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SYNTHESIS AND CHARACTERIZATION OF METAKAOLIN BASED GEOPOLYMER FROM NARATHIWAT AND PRACHIN CLAYS

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จีโอพอลิเมอร์เป็นวัสดุอะลูมิโนซิลิเกตอนินทรีย์เชื่อมประสานชนิดใหม่ที่ไม่มีแคลเซียมออกไซด์เป็นองค์ประกอบซึ่งสามารถพัฒนาเป็นวัสดุทางเลือกทดแทนปูนซีเมนต์ปอร์ตแลนด์ จีโอพอลิเมอร์มีโครงสร้างเป็นสามมิติที่มีสมบัติและลักษณะการใช้งานที่ยอดเยี่ยม เช่น ความสามารถในการทนกรด และอุณหภูมิได้สูง ทนทานการขยายตัวของชิ้นงานต่ำ และความสามารถซึมผ่านได้ต่ำ ฯลฯ

จีโอพอลิเมอร์ฐานดินขาวเคโอลินเผาถูกสังเคราะห์โดยมีดินขาวเป็นวัตถุดิบหลัก โดยมาจากแหล่งดินขาวของจังหวัดนราธิวาสและปราจีนบุรี จุดประสงค์ของงานวิจัยเพื่อศึกษาสภาวะที่เหมาะสมสำหรับการสังเคราะห์จีโอพอลิเมอร์ และวิเคราะห์ลักษณะเฉพาะต่างๆของวัตถุดิบ ได้แก่ การวิเคราะห์องค์ประกอบทางเฟสด้วยเทคนิค X-ray diffraction การวิเคราะห์เชิงความร้อนของวัตถุต่อการเปลี่ยนแปลงอุณหภูมิด้วยเทคนิค Differential thermal analysis และการกระจายตัวของขนาดอนุภาคดินขาวเผาได้จากการเผาแคลไซน์ที่อุณหภูมิ 650 องศาเซลเซียส เป็นเวลา 6 ชั่วโมง เพื่อให้เฟสของดินขาวกลายเป็นเฟสเมตะเคโอลินอย่างสมบูรณ์ จากนั้นวิเคราะห์องค์ประกอบทางเคมีด้วยเทคนิค X-ray fluorescence และนำค่าองค์ประกอบทางเคมีที่ได้จากการวิเคราะห์ไปคำนวณเพื่อสังเคราะห์จีโอพอลิเมอร์ โดยผสมดินขาวเคโอลินเผากับสารละลายแอลคาไลน์ที่มีเงื่อนไขต่างกันจนกระทั่งเป็นเนื้อเดียวกัน โดยเงื่อนไขต่างกัน ได้แก่ การสังเคราะห์จีโอพอลิเมอร์ที่ความเข้มข้นของสารละลายโซเดียมไฮดรอกไซด์ต่างกัน การสังเคราะห์จีโอพอลิเมอร์ด้วยอัตราส่วนของซิลิกอนต่ออลูมิเนียมที่ต่างกัน การบ่มชิ้นงานจีโอพอลิเมอร์ที่อุณหภูมิต่างๆ และเวลาที่ใช้ในการบ่มต่างกัน

นำชิ้นงานจีโอพอลิเมอร์นราธิวาสและปราจีนบุรีไปวิเคราะห์องค์ประกอบทางเฟสด้วยเทคนิค X-ray diffraction วิเคราะห์สัณฐานวิทยาด้วยเทคนิค Scanning electron microscopy วิเคราะห์หมู่ฟังก์ชันด้วยเทคนิค Fourier transform infrared spectroscopy และความต้านทานกำลังอัด ความหนาแน่นรวม ค่าการดูดซึมน้ำ และ ความพรุนตัวปรากฏ ลักษณะเฟสที่ปรากฏแสดงเฟสเมตะเคโอลินไนต์ที่มีความเป็นอสัณฐานมากขึ้น ชิ้นงานจีโอพอลิเมอร์ที่ให้ค่าความต้านทานกำลังอัดมีค่ามากที่สุดได้จากโซเดียมไฮดรอกไซด์ 12 โมลาร์ โดยมีอัตราส่วนของซิลิเกตต่ออลูมิเนียมของนราธิวาสและ ปราจีนบุรีจีโอพอลิเมอร์ เท่ากับ 1.49 และ 2.52 ตามลำดับ ระยะเวลาที่เหมาะสมสำหรับการบ่มชิ้นงานจีโอพอลิเมอร์ที่ดีที่สุด คือ 28 วัน ที่อุณหภูมิห้อง เนื่องจากการเกิดจีโอพอลิเมอไรเซชันอย่างช้าๆ

ภาควิชา วัสดุศาสตร์ ลายมือชื่อนิสิต ....
สาขาวิชา เทคโนโลยีเซรามิก ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
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ANCHALEE ANCHALEERAT: SYNTHESIS AND CHARACTERIZATION OF METAKAOLIN BASED GEOPOLYMER FROM NARATHIWAT AND PRACHIN CLAYS. ADVISOR: ASST. PROF. SIRITHAN JIEMSIRILERS, Ph.D., CO-ADVISOR: PARJAREE THAVORNITI, Ph.D., 56 pp.

Geopolymers are a new type of CaO-free inorganic alumino-silicate cementitious material, which have been developed as an alternative material to replace Portland cement. Geopolymers, are three dimensional structure, have excellent properties and high performance such as higher resistance to acid and fire, long-term durability, low shrinkage and low permeability, etc.

Metakaolin based geopolymers were synthesized by using kaolin from Narathiwat and Prachinburi provinces, Thailand as starting materials. The purposes of this research were to investigate the optimum conditions of geopolymers which give good properties. Raw materials were characterized by X-ray diffraction (XRD), Differential Thermal Analysis (DTA) and Particle size distribution. Metakaolins were obtained by calcination of Narathiwat and Prachinburi kaolins. The calcined temperature was 650°C and soaked for 6 h. in order to allow kaolinite transformed to metakaolinite completely then they were analyzed by XRF for chemical compositions which was calculated to mix the raw materials with alkali solutions. The obtained metakaolin was mixed with strong alkaline solution until homogeneous with the different conditions which were concentrations of sodium hydroxide (NaOH), Si/Al ratios, curing temperatures and curing time.

Narathiwat and Prachinburi geopolymers were characterized by XRD, SEM, FTIR, Compressive strength, Bulk density, Water absorption and Apparent porosity. XRD pattern showed that metakaolinite phases were change to were more amorphous phase. The best concentration for this study was 12 M of NaOH which gave the highest compressive strength with the Si/Al ratio of Narathiwat and Prachinburi geopolymers were 1.49 and 2.52, respectively. The optimum curing time was 28 days at ambient temperature, since the geopolymerization occurred slowly at room temperature. The FTIR spectra could confirm the developed geopolymeric structure.

Department:	Materials Science	Student's Signature	
Field of Study:	Ceramic Technology	Advisor's Signature	
Academic Year:	2014	Co-Advisor's Signature	

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CHAPTER 1

INTRODUCTION

1. BACKGROUND AND MOTIVATIONS

Portland cement has been used widely in construction. The demand of using cement has continuously increased. In 2006, the usage of cement was approximately 2540 million tons (Mt) and the estimate of cement production in 2050 is forecast around 3680 Mt to 4830 Mt which is a high volume [1]. From the cement manufacturing produces one ton of cement approximately 0.8 tons of carbon dioxide are released into the atmosphere [2]. To decrease this effect geopolymers were replaced the Ordinary Portland cement (OPC) due to geopolymers manufactured at relatively low temperature as Portland cement used high energy and temperature during the cement manufacturing process.

In 1972, Davidovits named “Geopolymer” an inorganic polymer that has three dimentional alumino-silicates [3],[4]. Geopolymers have excellent properties such as high mechanical properties, low shrinkage, fire resistance and durability [5]. It is formed by the reaction between an aluminosilicate source and a strong alkaline solution. The aluminosilicate sources can be found in nature and industry such as metakaolin, fly ash, and blast furnace slag etc. Metakaolin, which has homogeneous properties and ally friendly used in ceramic industry, is a common mineral [6], [7].

Metakaolin was obtained by calcination of kaolin with different temperatures from 500°C to 800°C, which depend on its structure, crystal size and degree of crystallinity. The structure which was obtained from calcination process has been affected to amorphous state and given highly pozzolanic property [7]. When metakaolin was mixed with a strong alkali solution the silicate monomers and aluminate monomers were dissolved from metakaolin. They were formed to be aluminosilicate by geopolymerization. This work aims to study the possibility to use Narathiwat and Prachin metakaolins in Thailand as raw materials in geopolymers and investigate the physical and chemical properties of geopolymers. The geopolymers are characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), Scanning electron microscope (SEM).

1.1. Objectives of this research

- To synthesis and characterize geopolymers using the local kaolin in Thailand.
- To study physical and mechanical properties of metakaolin based geopolymers.

1.2. Scope of research

Firstly, this research focused on the success of synthesis geopolymers from local kaolin in Thailand in order to substitute Portland cement which released large amount of CO_2 emission into the environment. Secondly, finding the optimum conditions to synthesis geopolymers with good properties.

CHAPTER 2

LITERATURE REVIEW

According to statistic data from the U.S. Geological Survey[8], the world's usage of cement is increasing at a geometric rate. The total consumption of cement in the world in 2010 is 3,310,000 tons and the total using estimation in 2014 is 4,180,000 tons. Moreover, the production of one ton of cement releases about one ton of carbon dioxide to the atmosphere. In order to reduce CO_2 emission in the cement production there are many effort to find the other cementitious materials to replace cement.

In 1972 Davidovits named "geopolymers" a new material with cementitious characteristics that produced by polymeric reaction of alumino-silicate and alkali activators, is the one of the other options due to the reduction of 80-90% of CO_2 emission to the atmosphere compared with the cement production [6], [9].

2. GEOPOLYMER

2.1. Definition of geopolymers

Geopolymer is a class of inorganic polymer which is able to synthesis at low temperature by using alumino-silicate sources such as fly ash (FA), kaolin and metakaolin (MK) with alkali activators such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and potassium silicate (K_2SiO_3) or sodium silicate (Na_2SiO_3). The alkali activators dissolved aluminosilicate oxide to be free SiO_4 and AlO_4 tetrahedral units, then they form three dimensional framework structure, with the negative charge due to Al^{3+} in four-fold coordination localized on the bridging oxygens in each aluminate tetrahedron and balanced by the alkali cations[10].

2.2. Structure of geopolymer

Geopolymer can be different in compositions and structures [9]. The structures of geopolymer are the linkage type of sialate (Si-O-Al) and siloxo (Si-O-Si). According to terms of the Si/Al atomic ratio can be called the sialate and siloxo as follows

Si/Al = 1, sialate, poly(sialate), (-Si-O-Al-O-)

Si/Al = 2, sialate- poly(siloxo), (-Si-O-Al-O-Si-O-)

Si/Al = 3, sialate- poly(disiloxo), (-Si-O-Al-O-Si-O-Si-O-)

Si/Al > 3, sialate link

In the sialate structure consists of SiO_4 and AlO_4 tetrahedra linked alternately by sharing all the oxygen atoms. Alkali cations or positive ions such as $Na^+$and K^+ are charged-balanced of the negative charge of Al^{3+}. A polymeric structure of (poly)sialate formed constitutes the main building blocks of geopolymeric structure and the types of polysilates are illustrated in Figure 2.1 The empirical formula of polysialates is displayed as follow:

$$M_n\,[(\text{-Si-O}_2)_z\text{-Al-O}_2\text{-}]_n,\ wH_2O \qquad (1)$$

Where M = Alkali element

n = Degree of polycondensation

z = Amount of $Si-O_2$ (1,2 or 3)

and w = Amount of water

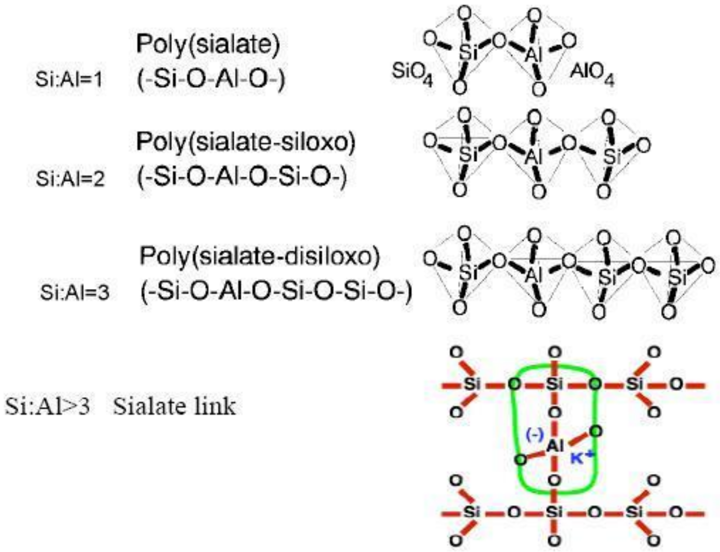


Figure 2.1 Chemical structure of polysialates[11]

2.3. Geopolymerization

The synthesis of geopolymers is successful by using the sol-gel method, which can be formed at ambient temperature. The polymerization is a reaction during sol-gel process. Geopolymerization is a reaction between aluminosilicate sources and strong alkali solutions. The mechanism of geopolymerization is divided into three stages[10].

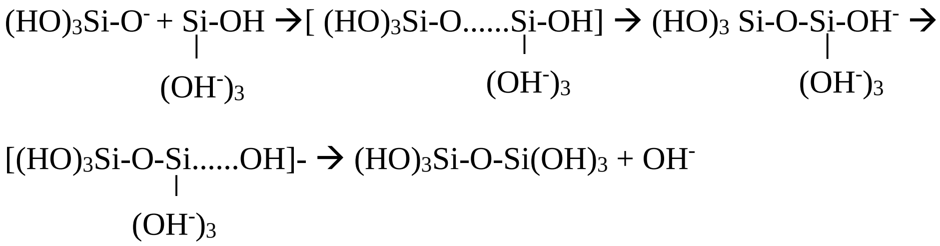
First stage : Destruction-Coagulation

The Si-O-Si, Al-O-Al and Al-O-Si bonds in the starting materials were attacked and dissolved by the high pH of alkali solutions. The OH^- ions from the alkali solution generate the rupture of Si-O-Si bonds and decompose into silicic acid ($Si(OH)_4$), oligomeric as well as anionic species containing Si-O groups; the Al-O-Si bond as well. The presence of alkali metal cations balances the negative charge in the structure.

The $-Si-O-Na^+$ complexes, which are stable in alkaline media, have a good condition to transport in the reacting structural units. The cations in this reaction destroy the covalent bonds to break bonds into a colloidal phase.

Second stage : Coagulation-Condensation

The condensability of silicic acid rises with high pH values. Thus, the Si-O-Si bond is ruptured by the high pH (pH<7). The rupture bonds create to form a new Si-O-Si bond and dimer as follows:



$$(HO)_3Si\text{-}O^- + \underset{(OH^-)_3}{\underset{|}{Si}}\text{-}OH \rightarrow [\ (HO)_3Si\text{-}O......\underset{(OH^-)_3}{\underset{|}{Si}}\text{-}OH] \rightarrow (HO)_3\ Si\text{-}O\text{-}\underset{(OH^-)_3}{\underset{|}{Si}}\text{-}OH^- \rightarrow$$

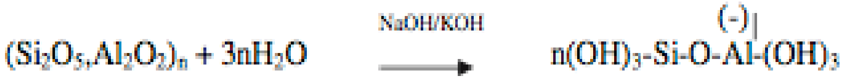
$$[(HO)_3Si\text{-}O\text{-}\underset{(OH^-)_3}{\underset{|}{Si}}......OH]\text{-} \rightarrow (HO)_3Si\text{-}O\text{-}Si(OH)_3 + OH^-$$

The OH^- ions are the catalysed in the reaction. From the polymerization process, the clusters of orthosilicic acid may grow in all directions to generate colloidal particles. The aluminate participates in the polymerization reactions, substituting isomorphously for silicate tetrahedra.

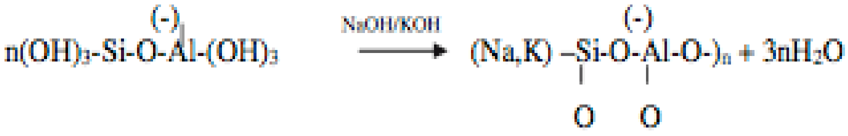
Third stage: Condensation-Crystallization

The presence of micro particles resulting from the condensed structure. The solid particles in the first period, which are different with the initial chemical composition is precipitated. Finally, It becomes to the hardening geopolymer.

The mechanism of geopolymerization exhibits in Figure 2.2 that show the transformation of solid aluminosilicate source turn to be geopolymer. Firstly, aluminosilicate source was attacked by alkali solution. The solid particles at surface area were dissolved into aluminate and silicate species. The amorphous aluminosilicates from dissolution that create a supersaturated aluminosilicate solution occur the formation of gel, then, the oligomers form to large networks by condensation. After gelation, the structure continues to reorganize and rearrange then it becomes to the three-dimensional aluminosilicate network commonly attributed to geopolymers[5]. The geopolymeric reaction can be expressed in equations 2-5 as below[12].

