CONTROLLING THE POROSITY OF CERAMIC MATERIALS BY
MICROWAVE TREATMENT

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A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of
Bachelor of Extractive Metallurgy

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ABSTRACT

Macroporous Ceramic Material (Commercial Water Filter Ceramic) was used as the initial material to be heated by microwave treatment. The compositions of this initial untreated ceramic material are silicon oxide, aluminium oxide, calcium oxide and magnesium oxide. The pore size of the initial ceramic is between macropores (>50 nm) and mesopores (2 nm to 50 nm). Reducing the pore sizes of the ceramic from macropores and mesopores to be the micropores (< 2 nm) by injection different type of mediums, polymers and monomers into the pores of initial ceramic samples by using a saturation vacuum technique, the mediums were water, mineral oil and methanol, polymers which were Polyethylene Glycol (PEG) and Polymethyl Methacrylate (PMMA), and monomers which were Ethylene Glycol (EG) and Methyl Methacrylate (MMA) to create polymerisation inside the pores then the injected samples were heated directly with Microwave for 30 min and also the injected sample were submerged in the methanol bath during be heated by Microwave for 30 min. SANS/USANS and BET of mediums, polymers and monomers injection into ceramics and heated without methanol bath show no decreasing of pore sizes or improving surface area of pores at Micropores size. The best condition improving surface area of pores from 0.6215 m²/g (the initial sample) to 32.7762 m²/g was the injection EG into ceramic and heating with methanol bath by microwave. EG has very high loss factor value that could adsorb the microwave energy and also the polymerisation of EG inside the pores. The interpretation of BET and SANS/USANS data, the best result that Macrocracks were filled up by PEG formed between ceramics gains, so Micropores could produce.

Keywords: Porosity Ceramic Materials, Sintering, Microwave Techniques, SANS/USANS, BET, Loss Factor, Macropores, Mesopores and Micropores.
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CHAPTER I

INTRODUCTION

1.1 Background

Porous ceramic material has been used in industry applications for the filtration, absorption, catalyst and heat exchange such as in the diesel engine filtration system to decrease the CO$_2$ emission (Meng et al., 2016) and waste water treatment in factories. Moreover, it has been used globally for household drinking water filter to eliminate bacteria, viruses and unwanted particles in the water (Abebe et al., 2016). The properties of porous ceramic material have special physical and mechanical properties. That is why it can offer many advantages such as high chemical resistance, low thermal expansion, corrosion, wear resistance and light weight, thermal and acoustic insulation, impact absorption, catalyst supports, lightweight structures, porous burners, energy storage and accumulation, biomedical devices, gas sensors and filtration in water treatment. However, there are some disadvantage of ceramic materials such as electromagnetic insulator, so it does not receive and transfer heat from microwave radiation. The selection of medium that can convert electromagnetic energy to heat energy become the important part of this thesis experiment.

Porous ceramic is the material that can be produced generally in a porous form, pore in the material can be an open pore channel, dead end pores and closed pores. Closed pores have a great effect to the physical properties of ceramic materials such as density and thermal conductivity. Open pores connect to the surface of materials that allow liquid or gas can pass through the sample.
Porosity (\( \varepsilon \)) of materials is defined by the ratio of the void volume \( V_v \) to the total volume \( V_{tot} \) of the sample.

\[
\varepsilon = \frac{V_v}{V_{tot}}
\]

And the total porosity is combined closed pores and open pores (open pore channel and dead-end pores)

\[
\varepsilon_{tot} = \varepsilon_{closed} + \varepsilon_{open}
\]

According to the International Union of Pure and Applied Chemistry (IUPAC), there are 3 categories of pore sizes which are micropores (< 2 nm), mesopores (2 – 50 nm) and macrospores (> 50 nm). Porous ceramic can be an organic material or an inorganic material.

This report focuses on the water filter ceramic and heat treatment by microwave to increase the surface area of pores and pore distribution. The pores size of the common ceramic filter is between macropores and mesopores size. Organic ceramic filters are commonly made of polyamides, polysulfones and cellulose acetate. Inorganic filters are made of the porous ceramic materials which can be oxides ceramics such as alumina,
silica, zirconia or non-oxide ceramics such as carbides, borides, silicides and nitrides (Yang et al., 2006). Many experiments and research found that these organic filters have poorer performance than inorganic filters, the inorganic filters ceramics are higher chemical and pH resistance, lower corrosion, wider range of temperature and pressure operation, longer operating lifetime and lower thermal expansion (Mallicoat et al., 2005). Over decades, scientists and material engineers have been trying to synthesis new inorganic filters by using numerous techniques such as using of low temperature aqueous synthesis or using pore former sintering (high temperature) or introducing the additives to develop the quality of ceramic (Salvini et al., 2000). The ceramic filter’s quality depends on the pore structures such as pore shape, size, distribution, connectivity and relative density. The benefit of porous ceramic filters can be used to improve the purification of water in the residential domestic (drinking water) and factories (water treatment). The macropores and mesopores ceramic filter can remove dust, turbidity, iron and E-Coli bacteria. In medical field, micropores ceramic can be used in the dialysis process for the treatment of patients with kidney failure.

1.2 Sintering Process

There are many methods to produce the porous ceramic materials such as sintering, replica Template method, direct foaming method and sacrificial fugitives method, etc. The sintering method (high temperature processing) is the most common method that use in the industry especially, in the water treatment industry. The commercial production of material is normally based on the conventional sintering process which take a long time to complete the process, but microwave heat treatment technique is faster process because the material is heated by microwave dielectric heating rather than thermal conduction in the convection heating process. It is the internal heating of the volume of ceramic material
The conventional sintering concern about the energy transfer, external heat source, heat flow from outside to inside, some energy losses and it is a contact method, but microwave sintering concerns the energy conversion, internal heating so heat flow from inside to outside, high efficiency and non-contact method.

There are several advantages of microwave heat treatment as mentioned above. However, there still are some disadvantages of using microwave for sintering such as, difficulty to control the temperature inside the microwave furnace, general ceramic materials (dielectric materials) are heat transparent of electromagnetic microwave and requiring a medium to absorb and transfer heat to the ceramics. Good mediums depend on the loss factor ($\tan \delta$) value where high $\tan \delta$ gives high microwave absorption (Kappe., 2004). The loss factors can be classified as high ($\tan \delta > 0.5$), medium ($\tan \delta$ between 0.1-0.5) and low microwave absorbing ($\tan \delta < 0.1$).

### 1.3 Microwave Theory

Heating materials by microwave radiation is also called dielectric heating, high-frequency heating or electronic heating. Microwave radiation is an electromagnetic
radiation which has the frequency between 0.3 to 300 GHz. Heating dielectric materials in the industry require the microwave frequency 2.45 GHz which is in S-band range. The way of heating materials by microwave depend on the materials size, shape and dielectric constant. The mechanism for the microwave heating is dipolar loss also known as the re-orientation loss mechanism and it can be explained by Debye theory (Bradshaw et al., 1998).

Microwave can use in the application of heating in mineral process such as drying coal (Monsef-Mirzai et al., 1995) extraction of gold in the process of the pre-treatment (Haque., 1987) and reduction of ore and it can be use in regeneration of granular activated carbon for the carbon-in-pulp (CIP) process. Moreover, it has been used in the process of combustion or heat treatment for the organic and inorganic ceramics materials (Bradshaw., 1998).

