cellulose-based carbon aerogels are used as the catalyst to support Proton Exchange Membrane Fuel Cell electrodes. Alumina aerogels is used as a catalyst for the reduction of nitrogen monoxide with hydrocarbons (Hirashima *et al.*, 1997).

2.6 Factors Affecting the Porous Network of Starch Aerogels

Starch aerogels can be prepared through many ways. The aerogels that prepared with the same concentration and condition have similar porous and homogeneous structures. The porous networks of the aerogels can be affected if they are prepared by using different concentration. Aerogels that are prepared by lower concentration of starch solution have thin fibers compared to the aerogels that are prepared by high concentration. Next, the porous network can also be affected by solvent exchange process. The aerogels that are dried using different types of solvent can give different morphology although they are prepared by using the same concentration of starch solution (Miao *et al.*, 2008).

3.0 Materials and Methods

3.1 Materials

Native sago starch used was purchased from a local grocery shop in Kuching, Sarawak, Malaysia. Acetone, absolute ethanol, liquid carbon dioxide and liquid nitrogen used were analytical grade and used without any further purification. Ultrapure water (18.2 M Ω) used was obtained from Water Purifying System (Model: ELGA UK, Ultra Genetic).

3.2 Synthesis of Starch Aerogel

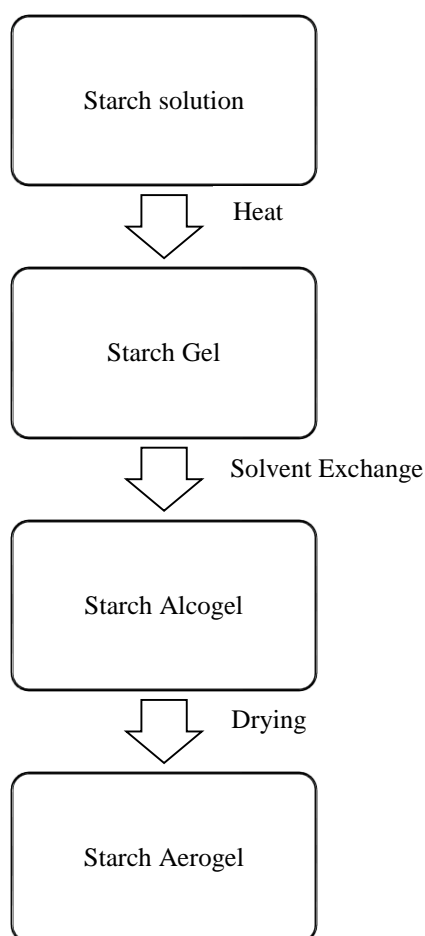


Figure 1: Basic processing method to synthesize starch aerogel

In this study, numerous starch aerogels of different morphology were synthesized by varying the time, temperature, solvent exchange method, solvent exchange ratio, drying method and native sago starch to water ratio. Figure 1 shows the basic processing method used to synthesize starch aerogels.

First of all, a measured amount of native sago starch was added into 10 mL of ultrapure water to produce starch dispersion of having desired concentration. Next, it was heated and stirred in the water bath at varies temperature for a specific amount of time until a clear starch gel was formed. Subsequently, the starch gel was formed and it was left to cool down to room temperature. The cooled starch gel was then placed into a clean beaker prior proceed to the step of solvent exchange.

Various solvent exchange methods as well as starch gel to solvent ratio were used for the process of solvent exchange (*Please refer to section 3.2.1, 3.2.2 and 3.2.3*). After that, starch alcogel was formed and two different drying methods were used to dry it (*Please refer to section 3.2.4, and 3.2.5*).

Table 1: Parameters involved in the synthesis of starch aerogel

Concentration (w/v %)	Time (minutes)	Temperature (°C)	Solvent Exchange Method	Starch Gel to Solvent Ratio	Drying Method
15.0	15	80 – 85	1	1:5	CPD
15.0	20	80 – 85	1	1:5	CPD
15.0	20	95 - 100	1	1:5	CPD
15.0	20	95 - 100	2	1:5	CPD
15.0	20	95 - 100	3	1:5	CPD
15.0	20	95 - 100	3	1:15	CPD
10.0	20	95 - 100	3	1:15	CPD
12.5	20	95 - 100	3	1:15	CPD
17.5	20	95 - 100	3	1:15	CPD
20.0	20	95 - 100	3	1:15	CPD
15.0	20	95 - 100	3	1:15	FD

3.2.1 Solvent Exchange Method 1

During the process of solvent exchange, 50 mL of absolute ethanol was used to soak the starch gel. For every interval of 30 minutes, the absolute ethanol was replaced with another same volume absolute ethanol. This step was repeated thrice. 24 hours was used for the fourth time of solvent exchange with absolute ethanol. After that, 50 mL of acetone was used for another solvent exchange with the starch gel for the next 24 hours. The ratio of starch gel to the solvent for solvent exchange was 1:5.