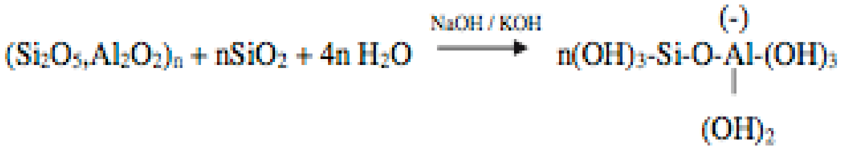


$$(\mathrm{Si_2O_5,Al_2O_2})_n + 3n\mathrm{H_2O} \xrightarrow{\mathrm{NaOH/KOH}} n(\mathrm{OH})_3\text{-Si-O-}\overset{(-)}{\mathrm{Al}}\text{-}(\mathrm{OH})_3 \qquad (2)$$

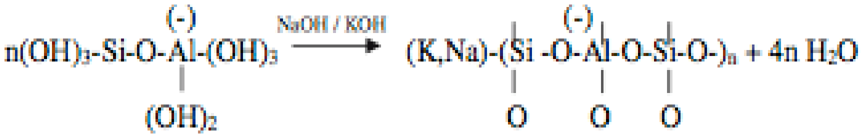


$$n(\mathrm{OH})_3\text{-Si-O-}\overset{(-)}{\mathrm{Al}}\text{-}(\mathrm{OH})_3 \xrightarrow{\mathrm{NaOH/KOH}} (\mathrm{Na,K})\ \text{–}\underset{\mathrm{O}}{\underset{|}{\mathrm{Si}}}\text{-O-}\underset{\mathrm{O}}{\underset{|}{\overset{(-)}{\mathrm{Al}}}}\text{-O-})_n + 3n\mathrm{H_2O} \qquad (3)$$

Orthosialate (Na,K)-Polysialate



$$(\mathrm{Si_2O_5,Al_2O_2})_n + n\mathrm{SiO_2} + 4n\ \mathrm{H_2O} \xrightarrow{\mathrm{NaOH\ /\ KOH}} n(\mathrm{OH})_3\text{-Si-O-}\underset{(\mathrm{OH})_2}{\underset{|}{\overset{(-)}{\mathrm{Al}}}}\text{-}(\mathrm{OH})_3 \qquad (4)$$



$$n(\mathrm{OH})_3\text{-Si-O-}\underset{(\mathrm{OH})_2}{\underset{|}{\overset{(-)}{\mathrm{Al}}}}\text{-}(\mathrm{OH})_3 \xrightarrow{\mathrm{NaOH\ /\ KOH}} (\mathrm{K,Na})\text{-}(\underset{\mathrm{O}}{\underset{|}{\overset{|}{\mathrm{Si}}}}\ \text{-O-}\underset{\mathrm{O}}{\underset{|}{\overset{(-)|}{\mathrm{Al}}}}\text{-O-}\underset{\mathrm{O}}{\underset{|}{\overset{|}{\mathrm{Si}}}}\text{-O-})_n + 4n\ \mathrm{H_2O} \qquad (5)$$

Ortho(sialate-siloxoxo) (Na,K)-Polysialate-siloxo

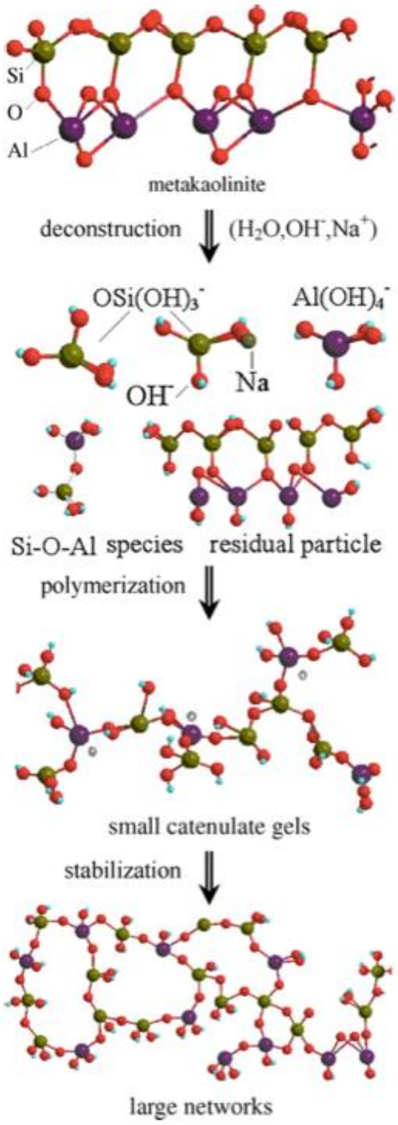


Figure 2.2 Geopolymerization process[13]

2.4. Geopolymer synthesis

a) Pozzolanic materials

A pozzolan is a material which mainly consists of silica and alumina. It is a supplementary cementing material and mineral additives that can react with calcium hydroxide to produce calcium silicate hydrated (CSH) gel at ambient temperature. Using pozzolan in a part of concrete industry because of their advantages such as high performance, high strength and lightweight concrete, etc. Generally, the commonly used pozzolanic materials are natural pozzolan (metakaolin, kaolin), fly ash, rice husk ash and etc. Pozzolans play an essential role in the formation of geopolymer as starting materials; moreover, they affect to their properties of geopolymers due to the various chemical compositions of starting materials which shown in Table 2.1.

Table 2.1 Chemical composition (wt%) of different silica materials from various origin [14].

Silica material	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**SO_3**	**Na_2O**	**K_2O**	**TiO_2**	**MgO**	**Other**	**LOI**
Fly ash	35.21	23.23	12.36	20.01	2.36	0.36	-	-	-	-	0.24
Fly ash	51.60	23.40	15.20	1.75	0.26	0.35	0.84	1.31	1.14	1.43	3
Rice Husk Bark Ash	81.36	0.4	0.12	3.23	0.85	-	-	-	-	-	3.55
Rice Husk Ash	87.75	0.38	0.19	1.04	0.56	0.05	2.83	0.02	0.69	1.38	3.04
Red Mud	1.20	14.00	30.90	2.50	-.	-	2.3	-	-	-	-
Kaolin	48.06	36.76	1.42	0.33	-	-	-	-	0.24	-	12.20
Kaolin	46.36	37.6	0.94	0.2	0.07	0.13	0.22	0.80	0.24	-	13.5
Metakaolin	53.68	42.0	1.70	0.21	-	-	-	-	0.10	-	1.95
Metakaolin based geopolymer absorbent	41.5	19.6	2.1	0.2	-	12.4	0.6	0.2	0.1	-	-
Granulated blast furnace slag	34.39	14.47	0.63	41.67	-	0.22	0.36	0.53	6.49	-	-

Note: LOI = lost in ignition

b) Alkali solution

The essential constituent of the initial geopolymerization is a chemical activator such as alkali hydroxides or silicates with high pH. The common alkali hydroxides used as activators in the geopolymer synthesis are sodium or potassium (NaOH or KOH) with high pH. The NaOH is the most popularly used hydroxide activator in geopolymer synthesis because it is the cheapest and most widely available of alkali hydroxides, so in this study NaOH was used as a hydroxide activator mix with an alkali silicate solution which is Na_2SiO_3 solution. The alkali solution plays a role in dissolving initial aluminate and silicate of raw material to rupture them into monomer, while the alkali silicate solution arranges the new alumino-silicate structures [10].

2.5. Kaolin and Metakaolin

Kaolin is a natural mineral which is a hydrous aluminium silicate of approximate composition $2H_2O{\cdot}Al_2O_3{\cdot}2SiO_2$. The structure of kaolinite includes alumina octahedral sheets and silica tetrahedral sheets that arrangement of atoms in its structure is shown in Figure 2.3. The general properties of kaolin are softness, small particle size and chemical inertness so, kaolin is used in many industry applications such as manufacture of ceramics, cement, porcelain and etc. [15].

Metakaolin (MK) is one type of pozzolanic materials which is obtained by the calcination of kaolin at temperatures ranging from 500 to 800°C the obtained metakaolin depends on their purities and temperature of the dehydroxylation of kaolinite. The impurities of metakaolin affect geopolymeric properties. The structure of metakaolin exhibits disordered because of leaving of hydroxyl groups from the layered kaolinite structure leads to the breaking down of crystal structure becomes to be amorphous phase during dehydroxylation of kaolinite. The metakaolin particle has microstructure as plate-like particle shape, therefore the surface area of particles is very high. The exothermal dehydroxylation reactions with different calcined temperature are exhibited by following equations [15] :

$$\sim 500^{\circ}C : \underset{\text{Kaolinite}}{Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O} \rightarrow \underset{\text{Metakaolinite}}{Al_2O_3{\cdot}2SiO_2} + 2H_2O \qquad (6)$$

$$\sim 925^{\circ}C : 2[Al_2O_3{\cdot}2SiO_2] \rightarrow \underset{\text{Silicon-spinel}}{2Al_2O_3{\cdot}3SiO_2} + SiO_2 \qquad (7)$$

$$\sim 1100^{\circ}C : 2Al_2O_3{\cdot}3SiO_2 \rightarrow \underset{\text{1:1mullite-type phase}}{2[Al_2O_3{\cdot}2SiO_2]} + SiO_2 \qquad (8)$$

$$\sim 1400^{\circ}C : 3[Al_2O_3{\cdot}3SiO_2] \rightarrow \underset{\text{3·2mullite}}{3Al_2O_3{\cdot}2SiO_2} + SiO_2 \qquad (9)$$

a) The physical properties of metakaolin

Metakaolin is the ideal and widespread used precursor because of its properties such as excellent chemical (high reactivity and purity), physical properties (Table 2.2), low cost and following:

-Increased durability and resistance to chemical attack

-Increased compressive and flexural strengths

-Reduced permeability and potential for efflorescence

-Reduced shrinkage due to particle packing, making concrete denser

Table 2.2 Physical properties of metakaolin [16]

Properties	**Values**
Specific gravity	2.60
Bulk density (g/cm^3)	0.4
Physical form	Powder
Color	Off-white
GE Brightness	80-82

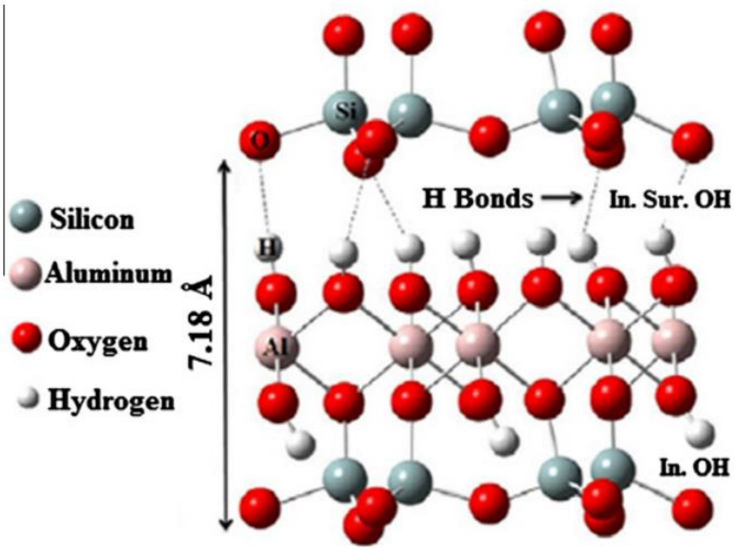


Figure 2.3 Schematic structural of kaolinite [15]

2.6. Geopolymer properties and applications

There are many attractive properties of geopolymer such as resistance to high temperature and chemical agents, durability, quick solidification with high strength, low shrinkage etc. From the excellent properties of geopolymer, it has been used as concrete and cement, composites and fire resistant matrix etc.

The type of applications of geopolymer materials assorted by the chemical structure in terms of the atomic ratio Si/Al in polysialate as shown in Table 2.3

Table 2.3 Applications of geopolymer materials based on Si/Al ratio atomic ratio[17]

Si/Al ratio	**Applications**
1	- Fire protection - Brick - Ceramics
2	- Low CO_2 cements and concretes - Radioactive and toxic waste encapsulation
3	- Fire protection fiber glass composite - Heat resistant composites, 200°C to 1000°C - Tooling for aeronautics titanium process
>3	- Sealants for industry, 200°C to 600°C - Tooling for aeronautics SPF aluminum
20-35	- Fire resistant and heat resistant fiber composites

2.7. Related research

Elimbi et al.[18] studied the effect of calcination temperature of kaolin clays on the properties of geopolymer cements. By using the three different clays sources as raw materials that consist of the density difference between quartz and kaolinite. The clays were calcined at 450 to 800°C for 10 h that a temperature of calcination depends on the purities of clays. The dehydroxylation of kaolinite is progressively between 400 and 620°C that coincide with the formation of metakaolinite, but the calcined clays at 450°C remained kaolinite in structure as shown in Figure 2.4. Thus, the calcined temperatures in this study are 600-800°C. From the linear shrinkage and compressive strength results, the best calcined temperature was 700°C and if the calcination of kaolin above 700°C, the compressive strength will decrease.

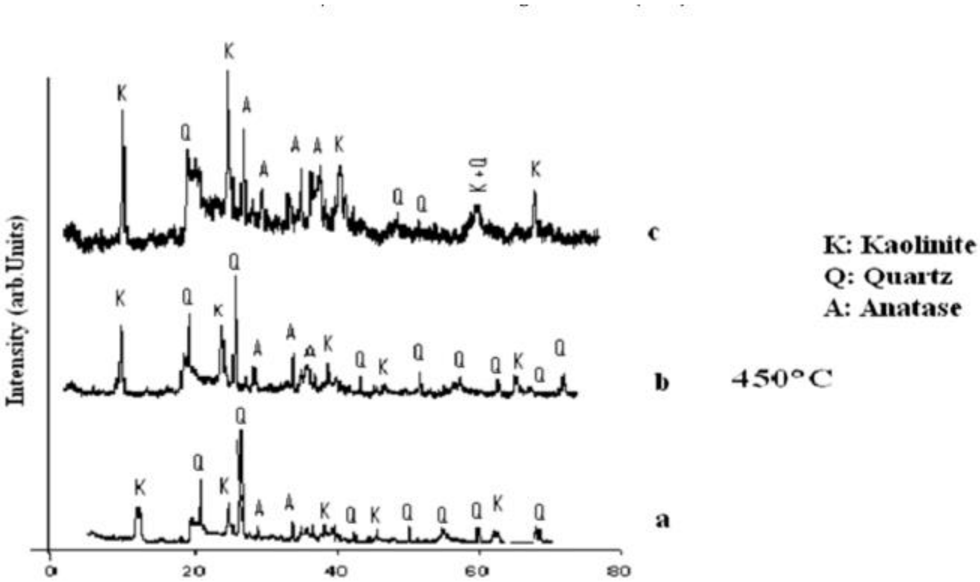


Figure 2.4 Calcined clays of different clays at 450°C

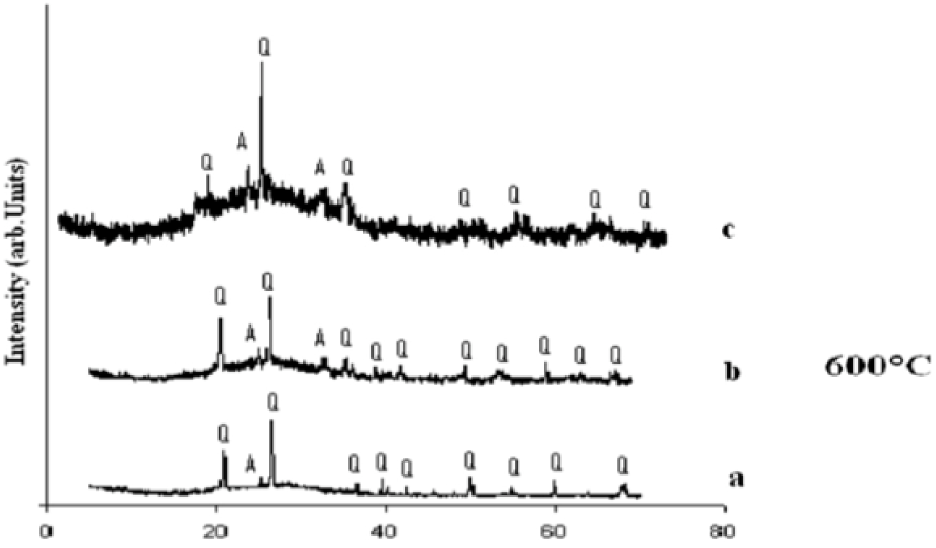


Figure 2.5 Calcined clays at 600°C

Wang et al.[19] examined the various of NaOH solution concentrations of 4-12 Molar. The mass ratio of the metakaolin and alkali activator is 3:1 that the activator included NaOH solution and sodium silicate solution at a mass fraction of 4.15:1. After mixing, the samples were cured at room temperature for 1 h, then cured at 65°C for 10 h to enhance its mechanical strength. The results showed that the more concentration of the NaOH solution increased, the higher compressive strength and apparent density of geopolymer were. Since the NaOH solution was able to dissolve the metakaolin particulates and better dissolving when the NaOH solution was higher. The dissolving particulates produced more reactive bond for the monomer resulting in geopolymerisation to form to aluminosilicate structure.

Duxson et al.[20] investigated the effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin based geopolymer. The raw materials are metakaolin (Metastar 402, Imerys Minerals) which have Muscovite as an impurity. The alkali solutions were varied sodium silicate solution composition SiO_2/M_2O = R = 0.0, 0.5, 1.0, 1.5 and 2.0, Na/[Na+K] = A = 0.00, 0.25, 0.50, 0.75 and 1.00 then, the geopolymer samples synthesized at five different Si/Al ratios from alkali solutions with five different alkali cation ratios. The Si/Al ratios are 1.15, 1.4, 1.65, 1.9 and 2.15, respectively. Next, all samples were cured in oven at 40°C for 20 h before keep them in sealed storage vessels for 7 and 28 days. After curing, samples were investigated by the compressive strength of the results showed that when the Si/Al ratios increase from 1.15 to 1.90 the compressive strength also increases. However, the Si/Al ratio is higher than 1.90 the compressive strength dropped.