1.4 Pores Characterisation

1.4.1 Pore Size is classified the materials into 3 categories, macropores, mesopores and micropores. It can be measured by many techniques and choice depends on which category of pore size.

1.4.2 Pore size distribution represent the pore volume in the function of pore size and normally result in derivative or percentage.

1.4.3 Specific surface area of pores is higher when the pore size of the sample is smaller.

1.4.4 Specific pore volume and porosity is the void volume and void space of the sample.
1.5 Polymerisation and Porous Polymers

Polymerisation or step growth of polymer is the forming of polymer by chemical reaction between functional group of monomers. Monomers can be the same type or different type of monomer reaction each other. Generally, there are 3 main types of polymerisation which are addition polymerisation, condensation polymerisation and elimination polymerisation.

Nowadays, porous polymer is very popular and useful in the industry. Porous polymer is material has a lot pores in it. There are several methods to synthesise the porous polymers such as the crosslink polymerisation, radiation-cast polymerisation at low temperature (Kumakure et al., 1988), multistage polymerisation (Gokmen et al., 2012).

In this experiment, the polymerisation of polymethyl methacrylate and polyethylene glycol by using the reaction from microwave radiation. These polymers are expected to form and coat on the surface of ceramic’s pores.

1.6 BET Theory

Brunauer-Emmett-Teller (BET) surface area analysis is one part of Langmuir Model which study kinetic behaviour of the gas (nitrogen) adsorption process and rate of arrival of adsorption and desorption. This technique is used to find the porosity, pore surface area and pore size distribution of porous materials. Adsorption mechanisms are mono-layer adsorption, multi-layer adsorption and capillary condensation. The isotherm curve of BET measurement is used to identify the porosity and pore size of sample. There are six types of isotherm curve that show in Figure 1.4. The y-axis of the isotherm curve represents in term of the quantity of gas adsorption by pores or cracks and x-axis represent
in term of the relative pressure \( \frac{P}{P_0} \). The section of the relative pressure can indicate size of pores which show in Figure 1.3

![Figure 1.3 Pore classified section on BET Isotherm (C. Solar et al 2009)](image-url)

Figure 1.3 Pore classified section on BET Isotherm (C. Solar et al 2009)

![Figure 1.4 Types of BET Isotherm curve (C. Solar et al 2009)](image-url)

Figure 1.4 Types of BET Isotherm curve (C. Solar et al 2009)

Table 1.1 Identify the porosity of material by BET Isotherm curve. (C. Solar et al 2009)

<table>
<thead>
<tr>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Microporous solids (pore size &lt; 2nm)</td>
</tr>
<tr>
<td>II</td>
<td>Non-porous or Macro porous (pore size &gt; 50 nm)</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>III</td>
<td>Multi-layer adsorption</td>
</tr>
<tr>
<td>IV</td>
<td>Capillary condensation in Mesoporous solids</td>
</tr>
<tr>
<td>V</td>
<td>Porous adsorbent / Mesoporous solids</td>
</tr>
<tr>
<td>VI</td>
<td>Stepwise multilayer adsorption / a uniform non-porous solids</td>
</tr>
</tbody>
</table>

These BET isotherm curves are used to compare with the results of this experiment.

1.7 SANS/USANS Theory

Small-angle neutron scattering is a powerful tool for analysis or measurement the materials at the nanoscale. It can measure very wide range of particles from proteins, viruses to the emulsion, polymers and rocks as show in Figure 1.5

Figure 1.5 The measurement range of SANS and USANS (IUPAC)
The neutron beam (incident beam) hits the sample and beam scatter as angle ($\theta$) from the normal line. Differences in scattering depend on the chemistry and physical of the materials. SANS measures the scattering intensity vs the scattering vector ($q$). The $q$ value can be calculated by the following equation

$$q = \frac{4\pi}{\lambda} \sin \theta$$

where $q = \text{half of the angle scattering}$

$\lambda = \text{wavelength of the incident beam}$

**Figure 1.6 Neutrons beam scattering (R. Zang et al 2015)**

**1.8 Objectives**

The properties of porous ceramic materials depend on the pore structures such as pore size, shape, distribution and topology or connectivity of pores and their density. This experiment has aimed to improve the connectivity, shape and distribution of the pores by microwave sintering and studied the appropriate time and temperature of reaction in microwave for the porosity controlling and improvement and then analyse the pore characteristics of the samples after heat treatment by the ultra-small-angle neutron scattering and small-angle neutron scattering technique (USANS/SANS) and the Brunauer-Emmett-Teller (BET) method. The results of this experiment have expected to
be able to change the pore size from micro-structure to be the nano-structure material, so it can give the benefit to the industries and human life.

CHAPTER II

LITERATURE SURVEY

Kappe (2004) discovered that the ability of substance to convert the electromagnetic energy into heat energy at a given temperature and frequency is determined by the loss factor (tan δ). This substance has known as medium. The reaction medium with high loss factor value can convert electromagnetics energy into heat energy rapidly. The loss factors for some common solvents are shown in Table 2.1.

Table 2.1 Loss Factor (tan δ) of different solvents. (C.O. Kappe 2004)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>tan δ</th>
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<tbody>
<tr>
<td>Ethylene glycol</td>
<td>1.350</td>
<td>DMF</td>
<td>0.161</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.941</td>
<td>1,2 Dichloroethane</td>
<td>0.127</td>
</tr>
<tr>
<td>DMSO</td>
<td>0.825</td>
<td>Water</td>
<td>0.123</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>0.799</td>
<td>Chlorobenzene</td>
<td>0.101</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.722</td>
<td>Chloroform</td>
<td>0.091</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.659</td>
<td>Acetonitrile</td>
<td>0.062</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.589</td>
<td>Ethyl acetate</td>
<td>0.059</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>0.571</td>
<td>Acetone</td>
<td>0.054</td>
</tr>
</tbody>
</table>

Chou (2012) found there are also media in state of gas can be used to control the porosity of ceramic materials. However, the gas medium is often used in the conventional furnace. Gas is injected into the pores of ceramic and be pressurised to keep the gas inside. The
most of them are the inert gas such as argon (Ar), helium (He), hydrogen (H₂), neon, xenon, and carbon dioxide (CO₂) then pressurised all these samples until make sure that all gas is stay inside the pores.

Karayannis (2016) reported the microwave sintering in the ceramic processing has been in use since 1940s and it became popular in 80s. It was used in the ceramic processing of drying, sintering and calcination.

Thomazini et al. (2011) found many research experiments have been trying to develop this technique in the commercial industry products for instance the experiment of density of alumina commercial product (A1K) by using both convention heating and microwave heating at the same temperature (1650 °C). After 60 minutes in the microwave process, density of A1K increased up to 4 g/cm³ but in the convention heating process, A1K increased the maximum density only 3.8 g/cm³ with time taken for 120 minutes.

Sauravet et al. (2015) reported there are numerous experiments that focus the controlling pore size and connectivity of the porous ceramic materials by convention heating techniques, the temperature condition and chemical solution for immersing the ceramic before heat treatment were the main factor. Porous magnesium oxide (MgO) ceramics increased the porosity and connectivity at 1300 °C for 1 hour then immersed into aluminium nitrate solution and reheated again at 1300 °C for 2 hours, SEM and XRD were used to measure the physical properties of ceramics and pore size.