3.2.2 Solvent Exchange Method 2

Before the process of solvent exchange, solvent with vary acetone to water ratio (30 %, 50 %, 70 %, 90 % and 100 % acetone) were prepared. 50 mL of 30 % acetone was first poured into the beaker containing the starch gel for the process of solvent exchange.

At every interval of 30 minutes, the solvent was replaced with another solvent of having higher acetone percentage. Meanwhile, 24 hours were used for the process of solvent exchange when 100 % acetone was used. This step was repeated twice. The ratio of starch gel to the solvent for solvent exchange was 1:5.

3.2.3 Solvent Exchange Method 3

Before the process of solvent exchange, solvent with vary absolute ethanol to water ratio (30 %, 50 %, 70 %, 90 % and 100 % ethanol) were prepared. 50 mL of 30 % ethanol was first poured into the beaker containing the starch gel for the process of solvent exchange. At every interval of 30 minutes, the solvent was replaced with another solvent of having higher ethanol percentage. Meanwhile, 24 hours were used for the process of solvent exchange when 100 % ethanol was used. After that, another 24 hours of solvent exchange by using 50 mL of acetone was performed. The ratio of starch gel to the solvent for solvent exchange was 1:5.

3.2.4 Critical Point Drying Method

The following were the critical point drying process used to dry the starch alcogel. Adequate amount of starch alcogel was placed into the chamber of critical point dryer. Then, acetone was poured into the chamber until it was half filled. Next, liquid carbon dioxide (at 10 °C) was used to flush the chamber for 5 times. After flushing, the temperature was raised to 40 °C to convert all the liquid carbon dioxide into gaseous state. The gaseous carbondioxide was then slowly released until the pressure inside the chamber was the same as the surrounding. Finally, the starch aerogel was formed.

3.2.5 Freeze Drying Method

The following were the freeze drying process used to dry the starch alcogel. For the sample preparation, liquid nitrogen was poured into a beaker containing starch alcogel to prefreeze the sample. The collector of the freeze dryer was then cooled to $-50\text{ }^{\circ}\text{C}$. After that, the beaker containing starch alcogel was placed into a flask followed by attaching it to the port of the drying chamber. Then, the vacuum condition was immediately created in the flask and started the drying process. When the drying process was completed, starch aerogel was formed.

3.3 Characterization of Starch Aerogels

3.3.1 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (JEOL –SM 6390 LA) was used to analyze the surface morphology of starch aerogels. Before SEM imaging, the samples were gold-sputtered with JEOL JFC-1600 auto fine coater to reduce charging effect and enhance the quality of the image (García-González *et al.*, 2012).

3.3.2 Swelling Studies

0.070 g of starch aerogel sample was weighed and immersed into 50 mL of pH 7 ultrapure water at room temperature for the swelling process. 12 hours were used for this process. The swollen aerogel was then filtered and weighed spontaneously after the surface water was removed. After that, the swollen starch aerogel was dried in an oven at $80\text{ }^{\circ}\text{C}$

until a constant dry weight, W_d was obtained. The swelling ratio of the starch aerogel was calculated according to equation (1):

$$\text{Swelling Ratio (SR)} = \frac{W_w - W_d}{W_d} \quad \text{— Equation (1)}$$

where W_w and W_d represent the weight of the wet and dry aerogel sample respectively (Alupei *et al.*, 2002).