Ozer et al.[21] were characterized metakaolin based geopolymers with different molar Si/Al ratios which are Si/Al ratio of 1.12, 1.77 and 2.20, respectively. The aluminosilicate source is metakaolin that was obtained by heat treatment at 700° for 1 h then kept it for 1 day before fabrication. The Si/Al ratio of 1.12 was synthesized using 8M NaOH as the activator solution while the other geopolymers were used 8M NaOH and $Na_2Si_3O_7$ to adjust Si/Al ratios to gain more Si content in samples which were Si/Al ratios of 1.77 and 2.20. To study the changes in structure and mechanical property to various curing temperature and molar Si/Al ratios. The samples were treated at 60°C and 25°C which cured i) cured at 60°C for 1 day then kept for 3 weeks at 25°C ii) cured at 60°C for 7 days then kept for 3 weeks at 25°C. Next, all samples were tested.

All samples were investigated by X-ray diffraction, Fourier transform infrared spectroscopy and Scanning electron microscopy displayed that samples with Si/Al ratio of 1.12 comprised of crystalline constituent that is zeolite A or sodalite. They were more brittle than 1.77 and 2.20 due to the different crystal structures. Si/Al ratio of 1.12 is crystalline, but Si/Al ratios of 1.77 and 2.20 were amorphous which were observed XRD patterns and microstructures. The compressive strength results of Si/Al ratios of 1.12, 1.77 and 2.20 were about 1 MPa and 13-23 MPa that interrelated to XRD and SEM results. IR spectra of the samp les showed the region of wavenumber indicated geopolymerization.

Zuhua et al.[22] studied the role of water in the geopolymer process. The major raw materials were fine kaolin, which calcined at 600°C, 700°C, 800°C, 900°C and 1000°C for 6 h blended with fly ash bFouriefore mixing into the alkali activator. The solid and liquid ratio was 1.25 and the mass ratio of calcined kaolin to fly ash was 1.5, after synthesis the samples were cured with five different conditions: in air (AC, 20±2°C), in sealed bag (BC, 20±2°C), in room temperature water (RWC, 20±2°C), in steam (SC, 80°C) and in elevated temperature water (EWC, 80°C) for 7 days.

From the X-ray diffraction results showed that at 700-900°C were completely turned to metakaolin and the best compressive strength were the SC and EWC gave higher values than the others because the expansion values were low and not too much water inside the samples.

Rovnanik et al.[6] investigated the effect of curing temperature on the development of hard structure of metakaolin based geopolymer. The starting materials used the metakaolin and alkaline silicate solution with solid sodium hydroxide. Standard quartz sand was added as an aggregate to prepare geopolymer mortar. Next, the samples were cured at 10, 20, 30, 40, 60 and 80°C for 1, 2, 3 and 4 h, respectively. Then, they were stored at room temperature for 1, 3, 7 and 28 days after curing, they were determined by flexural strength and compressive strength. The curing temperature affected to the hardness of samples at an ambient and elevated temperature the samples set within 4 h, but at 10°C it cannot be set. In the early-aging, showed that the higher curing temperatures increased the compressive and flexural strength which were aged for 1 day. However, the samples that were cured for 28 days with different temperatures showed that at an ambient or decreased temperatures had better mechanical properties than at high temperature. The elevated temperatures led to the increasing of pores in the samples which affect to the final mechanical properties of geopolymers.

CHAPTER 3
EXPERIMENTAL PROCEDURE

In this study, the kaolins from local sources in Thailand were chosen as pozzolan materials to synthesize metakaolin based geopolymers. The geopolymers were alternative materials to replace the Portland cement that can reduce the extravagant energy and carbon dioxide from the cement industry. The materials and experimental procedure were explained as the followings.

3. EXPERIMENTAL

3.1. Materials

1) Narathiwat Kaolin, Ceramics R US Co.Ltd
2) Prachin Kaolin, Aumnuaychai Co.Ltd
4) Na_2SiO_3, Chemmin Co. Ltd
5) NaOH , Ajax Finechem Pty Ltd
6) Distilled water

3.2. Preparation of raw materials

3.2.1. Metakaolin

Metakaolins were obtained by calcination of Narathiwat and Prachin kaolins which are from the local kaolin mines in Narathiwat and Prachinburi provinces, Thailand. Kaolins were ground then dried at 110°C to dehydrate water for 24 h then kaolins were screened through sieve size No.100 in an oven (aperture of 150 μm) and calcined at 650°C for 6 h to allow kaolinite to transform to metakaolin completely.

3.2.2. Alkali Solution

Sodium silicate (Chemmin Co. Ltd., SiO_2/NaOH = 3.09) and sodium hydroxide (Ajax Finechem Pty Ltd, 97%) were used as the alkali activators. The sodium hydroxide solution with various concentration of 6, 8, 10, and 12 molar, respectively was prepared by dissolving NaOH pellets in distilled water and left the solution until it cooled down and clear. Then mixed it with Na_2SiO_3 with the 1.5 ratio of Na_2SiO_3:NaOH. This solution was left for 24 h before use.

3.3. Experimental designs

Narathiwat and Prachin geopolymers have different Si/Al ratios and percent of solid/liquid ratios are presented in Table 3.1 and 3.2, respectively. Various concentration of NaOH of 6,8,10 and 12 molar were used.

Table 3.1 Mix designs with various Si/Al ratios for Narathiwat metakaolin

Mix design	Precursor	
Si/Al	Metakaolin (g)	Alkaline Solution (ml)
1.44	62	38
1.49	57	43
1.55	53	47
1.60	50	50

Table 3.2 Mix designs with various Si/Al ratios for Prachin metakaolin

Mix design	Precursor	
Si/Al	Metakaolin (g)	Alkaline Solution (ml)
2.46	73	27
2.52	68	32
2.60	63	37
2.65	60	40

3.4. Geopolymer synthesis

Geopolymer samples were prepared by mixing alkali activators with the Narathiwat metakaolin (NT-MK) and Prachin metakaolin powder (PJ-MK) until homogenous with the ratios as shown in Table 3.1 ad 3.2, respectively. The mixture was poured into acrylic molds with dimensions of 25x25x25 mm^3 and left it for 3 days then demolded, the samples were sealed to avoid water evaporation and cured at room temperature (RT) for 7,14 and 28 days and cured at elevated temperature at 40 and 60°C for 24 h then cured at room temperature for 7, 14, and 28 days after curing the samples were characterized.

METHODS

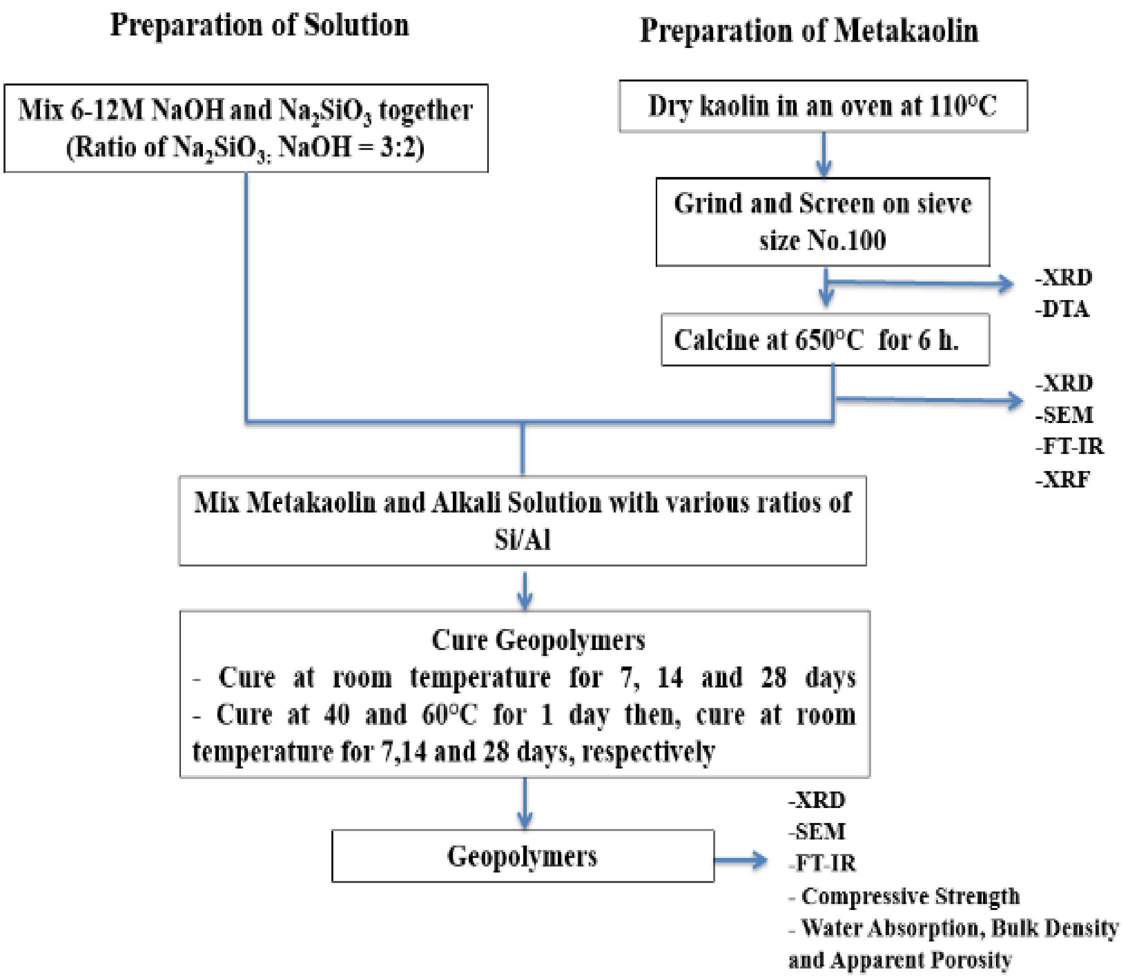


Figure 3.1 Flow chart of synthesis geopolymer process

3.5. Characterizations

3.5.1. Thermal Analysis

Differential Thermal Analysis (DTA) is equipment which analyzes the thermal changing of materials measured by the different of temperatures between sample and reference substances. During heating sample will change due to the Endothermic or Exothermic reactions results from phase transformation, melting and burning of organic. The raw materials were characterized thermal physical analysis by DTA7, Perkin Elmer.

3.5.2. Particle size distribution analysis

The particle sizes of raw materials were investigated by Laser Light Scattering technique (Mastersizer 2000 Malvern Instruments). The sample was prepared to powder form in order to disperse in a liquid media. The laser beam passes through the particles in a media and the particles scatter light at an angle which is inversely proportional to their size. The larger particles size were approximate by Fraunhofer theory, but the smaller particles size were explained by Mie theory.

3.5.3. Chemical composition analysis

The chemical composition of NT-MK and PJ-MK were analyzed by X-ray fluorescence (XRF) spectrometer (S8 Tiger, Bruker AXSX). XRF spectrometry is an elemental and chemical analysis technique. It can determine solid, liquid and colloid by measured amount of X-ray fluorescence that are released from elements of sample. The analysis method is X-ray tube generates X-ray which has high energy. X-ray passes through sample and bring about photons discharging which have a characteristic of energy to each element, thus can be able to indicate the element or chemical compositions in the sample.

3.5.4. Phase analysis

The mineral phases were performed on X-ray diffraction Bruker diffractometer model D8-Advance using Cu-Kα radiation at 40 kV, 25 mA. XRD pattern were obtained with a step width of 0.2 degree (2θ)/min and recorded from 2θ at 5 up to 80 degree. XRD is an x-ray diffraction analysis instrument in sample by using Bragg's law or $2d\sin\theta = n\lambda$ and matched peak with Joint Committee on Powder Diffraction Standard files (JCPDS) and the average crystallite size was estimated via Debye-Scherer equation:

$$Dc = \frac{K\lambda}{\beta cos\theta}$$

When	D_c	is average crystallite size (nm)
	K	is Debye-Scherer constant (normally taken as 0.89)
	λ	is wavelength of the X-ray radiation (0.154 nm)
	B	is line width at half –maximum height of the broadened peak (Full width at half maximum (FWHM)
	θ	is the half diffraction angle of centroid of peak (degree)

3.5.5. Fourier transform infrared spectroscopy

The chemical bonds in molecule were investigated by Spectroscopy Perkin Elmer (Spectrum one) Spectrometer. The information from FT-IR can be used to identify bonding in materials. The range of Infrared region is 12800 ~ 10 cm^{-1}and can be divided into near-infrared region (12800 ~ 4000 cm^{-1}), mid-infrared region (4000 ~ 200 cm^{-1}) and far-infrared region (50 ~ 1000 cm^{-1}). In this study use mid-infrared to determine the structures of molecules. The samples were prepared as powder and mixed with the Potassium Bromide powder (KBr) then pressed it to be a form pallet.

3.5.6. Scanning electron microscopy and Energy-dispersive X-ray spectroscopy (SEM and EDX)

The microstructure of samples were characterized by Scanning electron microscopy (JEOL, JSM-6480LV model). The elements distribution of samples was detected by an Energy dispersive X-ray spectroscopy (EDX, INDA x-sight). NT-K, PJ-K, NT-MK and PJ-MK were prepared by powders and the geopolymer samples used fracture surfaces of samples after the compressive strength testing at 28 days. From the SEM micrograph and EDX results could show microstructures that presented morphology of starting materials and reaction products and chemical compositions of raw materials and geopolymers, thus it could also explain the characteristic of them.

3.5.7. Compressive strength

The mixture of geopolymers were cast in 25x25x25 mm^3 cubic acrylic molds. Next, they were sealed and left in the box for 3 days. Then, they were remolded and sealed again and left them as it was mentioned in 3.4. The compressive strength of geopolymer samples were examined according to ASTM C109 by using Concrete Compression Machine, ELE international model ADR-Auto.

Compressive strength (MPa) = Force (N)/Area (mm^2)

Figure 3.2 Concrete Compression Machine

3.6.8 Water absorption, bulk density and apparent porosity

In this study, the sample after 7 days were prepared by immersed into hot water at 80°C for 2 h and left them for 24 h then weight them as W_w. The saturated weight was weighed in air as W_a. Next, the sample was dried at 85°C for 24 h then, weighed it as a dry weight (W_d). The equations of ASTM C 20-00 were used in calculating for water absorption, bulk density and apparent porosity, respectively [23].

The water absorption was calculated using Eq.1

$$\text{Water absorption (\%)} = [(W_a-W_d)/(W_d)] \times 100 \qquad (1)$$

The bulk density was calculated using Eq.2

$$\text{Bulk density (g/cm}^3\text{)} = [(W_d)/(W_a-W_w)] \qquad (2)$$

And the apparent porosity was calculated using Eq.3

$$\text{Apparent porosity (\%)} = [(W_a-W_d)/(W_a-W_w)] \times 100 \qquad (3)$$

Where
W_a is weight in air of saturated sample (g),
W_d is dry weight after 24 h in oven at 85 ± 5 °C (g) and
W_w is weight in water of saturated sample (g)

CHAPTER 4

RESULTS AND DISSCUSSION

4. CHARACTERIZATION

Firstly, the good starting materials are essential for geopolymerization process that have effect on geopolymer properties. Thus, analysis of raw materials is necessary to prepare the starting materials to synthesis geopolymers. The raw materials were characterized by different techniques such as Differential thermal analysis (DTA), X-ray diffraction (XRD), Fourier transform infrared (FTIR), Scanning electron microscope (SEM), X-ray fluorescence (XRF) and Particle size distribution (PSD).

Secondary, geopolymer samples were characterized to investigate characteristics and properties of geopolymers of the NT-GP and PJ-GP which were synthesized from local kaolin in Thailand.

4.1. Characterization of raw materials

4.1.1. Differential Thermal Analysis of kaolins

Narathiwat (NT-K) and Prachin (PJ-K) kaolins were obtained from Ceramics R US Co. Ltd and Aumnuaychai , in Narathiwat and Prachinburi provinces. Kaolins were ground and screened on a sieve size No.100.(150 μm) then they were calcined and analyzed by Differential thermal analysis (DTA) technique. The thermal analysis results show phase transformation of kaolins and the reaction of raw materials.

Figure 4.1 and Figure 4.2 show the DTA curves of the Narathiwat and Prachin kaolins. DTA thermograms exhibit the endothermic peaks with the maximum at 109, 93°C and 570, 550°C which are hydration and dehydroxylation (where kaolinite, $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ turns to be metakaolinite, $Al_2O_3{\cdot}2SiO_2$), respectively. The exothermic peaks with the maximum at 982 and 969°C are the point of phase transformation which metakaolinite transforms to mullite. Generally, Metakaolin (MK) was obtained by calcination of kaolin at different temperatures from 500°C to 800°C which depends on its structure, crystal size and degree of crystallinity. The calcined temperatures used in this experiment was around 650°C according to DTA result and soaked for 6 h.