Abourriche et al. (2015) researched by using the convention heating technique, the ceramic sample was synthesised from the raw materials, the red clay and the oil shale rock. The main components of this raw materials were silica (SiO₂), aluminium oxide (Al₂O₃), lime (CaO), alkalis (K₂O and Na₂O) and magnesia (MgO). The synthesised
ceramic samples were sintered in the furnace at various temperatures 1000 °C, 1050 °C and 1100 °C and SEM was used to measure of pore diameter sizes. A temperature of 1000 °C gave the smallest pore diameter sizes.

Sato et al. (2003) mentioned that in Japan, there was the successful research by using microwave sintering of commercial alumina ceramic for the application in the construction and high temperature optics. The 15 inch of alumina ceramic ring sample was sintered with microwave method could improve the bending strength by 30% greater and the shrinkage distortion by 60% smaller than the convention heating process. Moreover, it used less time and energy than the convention heating process. In study case of the nano-structure of ceramic was the difficult case to identify or control the properties of nanometric alumina particles by using direct microwave sintering.

Cheng et al. (2002) found the way to achieve the best results of small gain size and higher density, alumina ceramic sample was doped with magnesium oxide (MgO) and fired in hydrogen (H₂) atmosphere.

Kumar et al. (2016) reported that some type of ceramic material such as piezoelectric materials (PZT) was heated by microwave and compared with the convention heating at the same temperature 1150 °C, the dielectric and piezoelectric properties of PZT materials from both methods were not much different but the operation time by microwave was much shorter than the convention heating method.

Measuring the porosity of ceramic materials can be done by many techniques such as gas adsorption, fluid penetration, the frequency response method, small angle and ultra-small angle neutron scattering (SANS/USANS).
Jarvelaine et al. (2014) used the frequency response method by using pseudo-random binary sequence to measure the porosity of ceramics. This technique is measuring the behaviour of ceramic in alternating electric field and analysing the results by the capacitance of the capacitor.

The most common method to characterise macroporous ceramic materials is mercury intrusion porosimetry. Hassan et al. (2015) used mercury intrusion porosimetry to measure the pore size of anodes in solid oxide fuel cells. Mercury is filled into the pores of solid oxide under high pressure. This method is more precise and accurate when measuring macroporous materials than other methods but if the size of pores falls below macropores, increasing pressure is required.

Donchev (2005) found the common method to characterise of mesopores and micropores range of ceramic materials is Brunauer-Emmett-Teller (BET) method, liquid Nitrogen is used for the pores absorption of Nitrogen gas and the shape of pores should be sphere and very small size pores.

![Figure 2.1 Pore Size and the pore characterisation method (IUPAC)](image)

Xia et al. (2014) reported about the small pores size in microporous range, the small angle and ultra-small angle technique is applied for measurement of the pore distribution, connection and size. It is quite different from two techniques above. USANS/SANS has very wide range detection of pore size from sub-
micrometer to sub-nanometer (around $10^{-10} \text{ to } 10^{-6} \text{ A}$). It can measure the sample in liquid, solid and bulk samples.

All the study cases above concern only the high temperature to control the pore size, connectivity and density of ceramics.

Donchev et al. (2005) did some experiment study the pores controlling under very low temperature. Macrostructure ceramic materials was synthesised and prepared, then it was frozen under freezing low temperature from -15, -20, -25 and -30$^\circ$C respectively. The results show that at -30$^\circ$C gave the highest percentage of porosity. The main factors of this study are the bulk freezing temperature, the ice crystal growth, temperature gradient and the properties of the starting ceramic materials. This technique is known as the freezing-cast method.

Ingram-Ogunwumi et al. (2010) applied the catalyst pre-coating technique on the pore’s surface before do the microwave heat treatment. The materials that coated on the surface of the pore could reduce the microcrack space. The materials were ionene polymer, polyvinyl alcohol/vinyl amine and polyvinyl alcohol/vinyl formamide copolymers or gelatines. The filter ceramic is a combination of inorganic such as silica, titania and alumina and organic material then giving them a heat treatment to produce aluminium titanate ceramic filter.

Pakdeewanishsukho et al. (2006) synthesised the lead glycolate for the precursor of the piezoelectric ceramic material (PZT) via sol-gel process and heated by conventional furnace and microwave reactor. Microwave was easier to control condition than conventional furnace and it produce higher crystallinity and higher density surface of materials.
CHAPTER III

EXPERIMENTAL

3.1 Materials

The sample is the ceramic water filters (Stefani brand) were purchased from Bunnings. The clay that used to make this filter is Brazilian clay. The composition of this sample is 30% of aluminium oxide, 50% of silicon oxide, 10% calcium, 5% magnesium oxides and 5% others. The size of the pore is in the range of mesopores and macropores. Medium solvents that used to inject into the pores of ceramic samples in this thesis are laboratory grade methanol (CH$_3$OH), de-ionised water and mineral oil (parafin oil). Polymers that used to injection into the sample are polyethylene glycol (PEG 400) and polymethyl methacrylate (PMMA). Monomers that used for this thesis are ethylene (EG) and methyl methacrylate (MMA).

Mineral oil and polyethylene glycol have high viscosity and then ethylene glycol respectively. Methanol has the lowest boiling point. During the heat treatment process methanol evaporate faster than PEG, EG and mineral oil.

3.2 Experimental Instruments

High temperature microwave reactor (MW-HS06) is an industry microwave pyrolysis furnace that can give continuous microwave radiation flow and produce very high temperature (>2000 °C) in a short period of time. This microwave furnace is suitable for roasting, sintering, synthesis and heat treatment. This model can be adjusted the percentage of microwave radiation power and can set the temperatures and periods of each stage but temperature inside the furnace increase all the time of reaction. It cannot be held at the certain temperature.
A vacuum oven is an oven that can adjust the temperature up to 200 °C and vacuum pressure up to 100 Pa. It is used for injection the medium solvent, polymers and monomers into the pores of ceramic materials.

Surface area and porosity measurement (Micromeritics Tristar II) via the Brunaurer Emmett Teller (BET) method were obtained to identify surface area of pores by using isotherm to analyse the data of experiment.

Scanning electron microscopy was used to determine the product morphology and composition of materials. Small-angle neutron scattering (Quokka) is very powerful equipment for looking at structure on nanoscales from 1-10 nm. It has a wavelength between 4.5-43 Å. Source distance to sample and to the detector is from 1 m to 20 m. Maximum beam cross section is 50 mm x 50 mm. Instrument location is at a neutron-guide hall, cold guide CG1, ANSTO (Gilbert., 2001).

Ultra-small-angle neutron scattering (Kookaburra) is the technique for investigating or studying the shape and size of the materials’ size 10 µm and below by diffraction. This instrument is useful for studying pores and cracks in the materials, mesoscopic magnetic particles and molecules of polymer. It has a beam line CG3 cold neutron, wavelength $\lambda_{\text{Si(111)}} = 4.74$ Å at $\theta_{\text{Bragg}} = 49.1^\circ$ and $\lambda_{\text{Si(311)}} = 2.37$ Å at $\theta_{\text{Bragg}} = 46.4^\circ$ which is suitable for weakly and strongly scattering samples (Gilbert., 2001)

### 3.3 Initial Untreated Ceramic Material Preparation

Untreated sample is Stefani ceramic water filter cartridge as shown Figure 3.1. It was cut into a square section around 5 cm x 5 cm, followed by sanding all the surface to make the flat surface and washed the sample by deionised water to remove excess
activated carbon and silver on the surface of sample. Clean sample placed in the oven at 110 °C at least 5 hours to remove excess water in the sample.