4.0 Results and Discussion

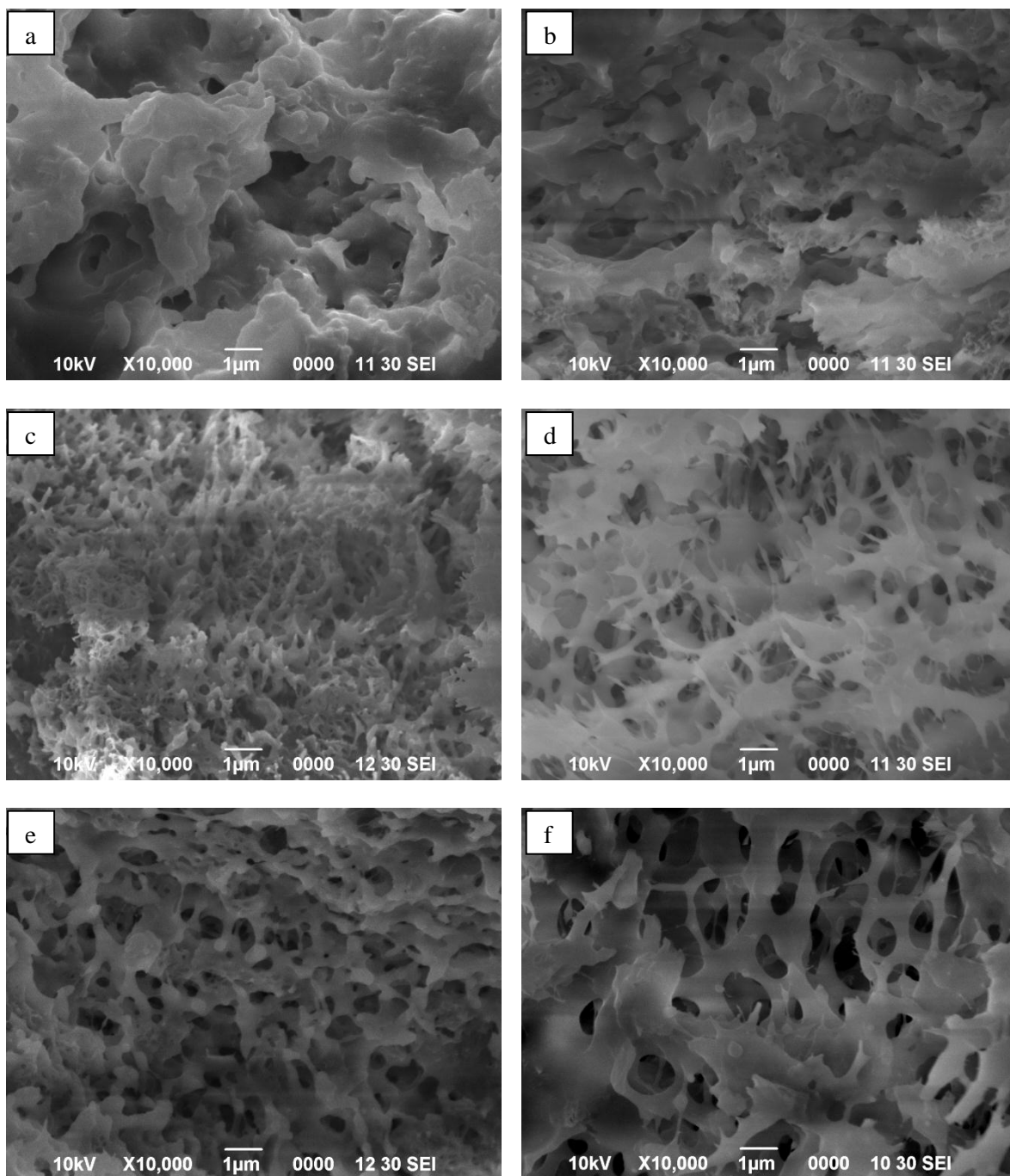


Figure 2: SEM micrographs of starch aerogels improved through various parameters: (a) without manipulation of parameter (b) time (c) temperature (d) solvent exchange method (e) solvent exchange method (f) ratio of starch gel to solvent for solvent exchange

In this study, starch aerogel was synthesized from native sago starch. At the beginning of the process, swelling of native sago starch had been taken place. Ultrapure water was absorbed by the native sago starch due to their natural hydrophilicity (Wootton and Bamunuarachchi, 1979). It causes an increased in the size of the granules. When heat was applied to the starch solution, gelatinization takes place and caused the destruction of the starch granules. The leaching of amylose from the starch granules helps the insoluble native sago starch particle to dissolve in the ultrapure water (Garcia-Gonzalez, 2011). When starch solution was slowly cooled down to room temperature, reorganization of amylose and amylopectin occurred. It causes the structure reformation which leads to the formation starch hydrogel.

Figure 2 (a) and (b) showed the SEM micrographs of starch aerogel prepared by heating the starch solution at 80 – 85 °C for 15 minutes and 20 minutes respectively. It can clearly be seen that the starch aerogel formed by heating starch solution for 15 minutes shows very little pore and they were in the clustered form. However, the structure shows improvement when the duration of heating increases from 15 minutes to 20 minutes. The extended heating duration provides more time for the leaching of the amylose and amylopectin from sago starch granules which they are responsible for the structure reformation. The increase in the degree of structure reformation had caused the starch aerogel on Figure (b) to be more porous compared to the one from Figure (a).

Figure 2 (b) and (c) showed the SEM micrographs of starch aerogel prepared by heating the starch solution at the temperature range of 80 – 85 °C and 95 – 100 °C respectively. A greater amount of the pore can be clearly observed in Figure 2 (c) compared to Figure 2 (b). The temperature used to heat the starch solution between 80 – 85