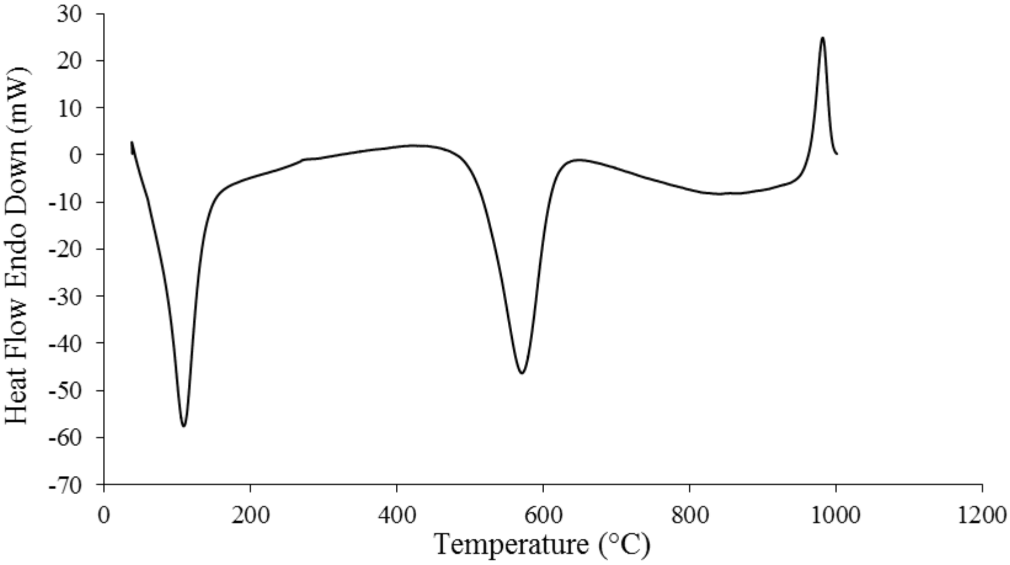


Figure 4.1 DTA curve of NT-K.

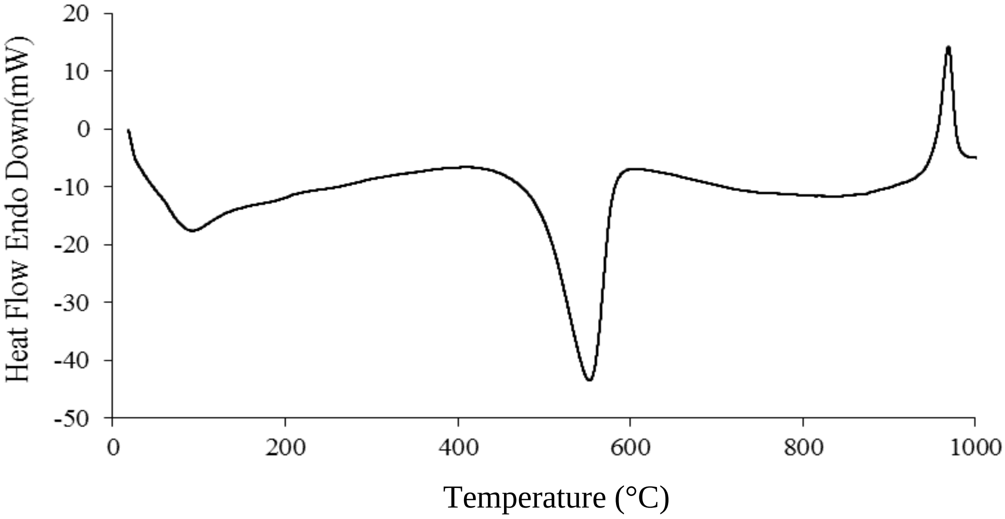


Figure 4.2 DTA curve of PJ-K.

4.1.2. X-ray Diffraction (XRD) analysis of kaolins and metakaolins

XRD analysis can be confirmed the phase of raw materials and characteristic of crystallinity. NT-K was dried, ground and screened on sieve size No.100 then, it was characterized by XRD. NT-MK obtained from calcination of the NT-K at 650°C for 6 h.

Figure 4.3 shows the X-ray patterns of NT-K and NT-MK. The major phases of NT-K are kaolinite (JCPDS: 01-089-6538), illite (JCPDS: 00-002-0056) and quartz (JCPDS: 01-086-1628) as impurities. NT-K, calcined at 650 °C, when compared with the XRD pattern of NT-K found that the kaolinite phase disappeared after the thermal treatment due to the dehydroxylation in molecules of kaolin resulting in the changing of kaolin structure from crystal to be amorphous, which coheres with the differential thermal analysis (DTA) result as shown in Figure 4.1 that the kaolin loses water by dehydroxylation at calcined temperature.

Figure 4.3 shows that NT-MK has amorphous characteristic that can be observed by low broad peak at 2 Theta around 18-25° peak band. XRD pattern displays the loss of crystallinity that still remained quartz as a minor impurity.

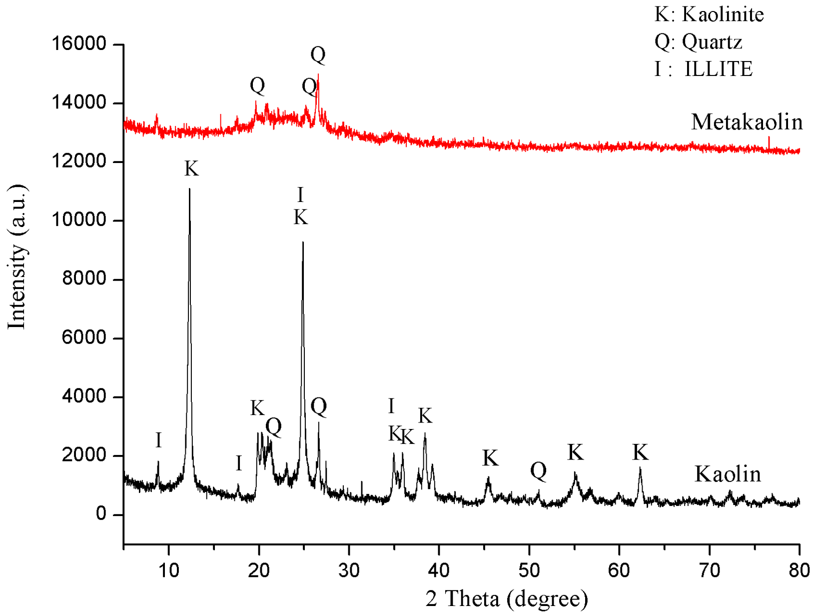


Figure 4.3 X-ray diffraction patterns of NT-K and NT-MK

Figure 4.4 shows XRD patterns of Prachin kaolin (PJ-K) and metakaolin PJ-MK. The PJ-K consisted of mainly kaolinite (JCPDS: 01-089-6538) with a minor phase of quartz (JCPDS: 01-089-8934). The high intensity of quartz peaks is due to its high content of silica or quartz in the raw materials that can be affirmed by the chemical composition as shown in Table 4.2. PJ-MK is obtained by thermal treatment of PJ-K at 650°C. The X-ray pattern shows the amorphous phase, but the amount of quartz or SiO_2 in NT-K or starting material was high (can observed in Table. 4.2), so it has high intensities of quartz (JCPDS: 01-086-1560) in the PJ-MK as impurity and kaolinite phase disappeared after heat treatment which corresponded to NT-MK X-ray pattern.

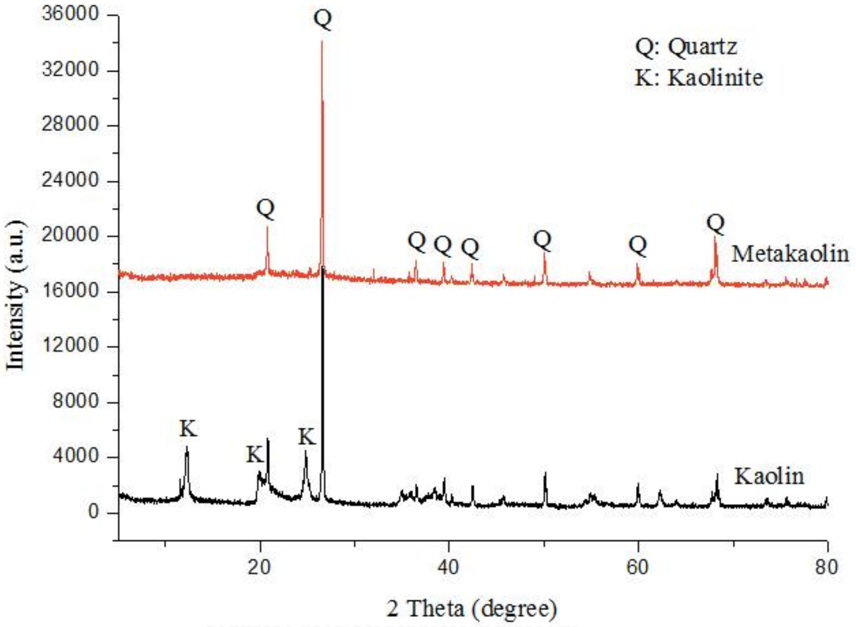


Figure 4.4 X-ray diffraction patterns of PJ-K and PJ-MK

4.1.3. Fourier Transform Infrared analysis of kaolins and metakaolins

The FTIR spectra shows the chemical bonding of molecules which can investigate bonding in raw materials. Figure 4.5 shows the FTIR spectra of NT-K and NT-MK. The band at 3694 and 3620 cm^{-1} of NT-K are related to OH stretching of inner hydroxyl groups that found in kaolin structure [24], [25]. The shoulder peak at 1114 is ascribed to Si-O stretching and the band at 1009 cm^{-1} is associated with Si-O stretching in plane which are vibrations in kaolin structure [26]. The peak at 1029 cm^{-1} is related to Si-O-Si lattice vibration in kaolin [27]. The sharp bands at 913 cm^{-1} is associated with octahedral coordination of Al^{3+} (Al-O stretching) in kaolinite. Low frequency bands positioned at 759, 694 and 536 cm^{-1} are ascribed to Si-O and Al-O bonds [21].

FTIR spectrum of NT-MK, the band at 1070 cm^{-1} is related to the asymmetric stretching of Si-O-T group (T=Si or Al) [27]and the last band at 800 cm^{-1} is assigned to Al-O bending vibration in metakaolin structure which changed from octahedral coordination of Al^{3+} in kaolinite structure to tetratrahedral coordination in metakaolinite [26], [28].

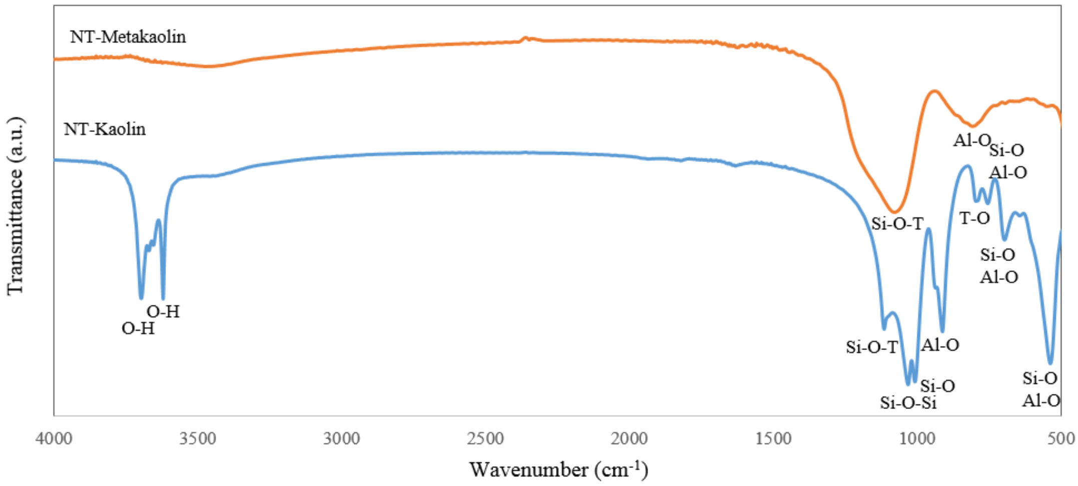


Figure 4.5 FTIR spectra of NT-K and NT-MK

Figure 4.6 exhibits the FTIR spectra of PJ-K and PJ-MK. The spectrum of PJ-K is same as NT-K in the band at 3696, 3620 cm^{-1} which are ascribed to OH stretching of inner hydroxyl groups, 1029 cm^{-1}, 1009 cm^{-1} and at low frequency band 694, 536 and 465 cm^{-1} which are all vibration bands in kaolin structure [24], [25], [26], [27]. The peak at 792 cm^{-1} is associated to a four-coordinated Al-O stretching vibration [27]

FTIR spectrum of PJ-MK, the broad band around 1077 cm^{-1} is asymmetric stretching of Al-O-Si bond and at 792 cm^{-1} is ascribed to a four-coordinated Al-O stretching vibration in metakaolin [27]. The last peak at 465 is the bending of T-O bond in TO_4 tetrahedra in metakaolin (T=Al or Si) [29].

All of the FTIR spectra of NT-K, PJ-K and NT-MK, PJ-MK show differences of bonding in their structures between kaolins and metakaolins that mean NT-K and PJ-K were completely changed to NT-MK and PJ-MK, respectively. Thus, the FTIR results are consistent with XRD and DTA results.

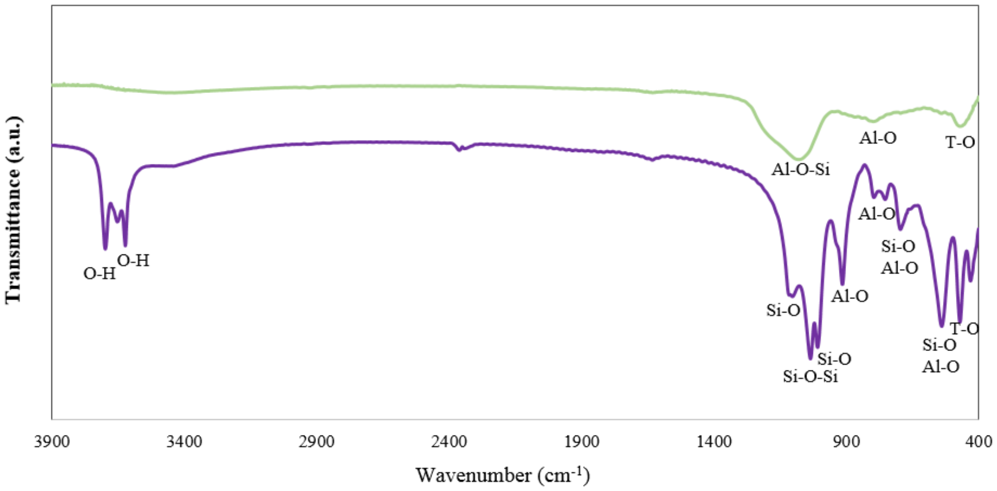


Figure 4.6 FTIR spectra of PJ-K and PJ-MK

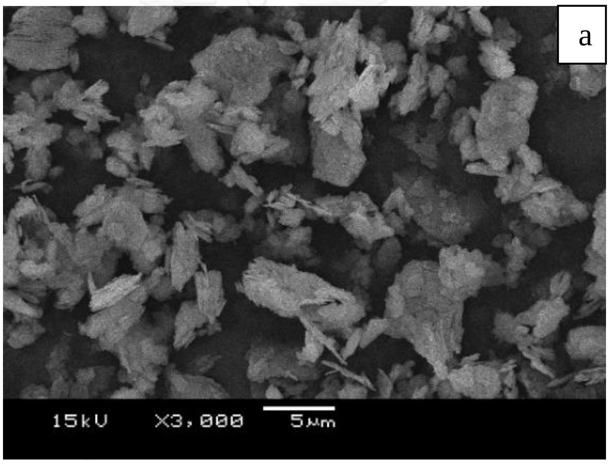
Table 4.1 Assignment of wavenumbers for molecular vibrations in absorption spectra of kaolin and metakaolin

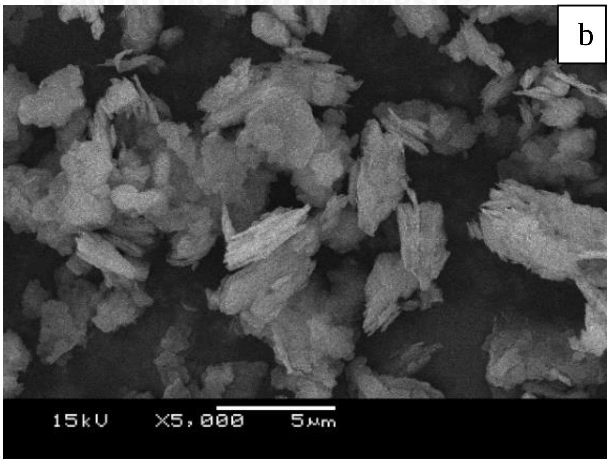
Wavenumber (cm^{-1})	**Vibrational assignments**
3696	OH stretching of inner-surface hydroxyl groups
3694	
3620	OH stretching of inner hydroxyl group
1114	Si-O Stretching
1077	Al-O-Si stretching
1070	Asymmetric stretching of Si-O-T group (T=Si or Al)
1030	Si-O-Si
1009	In-plane Si-O stretching
913	Al-O stretching
800	Al-O bending
792	Al-O Stretching
759	Si-O, Al-O
694	Si-O, Al-O
536	Si-O, Al-O
465	T-O bending (T=Si or Al)

4.1.4. Microstructure analysis of metakaolins

Microstructures can show approximate particle size and morphology of the particles or sample surface. One of the essential factors in reaction is the morphology of raw materials. The morphology which has a large surface area influences to the degree of reaction. The morphologies of NT-MK particulates are shown in Figure 4.7 (a)-(b). It was found that NT-MK particles were stacked layer by layer as the flake-plate layers with irregular angular shape. The flake of metakaolin is easy to react with the solution in geopolymeric reaction. The average particle size of NT-MK was less than 15 µm which corresponded to results of particle size distribution analysis.

Microstructure of PJ-MK are shown in Figure 4.7 (c)-(d) the particles were formed by agglomeration of small particles into larger agglomerate as sphere shape which was good for assault of the alkali solutions.