![Initial untreated ceramic water filter cartridge (Stefani product)](image)

**Figure 3.1 Initial untreated ceramic water filter cartridge (Stefani product)**

### 3.4 Injection Medium Solvent into the Untreated Sample

Untreated sample submerged into 3 different types of medium solvents which were deionised water, mineral oil (paraffin oil) and methanol then placed them in the vacuum oven and set the temperature of the oven around 40-50°C for the mineral oil, 30-40°C for the deionised water and no temperature setting for the methanol and set the pressure between -80 to -90 Pa (vacuum pressure) at least 6 hours until the bubbles disappeared. After 6 hours, the samples were taken out from the vacuum oven and they were kept submerged into the medium solvents at room temperature for further treatment.

### 3.5 Heat Treatment by Microwave Radiation for Medium Injection without Methanol Bath.

The injected deionised water, mineral oil and methanol ceramic samples were placed directly into the high temperature microwave furnace. Setting the thermocouple touched the top of the surface of ceramic samples for temperature reading. Operating the microwave reactor by setting the power at 70% and time of reaction for 30 min. The parameter of temperature were 5 stages controlling. The withdrawn current of the
microwave reactor should not be over 1.2 A and during the reactor was working the radiation leakage must be measured all the time. The samples were measured the temperature immediately after finishing the heat treatment by the infrared thermometer.

3.6 Injection Polymer Solution into Pores of Untreated Sample.

Untreated sample submerged into 2 different types of polymer solutions which were polyethylene glycol (PEG) and polymethyl methacrylate (PMMA) then placed them in the vacuum oven then set the temperature around 70-80°C and set the pressure between -80 to -90 Pa (vacuum pressure) at least 6 hours until the bubbles disappeared. After 6 hours, the samples were taken out from the vacuum oven and they were kept submerged into the medium solvents at room temperature for further analysis.

3.7 Heat Treatment by Microwave Radiation for Polymer Solutions Injection without Methanol Bath

The injected polyethylene glycol (PEG) and polymethyl methacrylate (PMMA) samples were placed directly into the high temperature microwave furnace. Setting the thermocouple touched the top of the surface of ceramic samples for temperature reading. Operating the microwave reactor by setting manually the power at 70% and time of reaction for 30 min. The parameter of temperature were 5 stages controlling. The withdrawn current of the microwave reactor should not be over 1.2 A and during the reactor was working the radiation leakage must be measured all the time. The samples were measured the temperature immediately after finishing the heat treatment by the infrared thermometer and rested in the room temperature then waited until the samples cool down before further analysis.

3.8 Injection Monomer Solution into Pores of Untreated Sample.
Untreated sample submerged into 2 different types monomer solutions which were ethylene glycol (EG) and methyl methacrylate (MMA) then placed them in the vacuum oven then set the temperature around 70-80 °C and set the pressure between -80 to -90 Pa (vacuum pressure) at least 6 hours until the bubbles disappeared. After 6 hours, the samples were taken out from the vacuum oven and they were kept submerged into the medium solvents at room temperature for further treatment and rested in the room temperature then waited until the samples cool down before further analysis.

3.9 Heat Treatment by Microwave Radiation for Monomer Solutions Injection without Methanol Bath.

The injected ethylene glycol (EG) and methyl methacrylate (MMA) samples were placed directly into the high temperature microwave furnace. Setting the thermocouple touched the top of the surface of ceramic samples for temperature reading. Operating the microwave reactor by setting manually the power at 70% and time of reaction for 30 min. The parameter of temperature were 5 stages controlling. The withdrawn current of the microwave reactor should not be over 1.2 A and during the reactor was working the radiation leakage must be measured all the time. The samples were measured the temperature immediately after finishing the heat treatment by the infrared thermometer and rested in the room temperature then waited until the samples cool down before further analysis.

3.10 Heat Treatment by Microwave and Freezing-Cast method of Injection Medium, Polymer and Monomer Solution Samples.

The injected deionised water, mineral oil, methanol, polyethylene glycol (PEG), polymethyl methacrylate (PMMA), ethylene glycol (EG) and methyl methacrylate
(MMA) samples were place directly into the high temperature microwave furnace. Setting the thermocouple touched the top of the surface of ceramic samples for temperature reading. Operating the microwave reactor by setting manually the power at 70% and time of reaction for 30 min. The parameter of temperature were 5 stages controlling. The withdrawn current of the microwave reactor should not be over 1.2 A and during the reactor was working the radiation leakage must be measured all the time. The samples were taken out of the microwave furnace and immediately placed in the liquid nitrogen then waited until the samples cool down before further analysis.

3.11 Heat Treatment by Microwave Radiation for the Injected Medium-Solutions into pores of the sample with Methanol Bath.

The injected deionised water, mineral oil and methanol ceramic samples were placed into the silica carbide crucible with full of methanol solution (300-400 ml) and put them in the high temperature microwave furnace. Operating the microwave reactor by setting the power at 70% and time of reaction for 30 min. The parameter of temperature were 5 stages controlling. The withdrawn current of the microwave reactor should not be over 1.2 A and during the reactor was working the radiation leakage must be measured all the time. The samples were taken out of the microwave furnace and rested in the room temperature then waited until the samples cool down before further analysis.

3.12 Heat Treatment by Microwave Radiation the Injected Polymer-Solutions into pores of the sample with Methanol Bath.

The injected polyethylene glycol (PEG) and polymethyl methacrylate (PMMA) ceramic samples were placed into the silica carbide crucible with full of methanol solution (300-400 mL) and put them in the high temperature microwave furnace. Operating the
microwave reactor by setting the power at 70% and time of reaction for 30 min. The parameter of temperature were 5 stages controlling. The withdrawn current of the microwave reactor should not be over 1.2 A and during the reactor was working the radiation leakage must be measured all the time. The samples were taken out of the microwave furnace and rested in the room temperature then waited until the samples cool down before further analysis.

3.13 Heat Treatment by Microwave Radiation for the Injected Monomer Solutions into pores of the sample with Methanol Bath

The injected Ethylene Glycol (EG) and Methyl Methacrylate (MMA) ceramic samples were placed into the silica carbide crucible with full of methanol solution (300-400 ml) and put them in the high temperature microwave furnace. Operating the microwave reactor by setting the power at 70% and time of reaction for 30 min. The parameter of temperature were 5 stages controlling. The withdrawn current of the microwave reactor should not be over 1.2 A and during the reactor was working the radiation leakage must be measured all the time. The samples were taken out of the microwave furnace and rested in the room temperature then waited until the samples cool down before further analysis.

3.14 Heat Treatment by Conventional Furnace

Untreated raw ceramic sample placed in the conventional furnace and set the temperature at 1,000 °C for 1 hour. The sample was taken out of the conventional furnace after 1-hour reaction and then took the sample out of the conventional furnace after 1 hour heat treatment and rested it in the room temperature then waited until the samples cool down before further analysis.
3.15 Sample Preparation for BET Analysis

These samples were ground and sieved under 53 µm. The empty tube must be weighted before placing the sample powder in it, then placed the power sample into the tube. This sample must be purified and completed dried by degassing under vacuum at 90 °C for 3 hours and then increased the temperature to be 130 °C for 3 hours and added helium gas in the tube for 10 seconds. Weigh the sample with tube again and calculate mass of purified sample.

3.16 Sample Preparation for SANS/USANS measurement

Preparation of samples for measuring the porosity by the ultra-small-angle neutron scattering and small-angle neutron scattering (USANS/SANS). These samples include:

1. Sample before microwave treatment and heat convection treatment
2. Injected deionised water sample after microwave furnace treatment at 70% power for 30 min without methanol bath
3. Injected mineral oil sample after microwave furnace treatment at 70% power for 30 min without methanol bath
4. Injected methanol sample after microwave furnace treatment at 70% power for 30 min without methanol bath
5. Injected PMMA sample after microwave furnace treatment at 70% power for 30 min without methanol bath
6. Injected PEG sample after microwave furnace treatment at 70% power for 30 min without methanol bath
7. Injected MMA sample after microwave furnace treatment at 70% power for 30 min without methanol bath

8. Injected EG sample after microwave furnace treatment at 70% power for 30 min without methanol bath

9. Sample after heat treatment by conventional furnace at 1000 °C for 30 min.

The above sample were grinded and sieved under 53µm and then prepared as thin sections, using quartz glass slides. We will prepare a few difference thicknesses of sample were prepared such as 0 mm and 1 mm for the ultra-small-angle neutron scattering and small-angle neutron scattering (USANS/SANS). Selected samples were measured for all 3 thicknesses to confirm whether multiple scattering is present and then the appropriate H₂O/D₂O mixture was used to further reduce contrast to avoid multiple scattering. Some samples even mixed with H₂O/D₂O mixture still cannot reduce the multiple scattering, so thickness of sample must be prepared as thin as possible. Therefore, all sample power above were brushed on the top of kaptan tape then run sample test then found this technique was suitable and reduce multiple scattering.
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterisation of Initial Untreated Ceramic Material.

Characterisation of the initial untreated ceramic material using SEM/EDS, figure 4.1, shows the morphology and composition of the sample. The compositions of sample are silicon oxide (SiO$_2$), aluminium oxide (Al$_2$O$_3$), calcium oxide (CaO), magnesium oxide (MgO) and potassium oxide (K$_2$O), table 4.1. The morphology clearly appears to be an amorphous phase; at this stage the crystalline and polymerisation have not yet formed.

![Figure 4.1 SEM/EDS of the initial untreated ceramic material](image)

Table 4.1 The chemical composition of the initial untreated ceramic material.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Mass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicon oxide (SiO$_2$)</td>
<td>51.56</td>
</tr>
<tr>
<td>aluminium oxide (Al$_2$O$_3$)</td>
<td>31.00</td>
</tr>
<tr>
<td>calcium oxide (CaO)</td>
<td>10.94</td>
</tr>
<tr>
<td>magnesium oxide (MgO)</td>
<td>4.89</td>
</tr>
<tr>
<td>Chemical</td>
<td>Percentage</td>
</tr>
<tr>
<td>---------------</td>
<td>------------</td>
</tr>
<tr>
<td>Potassium oxide (K₂O)</td>
<td>1.61</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

The general ceramic water filter that has been using in the industry is a combination of two mains chemical composition which are silica oxide and aluminium oxide.

From figure 4.1, BET adsorption isotherm of Initial untreated ceramic material show the materials is non-porous or macropores adsorption. The quantity of gas adsorbed (y-axis) is low around 0.2 cm²/g where the curve is quite flat gradient between 0 to 0.5 range of relative pressure (\(\frac{P}{P_0}\)) which can interpret that it is not a micropores material. The isotherm curve from this experiment is same as the isotherm type ii in figure 1.4, so it confirms that the untreated raw ceramic material is macropores or mesopores size.

Figure 4.1, BET adsorption isotherm of initial untreated ceramic material
4.2 Characterisation of Ceramic sample and Heat Treated by Conventional Furnace

Figure 4.2 represents The BET adsorption isotherm curve of heat treated by conventional furnace show no significant different from the untreated sample. The isotherm curve is same as Type II in Figure 1.4, so the sample has the large pore size and pore size distribution. The quantity of gas adsorption is less than 0.5 cm$^2$/g in the range of the relative pressure ($\frac{P}{P_0}$) from 0 to 0.5. The pores size is still larger than 2 nm and the microcracks of ceramic have some distance from each other. Thus, macropores and mesopores of alumina silica ceramic sample cannot change to be micropores by heating directly with the traditional conventional furnace. Chang et al., 200 reported that the cracked surface, the density and the grain size decreased at 850 °C for 5 min in the conventional furnace via Sol-gel synthesis process and the ceramic sample was the piezoelectric ceramic sample. With this temperature and heat treatment time duration in the conventional furnace cannot improve the surface area of pores.
4.3 Characterisation of Injected Medium solution-samples and Heat Treated by Microwave without Methanol Bath.

Figure 4.3 to 4.5 represent the BET adsorption isotherms. The relative pressure \( \frac{P}{P_0} \) around 0.2 to 0.5, the quantity of gas adsorption of sample is very low and low gradient that represent the treated sample is not different from the initial untreated sample. The surface area of the pore size (\(<2\) nm) of treated samples show significant low. The treated samples are still the macropores materials. The isotherm curve from this experiment is same as the isotherm Type II in Figure 1.4, so it confirms that the untreated raw ceramic material is macropores or mesopores size.

Figure 4.3 BET adsorption isotherm of injected water into ceramic and heat treat by microwave 70% power for 30 min without methanol bath
Figure 4.4 BET adsorption isotherm of injected mineral oil into ceramic and heat treat by microwave 70% power for 30 min without methanol bath

Figure 4.5 BET adsorption isotherm of injected methanol into ceramic and heat treat by microwave 70% power for 30 min without methanol bath
Ideally methanol has high loss factor, so it should be able to adsorb the microwave electromagnetic and convert to be heat energy the ceramic sample. In fact, it is not different from initial untreated sample or injected-water or injected-mineral oil. The amount of methanol that was trapped inside the pore was not enough to convert the heat energy and the boiling point of methanol is quite low around 65 °C, so it evaporated during the microwave heat treatment process.

Deionised water and mineral oil (paraffin oil) have low value of the loss factor, table 2.1, so the surface area of small pores (< 2 nm) is still in the low range and does not change macropores or mesopores to be micropores.

4.4 Characterisation of Injected Polymer solution samples and Heat Treated by Microwave without Methanol Bath.

Figure 4.6 and 4.7 represent the BET Isotherm curve of the injection polymer into the pores of sample and heated by microwave under 70% for 30 mins. The quantity gas adsorption is quite low (around 0.5 cm$^2$/g) where the relative pressure ($\frac{p}{p_0}$) between 0 to 0.5. This result indicates that injection PMMA does not show any improvement of increasing the mesopores surface area or decreasing the pore size. Therefore, polymethyl methacrylate is unsuitable to inject into the pores and no polymerisation into the surface of pore due to both of itself is a polymer, and also it is possible to burn out during microwave heat treatment process or PMMA has probably a low value of the loss factor (tan δ) that why it is not on the table 2.1. It is not a good medium can convert the microwave electromagnetic to be heat energy and the isotherm curves from this experiment are same as the isotherm Type II in Figure 1.4, so the results confirm that the
injected polymers and microwave heated ceramic material is still macropores or mesopores size.