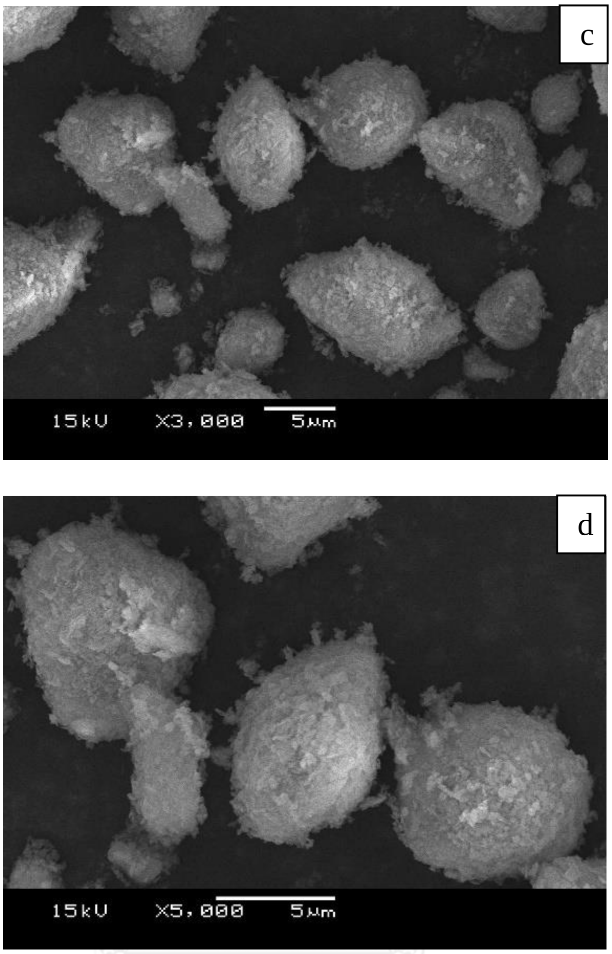


Figure 4.7 SEM micrographs of NT-MK and PJ-MK
(a), (b) NT-MK, Magnification x3000, x5000
(c), (d) PJ-MK, Magnification x3000, x5000

4.1.5. X-ray fluorescence analysis of metakaolins

The chemical compositions of raw materials were investigated by XRF as shown in Table 4.2. The main compositions of raw materials are rich in SiO_2 and Al_2O_3 which are an important sources of aluminosilicate to use as starting materials for synthesis geopolymer. The Si/Al ratios of geopolymer were calculated from the chemical compositions of metakaolin and alkali solutions. From the concentrations of SiO_2 and Al_2O_3 can estimate the ratios of Si/Al of geopolymer in the beginning. The ratios of Si/Al were used in the different applications due to their properties.

Table 4.2 Percentage by weight of chemical composition of metakaolins.

Chemical Compositions	**NT-MK Concentration (%)**	**PJ-MK Concentration (%)**
MgO	0.14	0.13
Al_2O_3	40.24	26.83
SiO_2	54.12	68.09
P_2O_5	0.04	-
SO_3	0.02	0.02
K_2O	1.88	0.16
CaO	0.04	0.11
TiO_2	1.14	1.16
Fe_2O_3	0.75	1.67
ZrO_2	0.02	0.08

4.1.6. Particle size distribution analysis of metakaolins

The particle sizes of raw materials were investigated by Laser Light Scattering (Mastersizer 2000 Malvern Instruments). The results exhibited that the particle size of NT-MK distributed from 2 to 30 µm which represented by the D_{10} , D_{50} and D_{90} were 2.61 µm, 9.60 µm and 30.61 µm, respectively, and for PJ-MK distributed from 9 to 65 µm which represented by the D_{10} , D_{50} and D_{90} were 9.73 µm, 33.12 µm and 65.18 µm, respectively as shown in Figure 4.8 and 4.9. Particle size of raw materials affected to the reaction. The small particle size of raw materials has a large surface area, thus it can occur reaction more than the large particle size which has a small surface area. For this reason the particle size of raw materials is important for the geopolymerization.

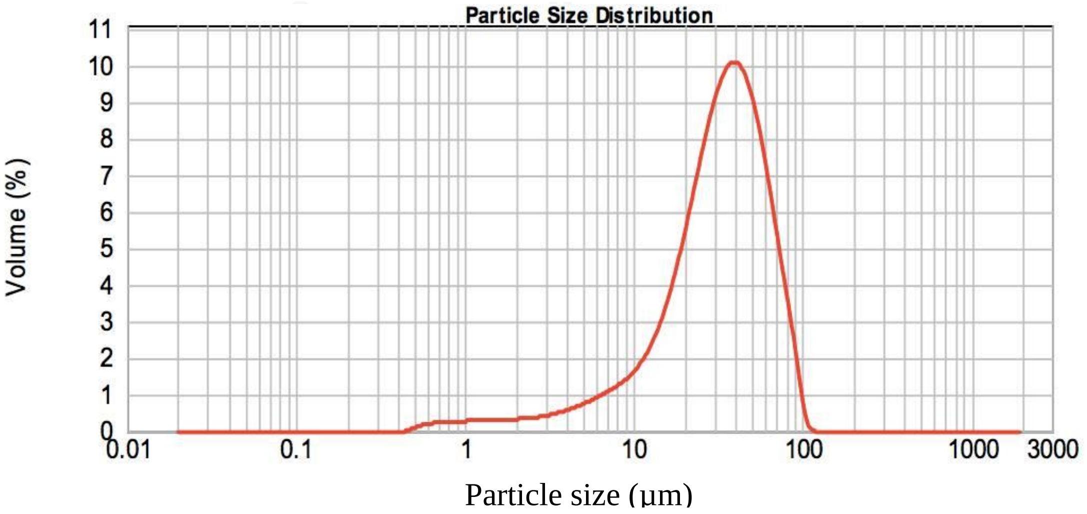


Figure 4.8 Particle size distribution of NT-K

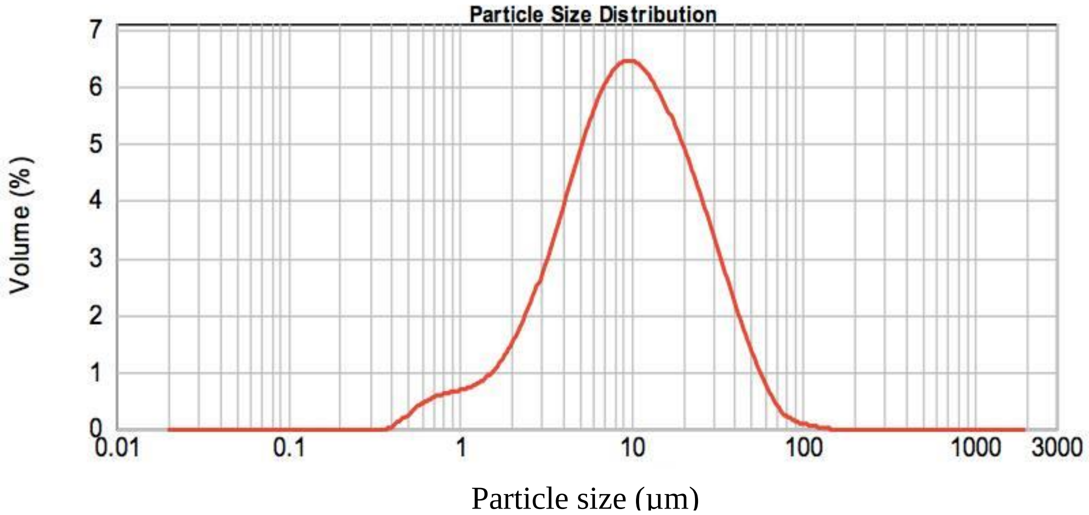


Figure 4.9 Particle size distribution of PJ-K

4.2.Characterization of geopolymers

4.2.1. X-ray Diffraction analysis of geopolymers

X-ray diffractrograms of geopolymers after stored for 7 days at room temperature, which have different concentrations of NaOH which are 6, 8, 10 and 12M has shown in Figure 4.10. The patterns of geopolymers were not obviously different when they were compared with the XRD pattern of metakaolin (see Figure 4.3). It can be noticed that the halo peak with 2 theta between 18-25° that indicates a peak of metakaolin was shifted to 20-45° which is a characteristic of geopolymers due to geopolymerization [30]. However, the amorphous peak of geopolymer still remained a quartz peak (JCPDS: 01-082-0511) as the impurity due to some undissolvable of metakaolin particulates during geopolymerization which corresponded to SEM images of NT-GP. XRD patterns of different Si/Al ratios displayed in Figure 4.11 the diffractrograms that were same as Figure 4.10.

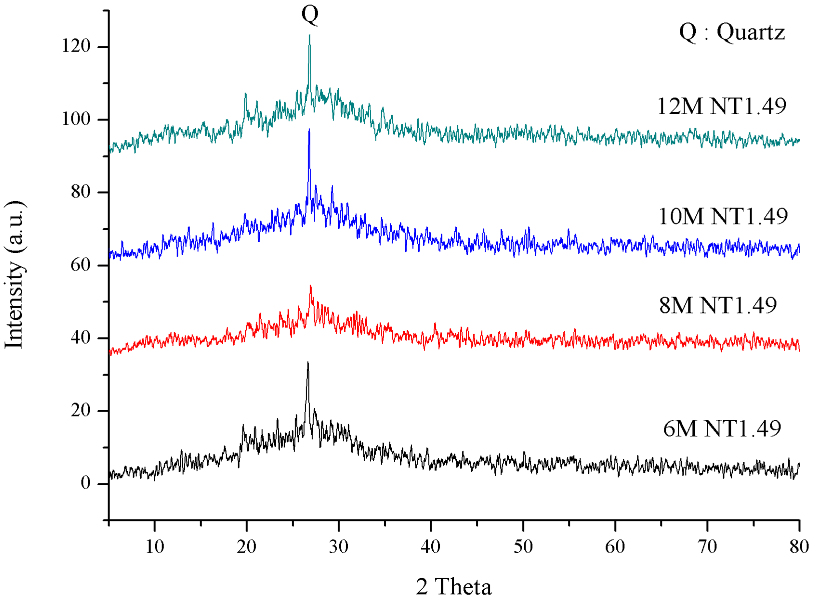


Figure 4.10 XRD patterns of NT-GP samples with different concentrations of NaOH

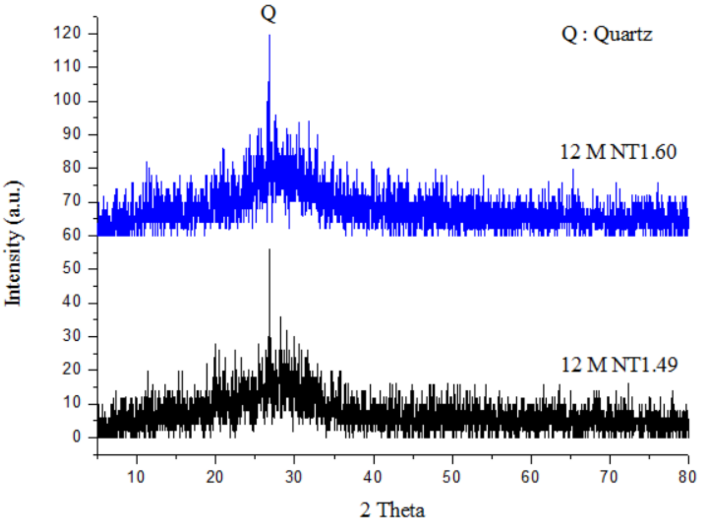


Figure 4.11 XRD patterns of NT-GP samples with different Si/Al ratios

XRD patterns of PJ-GP with different NaOH concentrations are given in Figure 4.12. It can be seen that the high intensities of quartz (JCPDS: 01-085-0794) are due to the unreacted metakaolin and quartz in the geopolymer structure. The semi-amorphous phase of geopolymers was quite difficult to notice since the high intensities of quartz. Figure 4.13 exhibits the XRD patterns of various Si/Al ratios have also same as XRD patterns in Figure 4.12.

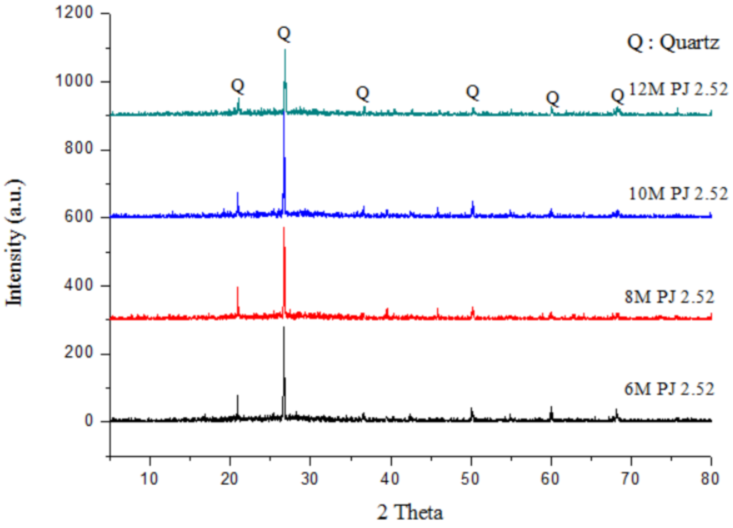


Figure 4.12 XRD patterns of PJ-GP samples with different concentrations of NaOH

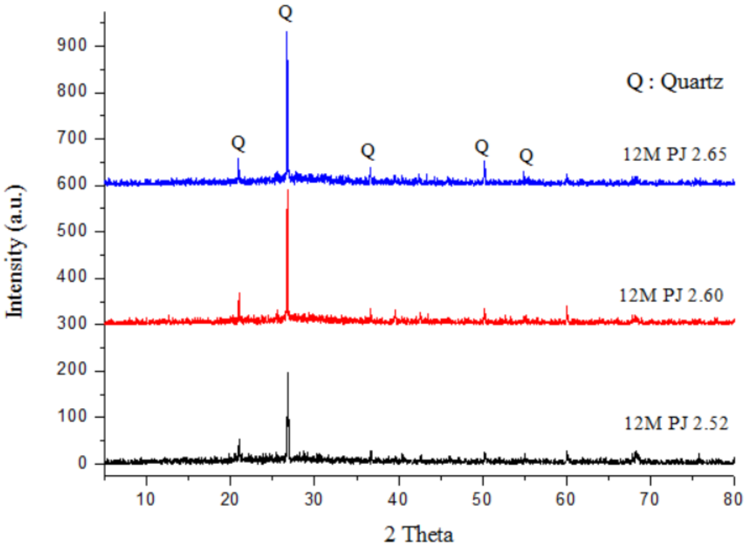


Figure 4.13 XRD patterns of PJ-GP samples with different Si/Al

4.2.2. Fourier Transform Infrared analysis of geopolymers

FTIR spectra can exhibit the comparison between starting materials and geopolymer products which have a variation of bonding structures. All FTIR spectra of the NT-GP with various concentrations of NaOH and Si/Al ratios are shown in Figure 4.14 which illustrated the broad band about 3450-3480 cm^{-1} and small band at 1650 cm^{-1} are assigned to stretching and deformation vibrations of O-H and H-O-H bonds of water molecules [31], [32]. The band range from 1030 to 900 cm^{-1} are ascribed to asymmetric stretching of Si-O and Al-O tetrahedral bonds and from these bonds confirmed that they turned from metakaolin to be geopolymer [28],[33]. The last band around 702 cm^{-1} is a C-O bond which is derived from Na_2CO_3. It is formed by the excess Na^+ from alkali solution reacted with CO_2 in the atmosphere on the surface of geopolymer. From Figure 4.14 a-c spectra are NT-GP samples with various concentrations of NaOH which are Si/Al of 1.49 with 6, 8, 10 and 12M, respectively that have the same characteristic of bonding structures. Whereas, Figure 4.14 d-e spectra are NT-GP samples with different Si/Al ratios are 1.49, 1.55 and 1.60 which have the same as the characteristic of the bonding structure as a-c spectra.

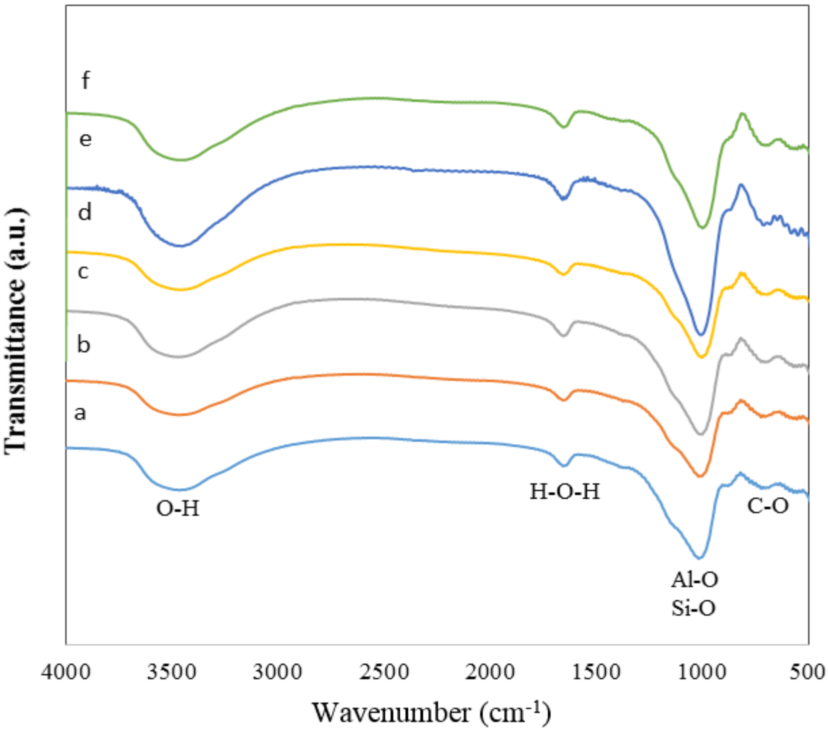


Figure 4.14 FTIR spectra of NT-GP samples with different conditions

(a) Si/Al = 1.49 with 6M NaOH, (d) Si/Al = 1.49 with 12M NaOH
(b) Si/Al = 1.49 with 8M NaOH, (e) Si/Al = 1.55 with 12M NaOH
(c) Si/Al = 1.49 with 10M NaOH, (f) Si/Al = 1.60 with 12M NaOH

Figure 4.15 shows FTIR spectra of all the PJ-GP with various in the concentrations of NaOH and Si/Al ratios are exhibited the broad band between 3450-3480 cm^{-1} and small band at 1650 cm^{-1} are related to stretching and deformation vibrations of O-H and H-O-H groups [31], [32]. The bands range from 1030 to 900 cm^{-1} are asymmetric stretching Al-O and Si-O bonding of AlO_4 and SiO_4 tetrahedrons of geopolymer. The low frequency bands at 696 and 456 cm^{-1} are associated with the Si-O or Al-O vibration and the range between 465 to 450 cm^{-1} are ascribed to the Si-O bending in plane of geopolymer bond [29].