Ethylene glycol has highest the loss factor value in term of monomer, table 2.1, but when it becomes the polymer (polyethylene glycol) should be able to transfer microwave electromagnetic to heat energy, so it should have any significant improvement of the pore size. Figure 4.7, there is improvement of pore size or pore size distribution. The quantity of gas adsorption is higher than medium and PMMA injection. It is around 1 cm$^2$/g where the relative pressure from 0 to 0.5 which is mesopores area. However, the curve shape is still same as Type II in Figure 1.4 that means this case, ceramic still contains the large pore size (macropores and mesopores) more than micropores size.

Ingram-Ogunwumi et al., 2010 indicated that the microcrack and pore gaps get closer when the ceramic has a pre-coating or injection with different type of polymers. Copolymers, ionone polymers, inorganics and organics were used to inject and pre-coated before heating by microwave, but the ceramic sample was aluminium titanate ceramic which is different from this thesis which alumina silica ceramic was used. Therefore, precoated pore surface of aluminium titanate ceramic can adsorbed microwave energy directly better than precoated pore surface of alumina silica ceramic without methanol bath during the microwave heat treatment process.
Figure 4.6 BET adsorption isotherm of injected polymethyl methacrylate solution into ceramic and heat treat by microwave 70% power for 30 min without methanol bath.

Figure 4.7 BET adsorption isotherm of injected polyethylene glycol solution into ceramic and heat treat by microwave 70% power for 30 min without methanol bath.
4.5 Characterisation of Injected Monomer solution-samples and Heat Treated by Microwave without Methanol Bath.

Injection monomer solution into the pores of sample and expected the polymerisation happened during the process of the microwave heat treatment and polymer should be coated on the surface of pore and decrease the diameter of pore size. Figure 4.8 represents the BET isotherm curve of injected MMA into the sample and heated by microwave shows the quantity of gas adsorption did not improve when compare with the untreated sample. It shows value less than 0.5 cm$^2$/g where the relative pressure ($\frac{P}{P_0}$) from 0 to 0.5 which is micropores section. Therefore, the Isotherm curve from this experiment is same as the isotherm Type II in Figure 1.4, so the pore sizes are still larger than 2 nm.
Figure 4.8 BET adsorption isotherm of injected methyl methacrylate (MMA) solution into ceramic and heat treat by microwave 70% power for 30 min without methanol

However, there is a sign of improvement of the quantity of gas adsorption after injected Ethyl Glycol (monomer solution) and microwave heated for 30 min shown in Figure 4.9. Even though, Ethylene Glycol has highest value of the loss factor and itself can become polymer and coat the surface of pores then create more Micropores size. On y-axis which is the quantity of gas adsorption is around 2 cm²/g where the relative pressure \( \frac{p}{p_0} \) on x-axis from 0 to 0.5 that indicate the surface area of pore size (< 2 nm) increase slightly increase but the shape of Isotherm curve is still same as Isotherm Type II in Figure 1.4, so this treated sample still has the pore size in range of macropores and mesopores.

Figure 4.9 BET adsorption isotherm of injected ethylene glycol (EG) solution into ceramic and heat by microwave 70% power for 30 min without methanol
4.6 Characterisation of Injected Medium solution-samples and Heat Treated by Microwave without Methanol Bath and then using Freezing-Cast Method

According to Hu et al., 2010 report that yttria-stabilized zirconia ceramics were sintered at 1450 °C for 2 hours in air and then freeze-dried sample at -50 °C under vacuum condition, the pore channel size decreased. Therefore, the freezing-cast method was applied in this experiment. Methanol solution as a good medium (high loss factor value) was injected in the pores of ceramic sample and heated in microwave furnace for 60 min then immediately freeze it in the liquid nitrogen under the vacuum pressure and measure the BET surface area and porosity. From Figure 4.10 show there is no significant improvement of pore size and pore size distribution. The quantity of gas adsorption is still low around 0.05 cm²/g and flat gradient curve where the relative pressure ($\frac{P}{P_0}$). The idea of shrinkage when material is frozen under vacuum pressure does not work in this case.

Figure 4.10 BET adsorption of injected medium-samples and heat by microwave 70% power for 30 min without methanol bath and freezing-cast method
4.7 Characterisation of Injected Polymer solution-samples and Heat Treated by Microwave without Methanol Bath and then using Freezing-Cast Method

Figure 4.11 show that injection polyethylene glycol (PEG) into the pore spaces of ceramic sample, heat by microwave and then freeze the sample in the liquid nitrogen under vacuum pressure, there is no sign of pore space get closer and improve pore shape and connection. the isotherm curve is same as Type II in Figure 1.4, so the pore sizes are still larger than 2 nm. Ceramic sample remains macropores and mesopores size.

![BET adsorption of injected polymer-samples (PEG) and heat by microwave 70% power for 30 min without methanol bath and freezing-cast method](image)

4.8 Characterisation of Injected Monomer solution-samples and Heat Treated by Microwave without Methanol Bath and then using Freezing-Cast Method

Methyl methacrylate was selected to inject in the pore and it was expected that BET isotherm curve should be the same as Type II in Figure 1.4 which the result of BET
isotherm show that is same as the expectation. Figure 4.12 indicate that the sample after injected and heated and frozen respectively, the pore size is still in range of Macropores and mesopores. The quantity of gas adsorption is still low. Therefore, MMA is confirmed that is not suitable for this experiment. The shrinkage of pores and decreasing pore size by dipping into liquid nitrogen is not suitable to apply in this case experiment.

Figure 4.12 BET adsorption of injected monomer-samples (MMA) and heat by microwave 70% power for 30 min without methanol bath and freezing-cast method

4.9 Characterisation of Injected Monomer solution-samples and Heat Treated by Microwave in Methanol Bath

Several analysis and measurement information, ethylene glycol is the best option for injection in the pores of sample. ethylene glycol (EG) is a pre-coating on the surface of pores. It received the microwave electromagnetic and convert it to be heat energy and itself form the polymerisation during heat treatment. However, only small improvement
on micropores size of ceramic sample, so it requires more heat conversion. Thus, methanol bath was introduced at this case. Injected EG sample was submerged in the methanol bath (300-400 ml) to make sure the heat conversion is enough to form the polymer and react to the surface of the pores. The surface area of pore size in Micropores region should show significant improvement. The pore size decrease and BET surface area of material increase. From Figure 4.13 show exactly same as the expectation. The quantity of gas adsorption of sample increase over 10 cm$^2$/g. where the relative pressure ($\frac{p}{p_o}$) from 0 to 0.3 (micropores region), moreover, the shape of the BET isotherm curve is similar with the isotherm curve Type I in Figure 1.4. This experiment case shows totally different any Isotherm curves of heat treatment without methanol bath. The methanol bath is the factor of developing and the microcracks of ceramic sample get closer and the pore size of untreated sample which is macropores or mesopores turn to be mesopores. the combination of ethylene glycol and methanol bath indicate the best condition for the thesis. this technique has been replicated many times and every time show increasing of bet surface area and micropores size.
4.10 Characterisation of BET Surface area of Untreated with Microwave and Conventional Furnace Heat Treatment, Injected Medium, Polymer and Monomer without Methanol Bath and Injected Medium, Polymer and Monomer with Methanol Bath by Microwave Heat Treatment.

BET surface area indicates the amount of micropores size of sample. If BET surface area of sample is high, so the quantity of micropores size and porosity of sample is also high. From Table 4.3 show the maximum of BET surface area is the sample of injected eg with methanol bath during microwave heat treatment. It is much higher than the untreated sample over 50 times. Therefore, this experiment shows successful process to decrease the pore size and increase porosity of ceramic materials.
Table 4.2 Summary of BET surface area samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET Surface Area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Untreated sample</td>
<td>0.6215</td>
</tr>
<tr>
<td>2. Raw ceramic heated at 1000 °C for 1 hour by conventional furnace</td>
<td>1.1582</td>
</tr>
<tr>
<td>3. Injected methanol in ceramic and heat by microwave furnace at 70%</td>
<td>1.1247</td>
</tr>
<tr>
<td>power for 30 min without methanol bath</td>
<td></td>
</tr>
<tr>
<td>4. Injected methanol in ceramic and heat by microwave furnace at 70%</td>
<td>1.3965</td>
</tr>
<tr>
<td>power for 30 min with methanol bath</td>
<td></td>
</tr>
<tr>
<td>5. Injected deionised water in ceramic and heat by microwave furnace</td>
<td>0.9961</td>
</tr>
<tr>
<td>at 70% power for 30 min without methanol bath</td>
<td>X</td>
</tr>
<tr>
<td>6. Injected deionised water in ceramic and heat by microwave furnace</td>
<td>X</td>
</tr>
<tr>
<td>at 70% power for 30 min with methanol bath</td>
<td></td>
</tr>
<tr>
<td>7. Injected mineral oil (paraffin oil) in ceramic and heat by microwave</td>
<td>0.6606</td>
</tr>
<tr>
<td>furnace at 70% power for 30 min without methanol bath</td>
<td>X</td>
</tr>
<tr>
<td>8. Injected mineral oil (paraffin oil) in ceramic and heat by microwave</td>
<td>X</td>
</tr>
<tr>
<td>furnace at 70% power for 30 min with methanol bath</td>
<td></td>
</tr>
<tr>
<td>9. Injected polymethyl methacrylate (PMMA) in ceramic and heat by</td>
<td>0.7874</td>
</tr>
<tr>
<td>microwave furnace at 70% power for 30 min without methanol bath</td>
<td>X</td>
</tr>
<tr>
<td>10. Injected polymethyl methacrylate (pmma) in ceramic and heat by</td>
<td>X</td>
</tr>
<tr>
<td>microwave furnace at 70% power for 30 min with methanol bath</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>11. Injected polyethylene glycol (PEG) in ceramic and heat by microwave furnace at 70% power for 30 min without methanol bath</td>
<td>1.8996</td>
</tr>
<tr>
<td>12. Injected polyethylene glycol (PEG) in ceramic and heat by microwave furnace at 70% power for 30 min with methanol bath</td>
<td>X</td>
</tr>
<tr>
<td>13. Injected methyl methacrylate (MMA) in ceramic and heat by microwave furnace at 70% power for 30 min without methanol bath</td>
<td>0.7352</td>
</tr>
<tr>
<td>14. Injected methyl methacrylate (MMA) in ceramic and heat by microwave furnace at 70% power for 30 min with methanol bath</td>
<td>0.8247</td>
</tr>
<tr>
<td>15. Injected ethylene glycol (PEG) in ceramic and heat by microwave furnace at 70% power for 30 min without methanol bath</td>
<td>4.6215</td>
</tr>
<tr>
<td>16. Injected ethylene glycol (PEG) in ceramic and heat by microwave furnace at 70% power for 30 min with methanol bath</td>
<td>32.7762</td>
</tr>
</tbody>
</table>

Note: X = no analysis of the sample and Freezing Cast results are not on the table because the BET surface area results are so small.

4.11 Characterisation of SANS/USANS of Untreated sample by Microwave and Conventional Furnace, Injected Medium, Polymer and Monomer Sample and Heat Treatment by Microwave Furnace.

SASFit is software that uses to analyse the data of SANS and USANS measurement. Figure 4.13 represent the SANS/USANS results show PEG and mineral indicate high intensity in the mesopores (large pore) and micropores (small pore) area.
Figure 4.14 represent the SANS/USANS results

The peaks of PEG and mineral oil show intensity higher than any sample curves. Ideally, they should be same line position as others, according to BET results but they are different. BET result has no significantly improving by using PEG as a precoat before the microwave treatment. The polymerisation of PEG (distinct from EG) and the relatively high carbon number of the alkanes in the mineral oil mean they both interact more strongly with neutrons than the ceramic other treatments. The result is that there are more scattering centres off the carbon atoms in mineral oil and PEG, resulting in multiple scattering. Multiple scattering results in incoherent scattering (i.e. structureless, flat, scattering) at higher q values, which is what this experiment observe. Scattering off the heavy organic molecules, it's a molecular scale effect, which show at higher q.
Multiple scattering is one of the banes of SANS and is always challenging to deal with. If it's happening because the overall sample is too thick, then aiming to use a thinner sample. But that approach may not work where the scattering is molecular scale (q > 0.1, 1/Å, size scale < 6 nm). Reducing a 300 μm sample down to 100 μm, to reduce micron scale multiple scattering. However, reducing 6 nm scale scattering is not so simple. Some carbon samples have the same problem. In this case, using a rotating sample holder for future measurements with a much smaller amount of sample suspended in fluid, to reduce multiple scattering.

Contrast matching can also help reduce it. When measuring the samples with 60% D₂O, the background intensity at high q got reduced by an order of magnitude, which is the effect you need introduce multiple scattering. Thus, the future work can recommend repeating measurements using contrast solution (probably 80% D₂O is best since it has the same reduced background at high q as 60%, but with better signal at low q.

Other interpretation: all the intensities are flat above q > 0.1, 1/Å. This means there is no nanoscale structure, which is consistent with the BET data which indicated no nanopores. PEG shows a small peak around q ~ 0.045, 1/Å. That indicates some PEG structure at a size around 14 nm. It's probably a combination of PEG molecules themselves, and the pore space between them. It corroborates the EG/MeOH bath result, that PEG forms nanoscale structure. In the case of Pre-polymerised PEG, it's not strong enough to show up in BET but does show up in this SANS peak. The BET surface area data for EG/MeOH bath indicates that the result is better than PEG result by polymerising in-situ using the microwave/MeOH bath method.
For the future work measuring the SANS of your EG/MeOH bath will show a high q peak like PEG does, probably at even higher q than 0.045 1/Å.