From Figure 4.15 a-c spectra are PJ-GP samples with different concentrations of NaOH which are Si/Al of 2.52 with 6, 8, 10 and 12M, respectively that have the same characteristic of bonding structures. Whereas, Figure 4.15 d-e spectra are PJ-GP samples with different Si/Al ratios are 2.52, 2.60 and 2.65 which have the same as the characteristic of the bonding structure as a-c spectra.

From the FTIR results of NT-GP and PJ-GP can verify that the bonding of metakaolin turn to the bonding of geopolymer as a result of geopolymerization of metakaolin with alkali solutions.

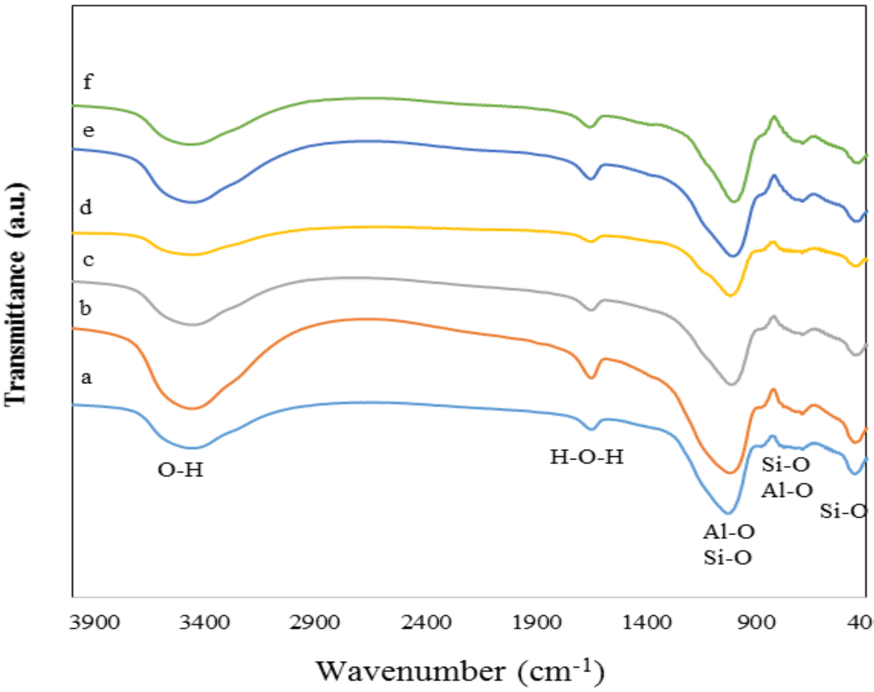


Figure 4.15 FTIR spectra of PJ-GP samples with different conditions
(a) Si/Al = 2.52 with 6M NaOH, (d) Si/Al = 2.52 with 12M NaOH
(b) Si/Al = 2.52 with 8M NaOH, (e) Si/Al = 2.60 with 12M NaOH
(c) Si/Al = 2.52 with 10M NaOH, (f) Si/Al = 2.65 with 12M NaOH

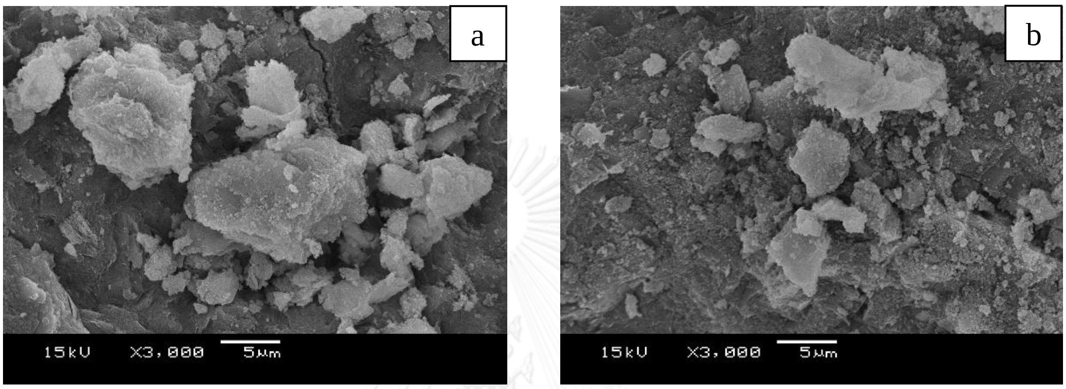
Table 4.3 Assignment of wavenumbers for molecular vibrations in absorption spectra of geopolymer

Wavenumber (cm^{-1})	**Vibrational assignments**
3450-3480	OH stretching
1650	Deformation of H-O-H
1030-900	Si-O, Al-O
702	C-O
696	Si-O, Al-O
465-450	Si-O bending
456	Si-O, Al-O

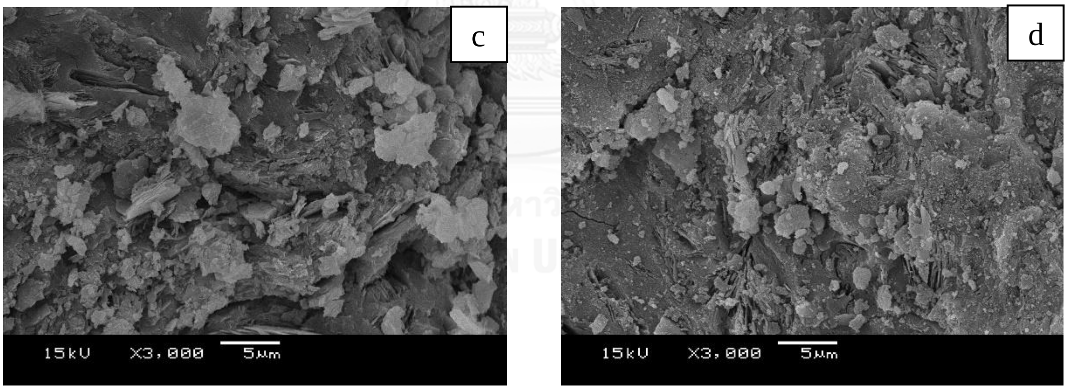
4.2.3. Microstructure analysis of geopolymers

The microstructures of the fracture surface of NT-GP samples with different conditions were characterized. Figure 4.16 (a) the dissolution of metakaolin was not good enough to form geopolymer under geopolymerisation, since the low concentrations of NaOH in the reaction. From the micrographs noticed that the particulates were smaller when the concentrations of NaOH were higher. The particulates were dissolved by the high pH alkali solution, since the NaOH solution attacked on the surface of particulates to produce more reactive bond for the monomer to form polymerized network [19]. However, all of the samples showed that the unreacted metakaolin particles still remain in geopolymers, which is consistent with XRD patterns results.

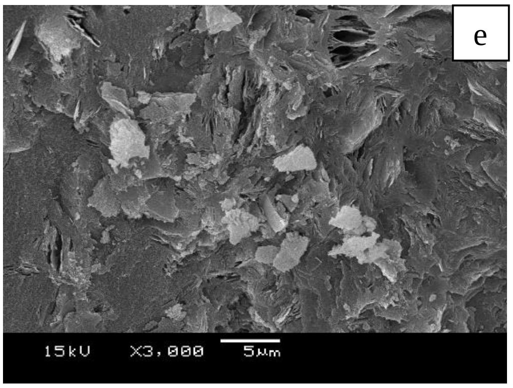
Figure 4.16 (e) displays the particulates are most dissolved and can observe the geopolymer gel which was Si/Al= 1.60 with 12M NaOH because the ratio of solid/liquid is also affected to the dissolving of metakaolin particulate. However, this ratio was not the optimum for synthesis NT-GP due to the high ratio of liquid results in the porosity and bulk density in the NT-GP samples.



(a) Si/Al = 1.49 with 8M NaOH (b) Si/Al = 1.49 with 10M NaOH



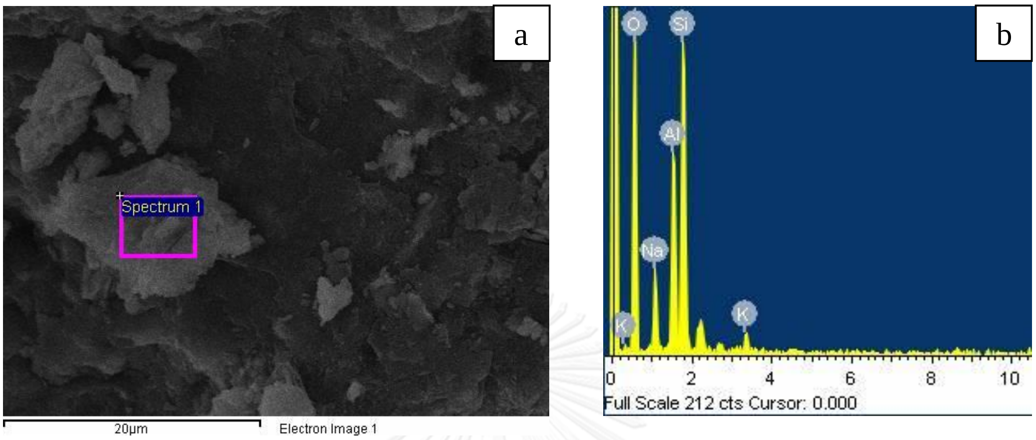
(c) Si/Al = 1.49 with 12M NaOH (d) Si/Al = 1.55 with 12M NaOH



(e) Si/Al = 1.60 with 12M NaOH

Figure 4.16 (a)-(e) SEM micrographs of NT-GP samples

The EDX results show that the particle contains Na, K, Si, Al and O elements as shown in Figure 4.17 (a) and (b) which can see the K element in Table 4.2 of XRF results as well. Figure 4.17 (c) and (d) display the geopolymer matrix that consists of Na, Si, Al and O which were ingredients of geopolymer gel.



(a)-(b) Particle area of NT-GP sample

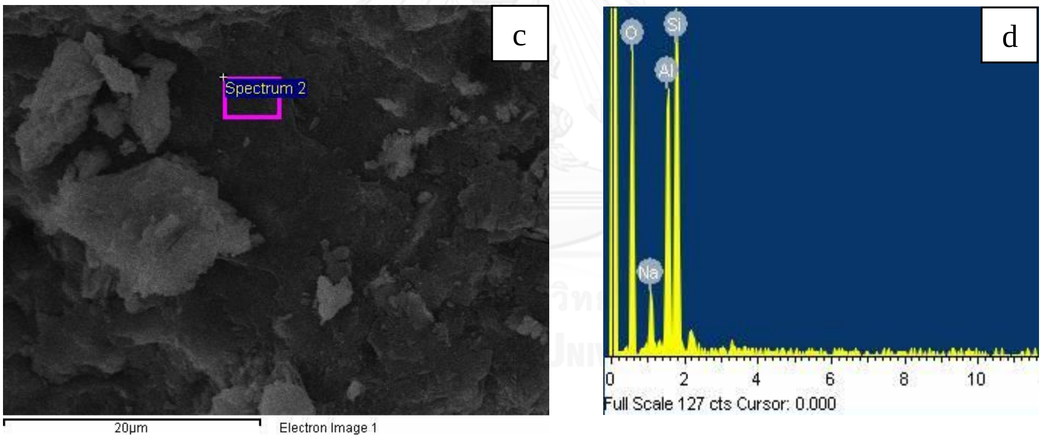
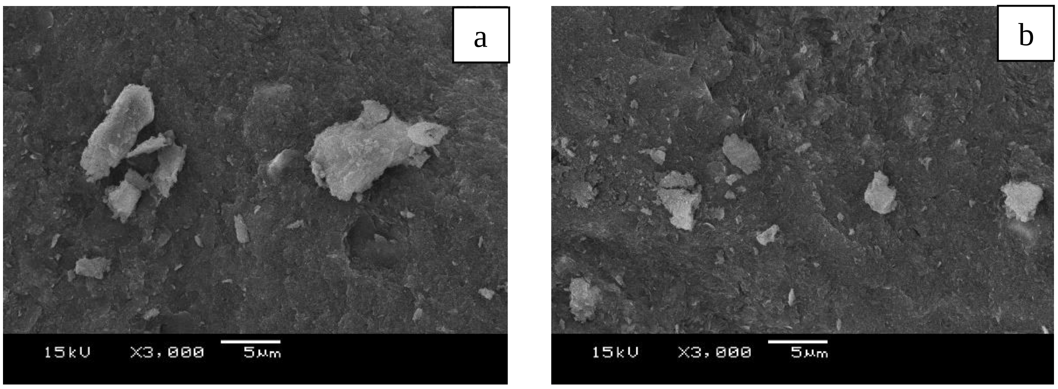
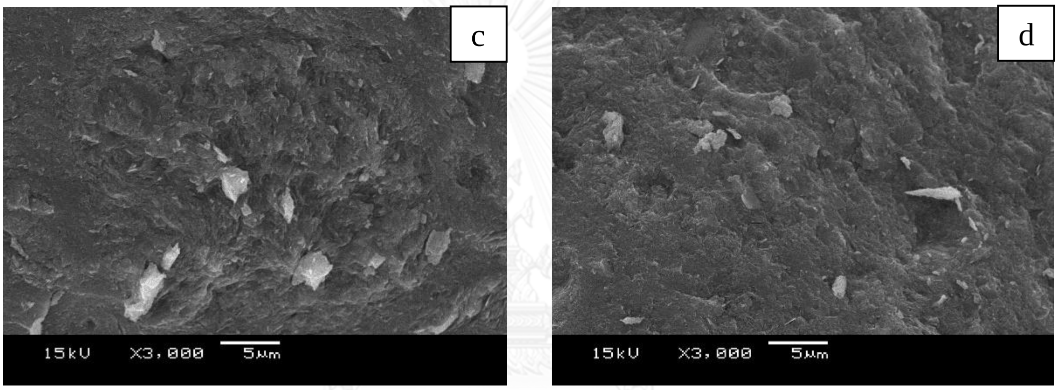


Figure 4.17 (a)-(d) EDX of NT-GP sample with Si/Al= 1.49 (8MNaOH)
(c)-(d) Matrix area of NT-GP sample

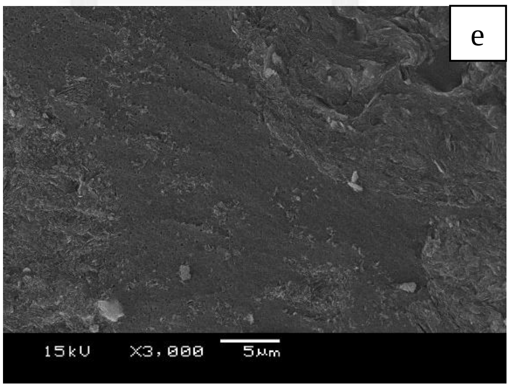
The particle size of PJ-MK is so small resulting in the agglomerate of small particle sizes as the larger particles that shows the SEM images of PJ-MK. Thus, the dissolving of metakaolin particulates was excellent as shown in Figure 4.18 (a)-(e) which display the microstructures of fracture surface of PJ-GP samples with various conditions. Figure 4.18 (a) has large metakaolin particles because of unreacted metakaolin during a geopolymerization. The particles of metakaolin dissolved by the high concentration of NaOH which can be observed in Figure 4.18 (a)-(c). Moreover, the best of particle dissolution was Figure 4.18 (e) or the PJ-GP ratio of Si/Al= 2.65 which showed the matrix of geopolymer without metakaolin particles. However, it was not the best due to the high porosity and low bulk density from evaporation during geopolymerization.