The high q noise in the other samples is somewhat irritating, indicating the measurements need to be run for longer, to collect more neutron counts.
CHAPTER V

CONCLUSIONS

In this thesis work, we demonstrated five techniques to control the porosity of ceramic material by microwave treatment. The ceramic sample was an existing ceramic water filter that been selling in the market. The chemical compositions of this ceramic water filter base on silicon oxide and aluminium oxide and it has pores size between Mesopores (pore size 5 nm to 50 nm) and Macropores (pore size > 50 nm). The expectation of these five techniques could be able to decrease the pores size to be in range of Micropores (pore size < 2 nm). In general, the ceramic material cannot absorb the microwave energy directly, so it needs some solvent to absorb and convert the heat energy.

The first technique, injection of medium solution into the pores of sample by using the saturation vacuum method to suck the medium to pore under vacuum condition and controlled temperature. Selection of medium depended on the loss factor, higher loss factor was the better medium for this experiment. When the loss factor is high value (< 0.5), it has high ability to absorb the electromagnetic of microwave and convert to be the heat energy to the ceramic materials rapidly. Thus, three mediums were selected in this experiment, they were deionised water, mineral oil (paraffin oil) and methanol. Methanol is selected due to high tan δ value. Mineral oil is selected because it has high viscosity that can stay inside the pore after completing the vacuum injection process. Water has quite low tan δ value to adsorb microwave energy. It is selected in this experiment to compare the data with methanol and mineral oil. Water injection into the ceramic’s pore should produce lowest improvement of the surface area of pores.
Three mediums were injected into the pores of ceramic sample then heat treated in microwave furnace for 30 min with 70% power of microwave. There were two conditions during the heat treatment in the microwave furnace which were sample submerged in the methanol bath and without the methanol bath. From BET and SANS/USANS analysis indicated there was no significant improvement of the porosity of the ceramic material. The ceramic material remained as mesopores and macropores.

The second technique, decreasing the pores space by injection polymer solution into the pores and heated by microwave. Ideally, polymer would trap inside the pores and bonded with the surface of the pores, so it could reduce the macrocracks. Two polymers were selected which were polymethyl methacrylate (PMMA) low viscosity polymer solution and polyethylene glycol (PEG) very high viscosity polymer solution. After injecting polymer into the pores then heat treated in microwave furnace with same condition as the first technique. There were two conditions during the heat treatment in the microwave furnace which were sample submerged in the methanol bath and without the methanol bath. From BET and SANS/USANS analysis indicated there was no significant improvement of the porosity of the ceramic material. The ceramic material remained as mesopores and macropores.

The third technique was applied the freezing cast method after injecting medium, polymer and monomer into the pores and heat treated by microwave with same condition as the first technique then followed by submerging the samples in the liquid nitrogen under vacuum condition (around -90 Pa) for 5 min. The results of BET analysis did not show any significant improvement at all.
The fourth technique was using the conventional furnace for heat treatment of the ceramic sample. The raw ceramic sample placed into the conventional furnace and set the temperature at 900 °C and 1000 °C for 1 hour. The results of BET and SANS/USANS did not show any significant improvement. The ceramic samples were remained as mesopores and macropores. Pores reduction did not occur from this technique.

The last technique, injection monomer into the pores space of ceramic sample then heat treated by microwave with same condition as the first technique. Ideally, the polymerisation should occur and bond with the pores’ surface that cause to decrease the pores size and increase the surface area of pores also porosity. Ethyl glycol (EG) and methyl methacrylate (MMA) were two monomers that were selected in this technique. After injecting monomer into the pores and then followed by heat treated by microwave with same condition as the first technique. There were two conditions during the heat treatment in the microwave furnace which were sample submerged in the methanol bath and without the methanol bath. The BET and SANS/USANS results did not show any significant improvement when methyl methacrylate (MMA) was used but totally different story with ethylene glycol (EG). The best condition of this experiment that improving the porosity and decreasing the pores of sample was injection ethyl glycol in the pores and heat treated by microwave with the sample submerged in the methanol bath. The BET surface area increased 50 times when comparing with the initial untreated ceramic sample and BET Isotherm curve indicated this sample was changed from mesopores/macropores to be micropores. Two main factors that could make this thesis work successful were combination of monomer (EG) with methanol bath and polymerisation. Ethylene glycol is the highest loss factor value and methanol helped to absorb microwave energy to transfer heat and formed polyethylene glycol and coated on the pores’ surface.
CHAPTER VI

FUTURE WORK

In this thesis work, the condition of microwave treatment was only one control condition. There are many conditions and factors that would be able to research and consider.

The power and parameter of microwave during the heat treatment can be set differently from this thesis work such as power can be set 60%, 80%, 90% or even 100%. Time duration of heat treatment can be varied from 15 min, 20 min and 45 min.

Replicate the experiment work but select the solvent bath during the microwave heat treatment differently such as ethanol because ethanol has high loss factor even higher than methanol bath that used in this thesis work.

SANS/USANS measurement, the heat treatment sample with methanol bath should be analyse by SANS/USANS to compare with the results without methanol bath.

In this thesis work used the existing commercial ceramic material but in the future, we can synthesis the initial ceramic materials then use it for experiment to get the better result and can real apply in the industry and give us the benefit.
REFERENCES


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APPENDICES

Appendix A: The International Union of Pure and Applied Chemistry (IUPAC) of pore sizes and pore size of a generic ceramic water filter.

![Pore size diagram](image1)

<table>
<thead>
<tr>
<th>Separation Process</th>
<th>Reverse Osmosis</th>
<th>Ultrafiltration</th>
<th>Nanofiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Size of Materials</td>
<td>Aqueous Salts</td>
<td>Metal Ions</td>
<td>Sugars</td>
</tr>
<tr>
<td>Size</td>
<td>1nm</td>
<td>10nm</td>
<td></td>
</tr>
<tr>
<td>Approximate Molecular Weight (Daltons)</td>
<td>100</td>
<td>200</td>
<td>1,000</td>
</tr>
</tbody>
</table>
Appendix B: SANS/USANS analysis pattern by using SASfit software.

Pore Diameter can calculate from.

\[ q = \frac{2\pi}{D} \]

where \( q \) = intensity vector (A\(^{-1}\))

\( D \) = the diameter of pore (nm)
Appendix C: BET Equation

\[
\frac{P/P_0}{w(1-P/P_0)} = \frac{1}{CW_0} + \frac{C-1}{CW_0}(P/P_0)
\]

Where \(\frac{P/P_0}{w(1-P/P_0)}\) is the value of y-axis from the BET Isotherm Linear curve.

\(P/P_0\) is the value of x-axis from the BET Isotherm Linear curve.

\(\frac{C-1}{CW_0}\) is the gradient of the BET Isotherm Linear curve.

\(\frac{1}{CW_0}\) is the y-intercept of the BET Isotherm Linear curve.

Then, C and \(W_0\) will be able to calculate.

Where \(W_0\) = the BET total surface area which is the most important data that require in this thesis work.

\(C = \) the energy of interaction between the adsorbent and adsorbate.
Appendix D: Polyethylene Glycol polymerisation

\[
\text{OH-CH}_2\text{-CH}_2\text{-OH} + \text{OH-CH}_2\text{-CH}_2\text{-OH} \rightarrow \text{H-(O-CH}_2\text{-CH}_2)_n\text{-OH}
\]

This thesis work used 32% of Hydrochloric acid as the catalyst.
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  - ISO14001: The international recognised standard for the environmental management of business
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