(a) Si/Al = 2.52 with 8M NaOH (b) Si/Al = 2.52 with 10M NaOH



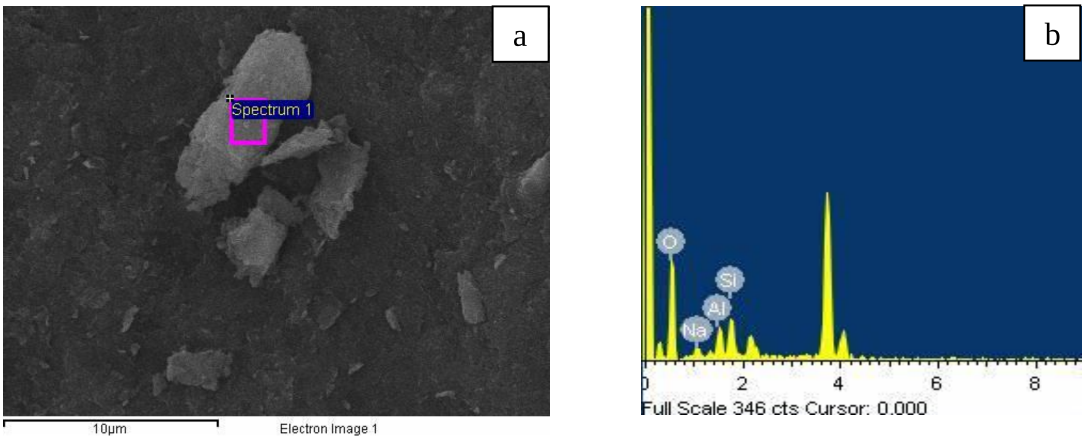
(c) Si/Al = 2.52 with 12M NaOH (d) Si/Al = 2.60 with 12M NaOH



(e) Si/Al = 2.65 with 12M NaOH

Figure 4.18 (a)-(e) SEM micrographs of PJ-GP samples

The microstructure of PJ-MK confirmed the element compositions by EDX results. The results exhibited that the major of particle and matrix inside a geopolymer sample composed of Si, Al, O and Na as Figure 4.19 (a)-(d) which was Si/Al= 2.52 with 8M NaOH.



(a)-(b) Particle area of PJ-GP sample

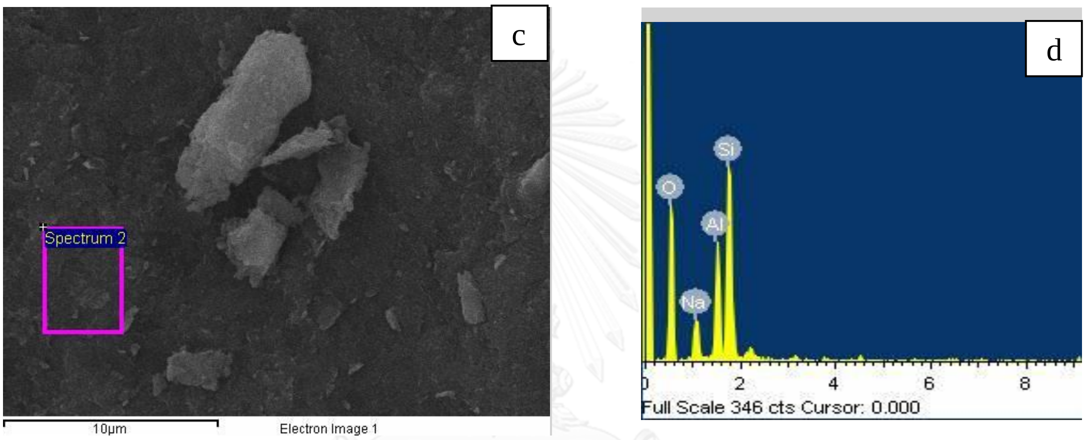


Figure 4.19 (a)-(d) EDX of PJ-GP sample with Si/Al= 2.52 (8MNaOH)
(c)-(d) Matrix area of PJ-GP sample

4.2.4. Bulk density, apparent porosity and water absorption

The range of bulk density of NT-GP samples in this study estimated 1.25-1.4 g/cm^3 as shown in Figure 4.20 The highest value of bulk density was 1.40 g/cm^3 (Si/Al= 1.49 with 12M NaOH) corresponded to the compressive strength result. The low ratio of solid/liquid affected to the dissolvable of metakaolin particulates. The apparent porosity and water absorption were exhibited in Figure 4.20 (b). Porosity was increased when the Si/Al ratios were higher due to the ratio of liquid increasing as evaporation of OH group in the structure.

Figure 4.21 (a) exhibits that the maximum bulk density of PJ-GP sample was 1.50 g/cm^3 that was the Si/Al ratio of 2.52 with 8M NaOH and the lowest value was Si/Al ratio of 2.65 with 12M NaOH. The range of bulk density was 1.36-1.46 g/cm^3. The apparent porosity and water absorption were shown in Figure 4.21 (b). The reason of characteristic of bulk density and porosity of PJ-GP was the same as NT-GP.

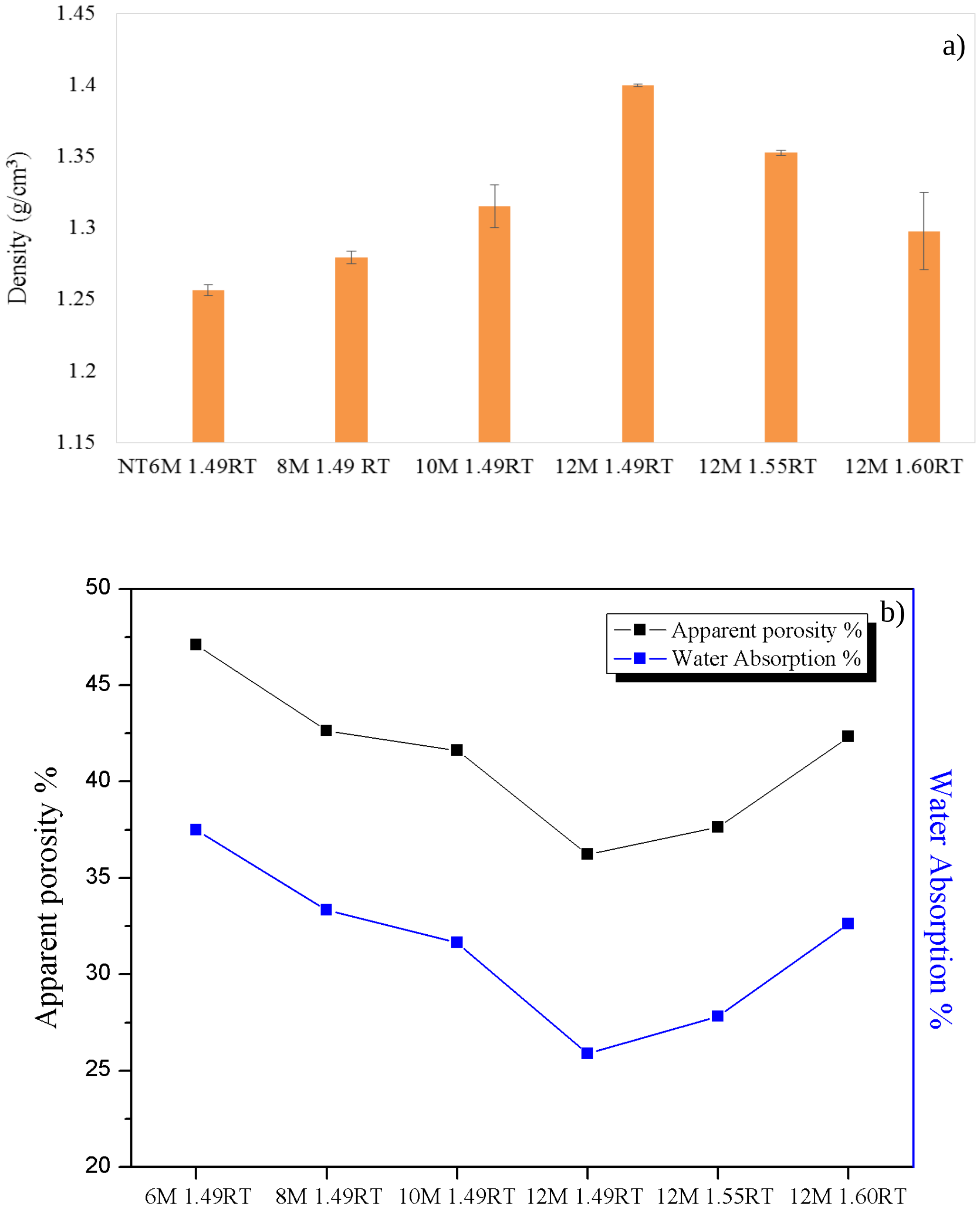


Figure 4.20 (a) Bulk density (b) Apparent porosity and water absorption of NT-GP with different Si/Al ratios

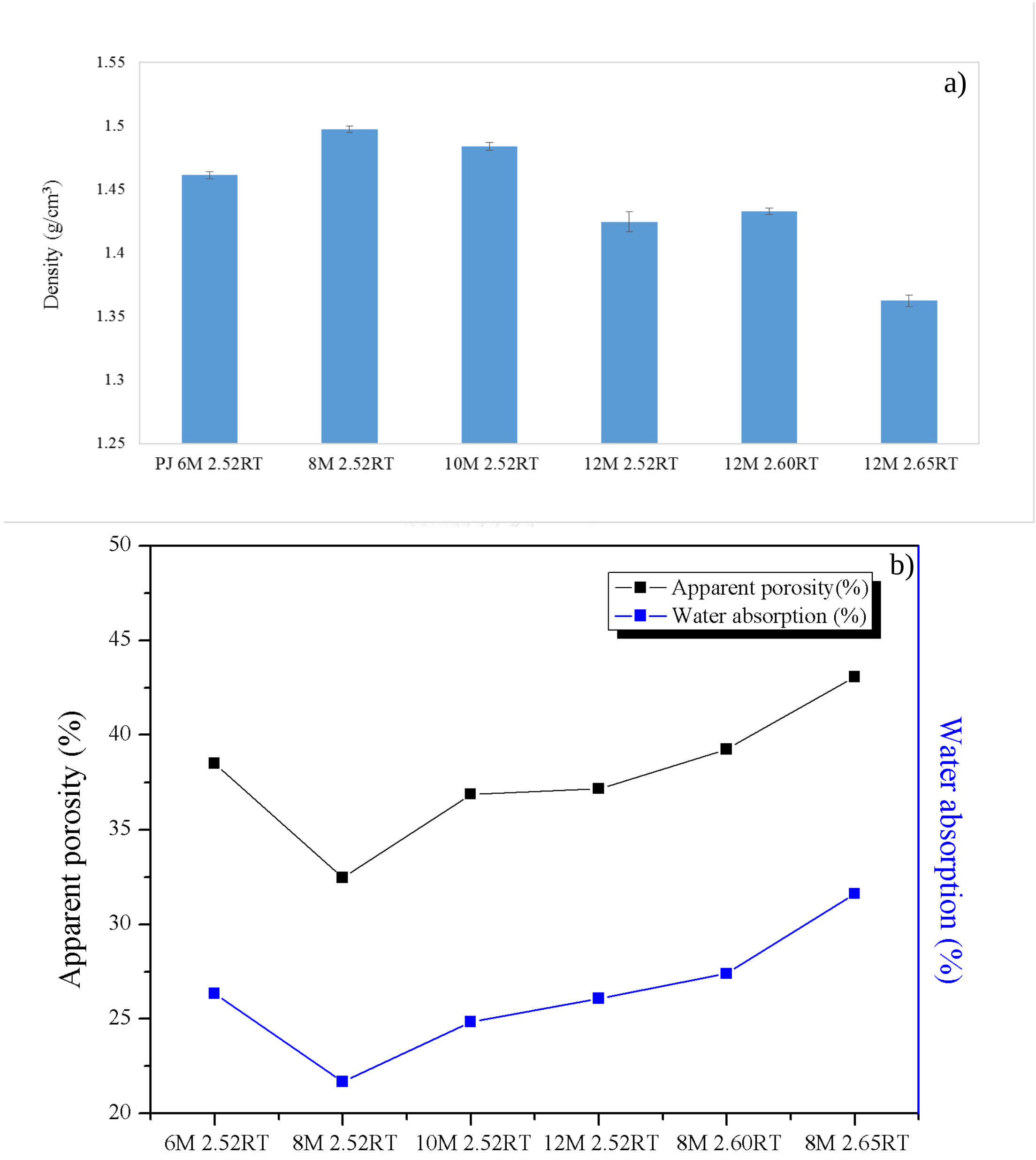


Figure 4.21 (a) Bulk density (b) Apparent porosity and water absorption of PJ-GP with different Si/Al ratios

4.2.5. Compressive strength

4.2.5.1.The effect of solid/liquid on compressive strength

All of NT-GP samples set and formed hard structure within 24 h after casting and they were kept at room temperature in the closed container for 7, 14, and 28 days, respectively then all NT-GP samples were tested compressive strength.The NT-GP samples with various Si/Al ratios can be fabricated by modification of the amount of solid/liquid. NT-GP samples with the lowest molar ratio of Si/Al of 1.44 obtained lower compressive strength because the liquid was not enough for the reaction to occur in geopolymer sample. The high bulk density of Si/Al of 1.44 was from the pressing during casting geopolymer pastes into the mold due to a bad flowability of geopolymer pastes, however the compressive strength was slightly higher when curing time was longer which showed that the reaction might occur slowly. The Si/Al ratios of 1.49 exhibited the higher compressive strength than 1.44 and the highest of 1.49 was 54 MPa curing for 28 days as shown in Figure 4.22.

Figure 4.23 illustrates the compressive strength of various Si/Al ratios of NT-GP. All NT-GP samples with different Si/Al ratios were cured at room temperature and controlled the moisture in the air by left in a container, then NT-GP samples were characterized the compressive strength. The compressive strength of samples decreased with increasing of the Si/Al ratios when the molar ratio was higher than 1.49. From this result, the molar ratio of 1.49 was an optimum for solid/liquid ratio. Because, water content is an essential factor that has effect on the mechanical strength, the higher water content will create more porosity, thus the total porosity increased [34] . Bulk density of NT-GP samples corresponded to this reason and the NT-GP which was Si/Al ratio of 1.49 gave the highest compressive strength and bulk density as shown in Figure 4.20. The solid/liquid ratios of Si/Al 1.55 and 1.60 were not good due to the higher water content which increased porosity in the samples that resulting in the lower bulk density compared to Si/Al 1.49.

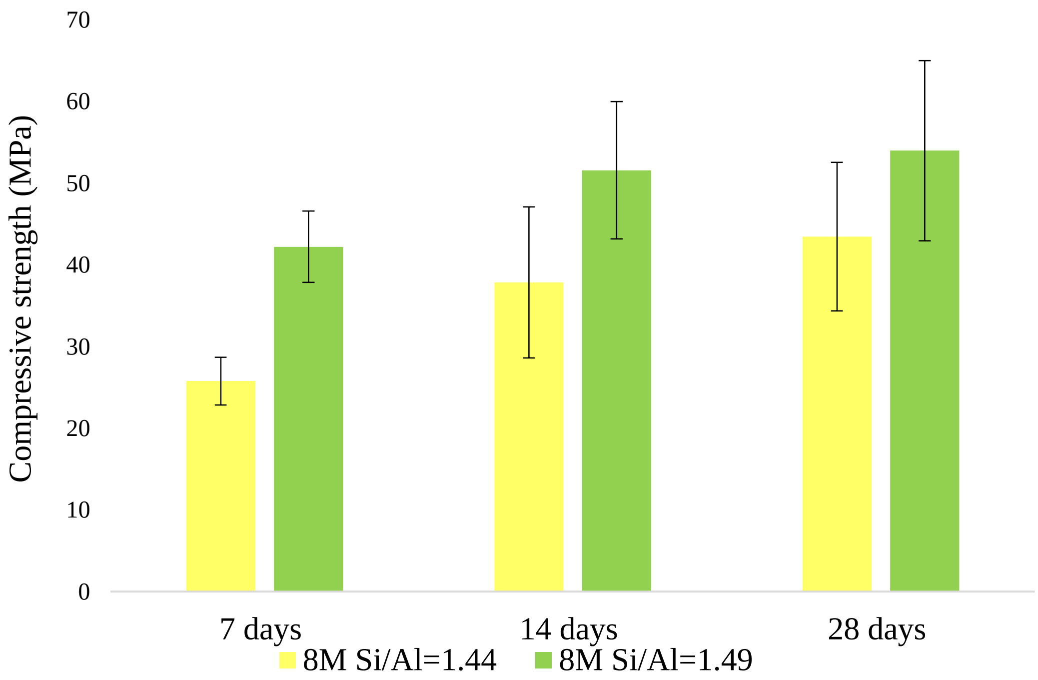


Figure 4.22 Compressive strengths of NT-GP with different Si/Al ratios (Si/Al=1.44 and 1.49)

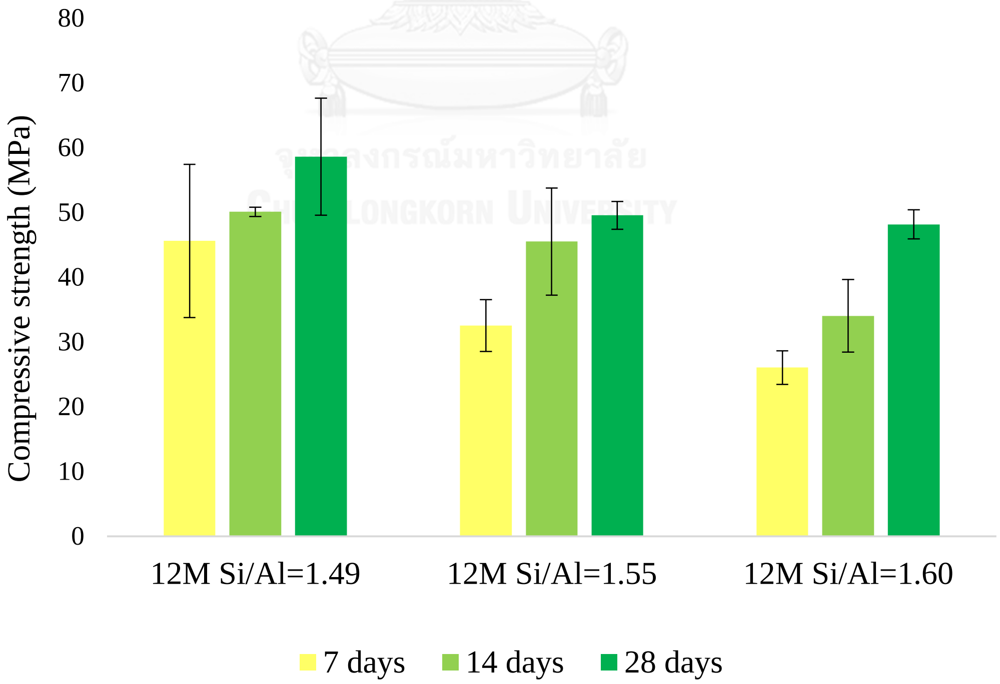


Figure 4.23 Compressive strengths of NT-GP with different Si/Al ratios
(Si/Al=1.49, 1.55 and 1.60)

The PJ-GP samples with different Si/Al ratios can be set within 24 h at the ambient temperature in the closed container for 7, 14 and 28 days, respectively after that PJ-GP samples were examined the compressive strength. The PJ-GP samples with the Si/Al of 2.46 gave the lowest compressive strength due to the lack of liquid solutions to dissolve and react in geopolymer paste, hence at this ratio is not proper for fabrication of geopolymer. Whereas, the higher compressive strength was the Si/Al ratio of 2.52 in all conditions and the highest strength was Si/Al ratio of 2.52 that cured for 28 days. Figure 4.24 shows the average compressive strength of PJ-GP samples with the Si/Al ratios of 2.46 and 2.52 with different conditions.

Figure 4.25 displays the compressive strength of various Si/Al ratios of PJ-GP. All PJ-GP samples which the ratios of Si/Al were 2.52, 2.60 and 2.65, respectively then the compressive strength of PJ-GP samples were investigated. The optimum Si/Al ratio was 2.52 which had the compressive strength of 62 MPa. The main reason was the ratio of 2.52 had proper amount of liquid for geopolymerization and provided the highest density of geopolymer samples.

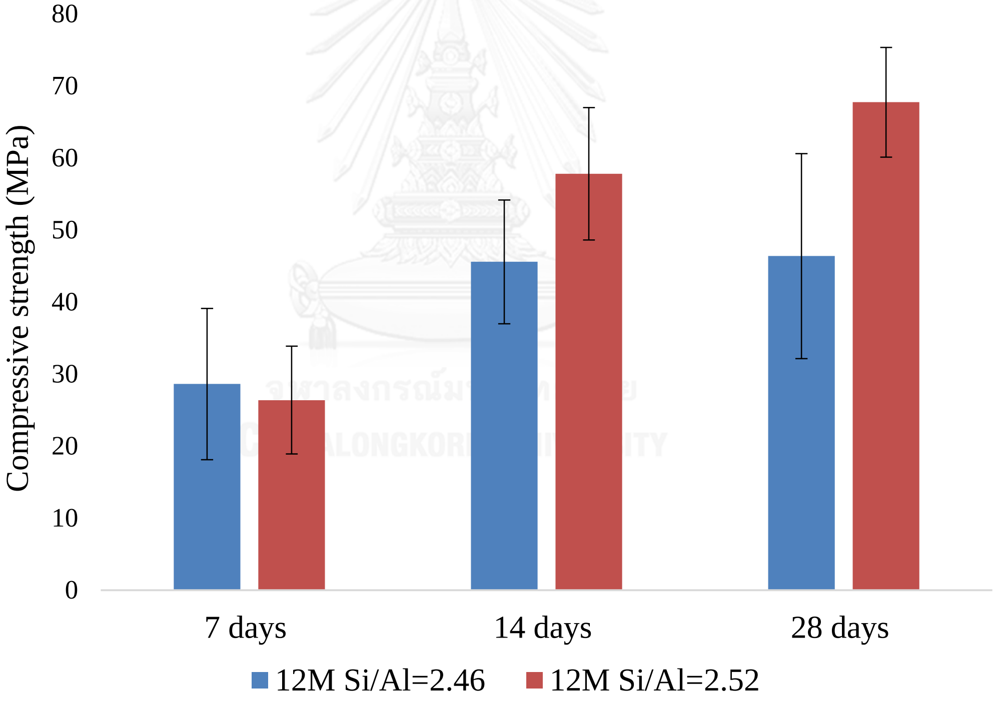


Figure 4.24 Compressive strengths of PJ- GP with different Si/Al ratios (Si/Al= 2.46 and 2.52)

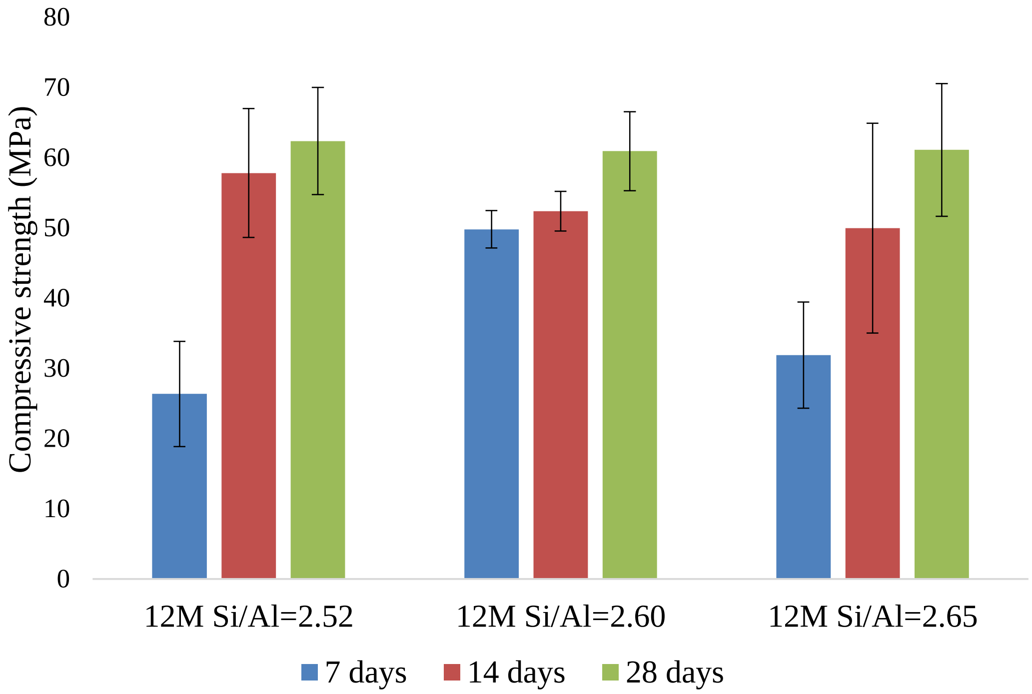


Figure 4.25 Compressive strengths of PJ- GP with different Si/Al ratios (Si/Al= 2.52, 2.60 and 2.65)

4.2.5.2.The effect of NaOH concentration on compressive strength

Narathiwat metakaolin was mixed with alkali solutions which modified the concentrations of NaOH were 6, 8, 10, and 12M, respectively at the room temperature, then cured for 7, 14 and 28 days. The results of the effect of NaOH concentrations on the compressive strength of NT-GP exhibited that the increasing of NaOH concentration can improve the compressive strength, because the dissolutions of metakaolin particulates increased and thus it had more monomer resulting in the higher rate of reaction [9]. This reason is consistent with the results of compressive strength that the optimum concentration of NaOH for NT-GP was 12 Molar of NaOH which gave the highest compressive strength at 28 days up to 58 MPa for the Si/Al ratio of 1.49 as shown in Figure 4.26.

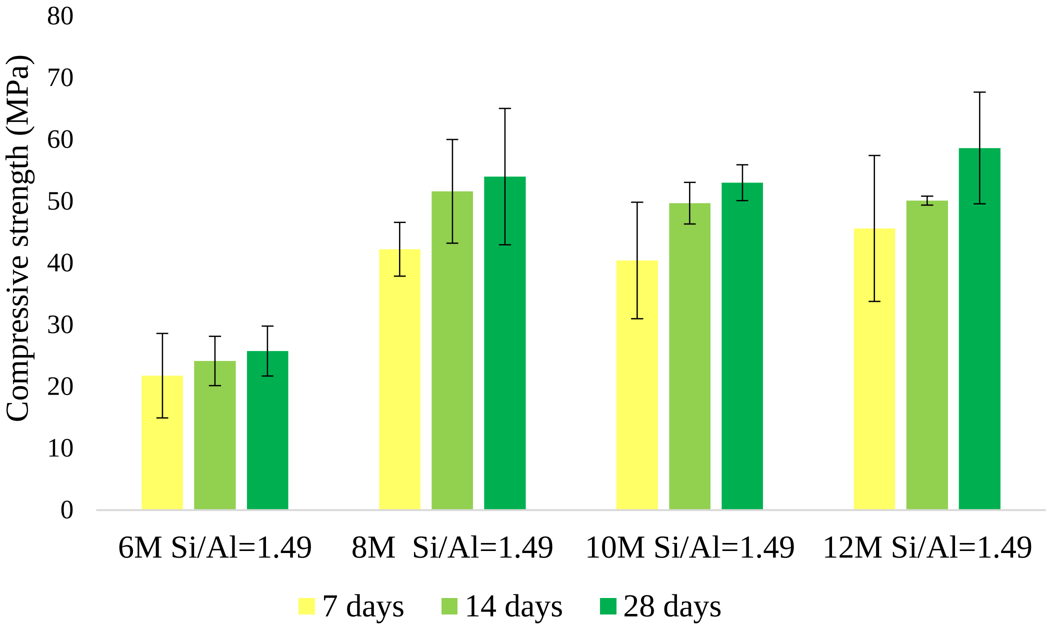


Figure 4.26 Effect of NaOH concentrations on NT-GP in the compressive strengths

PJ-GP samples were synthezised by using Prachin metakaolin and alkali solutions which varied concentrations of NaOH from 6-12 M to investigate the effect of NaOH concentrations on the compressive strength. The compressive strength shows that high concentrations of NaOH will provide an increasing of compressive strength, since it has more monomer which are from the dissolution of metakaolin particulates resulting in the higher degree of condensation. However, if the concentration of NaOH is very high, it will be hard to prepare a solution due to precipitation in a short time. Figure 4.27 shows the compressive strength of PJ-GP that the maximum value was 62 MPa which was Si/Al ratio of 2.52 with 12 Molar of NaOH

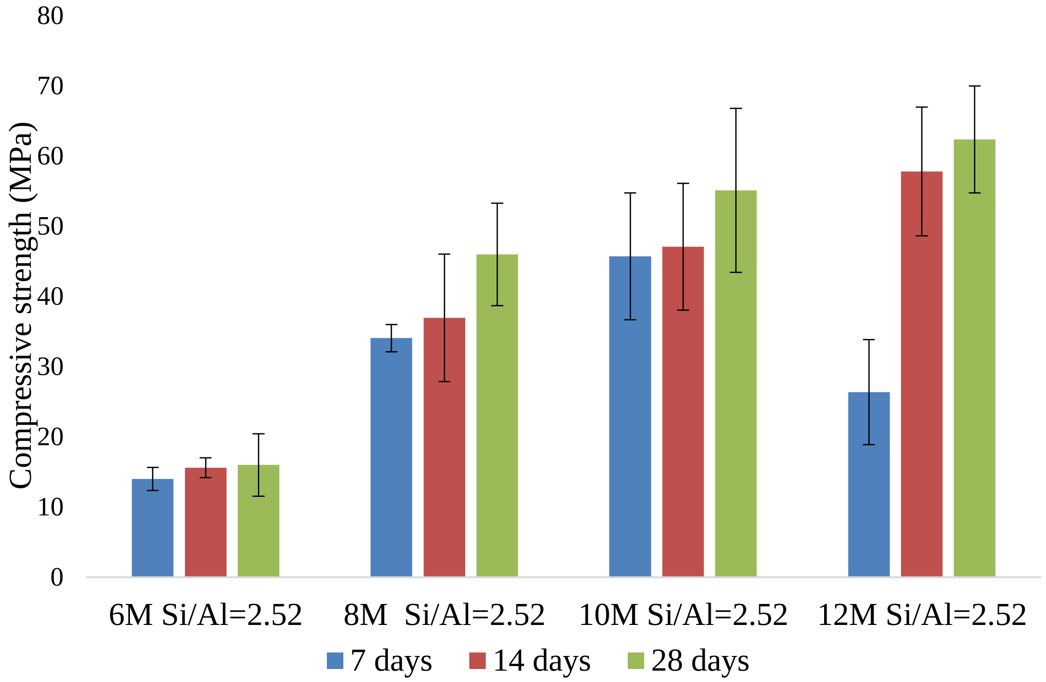


Figure 4.27 Effect of NaOH concentrations on PJ-GP in the compressive strengths

4.2.5.3. The effect of curing temperature and curing time on compressive strengths

NT-GP paste can form a hard structure within 24 h at room temperature. The NT-GP samples were divided into three groups for different curing temperature: first group, the geopolymer paste of the ratio of Si/Al = 1.49 with 8M NaOH was cast into the cubic mold at room temperature (RT) for 7, 14, and 28 days. Second and third groups, they were cast as the same condition as the first group, except the curing temperatures ,the geopolymers were wrapped with plastic film and kept in the oven at 40 and 60°C, respectively for 1 day then, kept at room temperature for 7, 14 and 28 days.

PJ-GP paste was cast with the ratio of Si/Al = 2.59 with 8M NaOH. They were classed to three groups for various curing temperature; first group, the geopolymer samples were cured at room temperature (RT) for 7, 14 and 28 days, second and third groups were cast and cured at 40 and 60°C, respectively in an oven for 1 day by covered plastic film then, left them at room temperature in closed container for 7, 14 and 28 days. Finally, they were tested compressive strength.

The compressive strength of NT-GP and PJ-GP results display that the elevated temperatures (40 and 60°C) deteriorated the compressive strength owing to the fast moisture evaporation. The loss of moisture during the geopolymerization will break down the gelular structure of geopolymer and generate dehydration and excessive shrinkage, however curing at room temperature is an advantage for strength development [9] as results in Figure 4.28 and 4.29.

Moreover, the curing time has an influence or strength development of NT-GP and PJ-GP samples. The enhancement of strength as the geopolymerization occurred slowly at room temperature thus, when curing time increased the strength was higher as shown in Figure 4.28-4.29. The NT-GP samples that were cured at 40°C shows the same results as the specimens cured at room temperature, which were higher compressive strength when the curing time increased. Whereas, NT-GP samples that were cured at 60°C bring about the reduction of compressive strength when increasing the curing time because an amount of moisture evaporation was higher than curing at 40°C.

PJ-GP samples that were cured at 40 and 60°C showed an increasing of the when the curing time increased in the same pattern as curing at room temperature. The different in curing temperature of NT-GP and PJ-GP at 60°C might be the quantity of liquid in the content was not equal: NT-GP had a higher amount of liquid than PJ-GP. Thus, the quantity of moisture in the geopolymer was not the same.

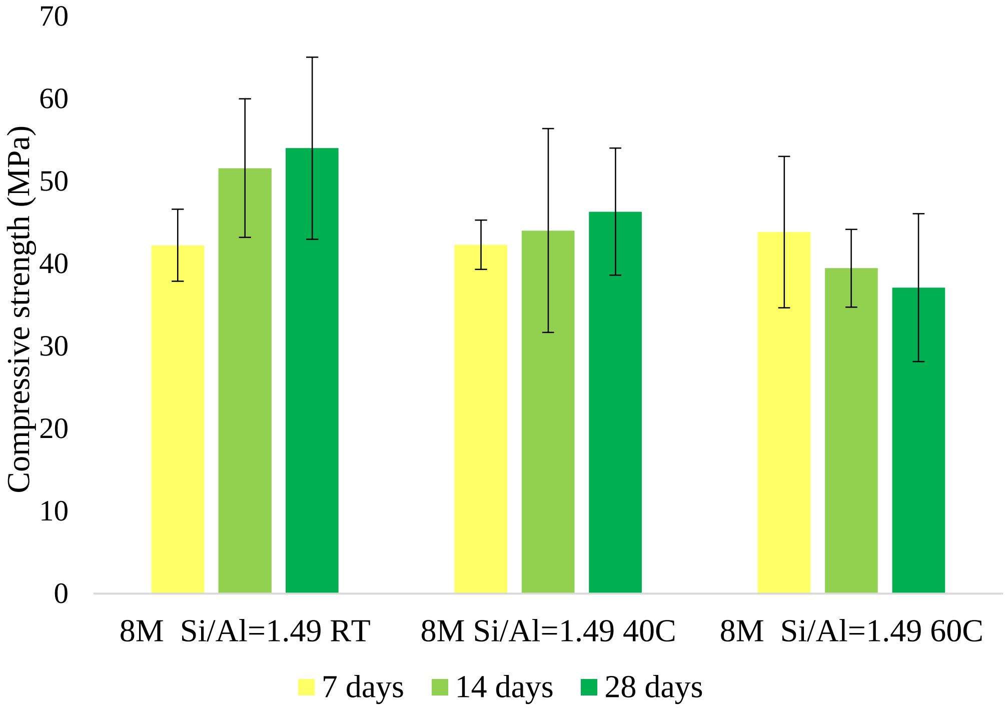


Figure 4.28 Influence of curing temperature on compressive strengths of NT-GP cured at room temperature and elevated temperatures (40 and 60°C)

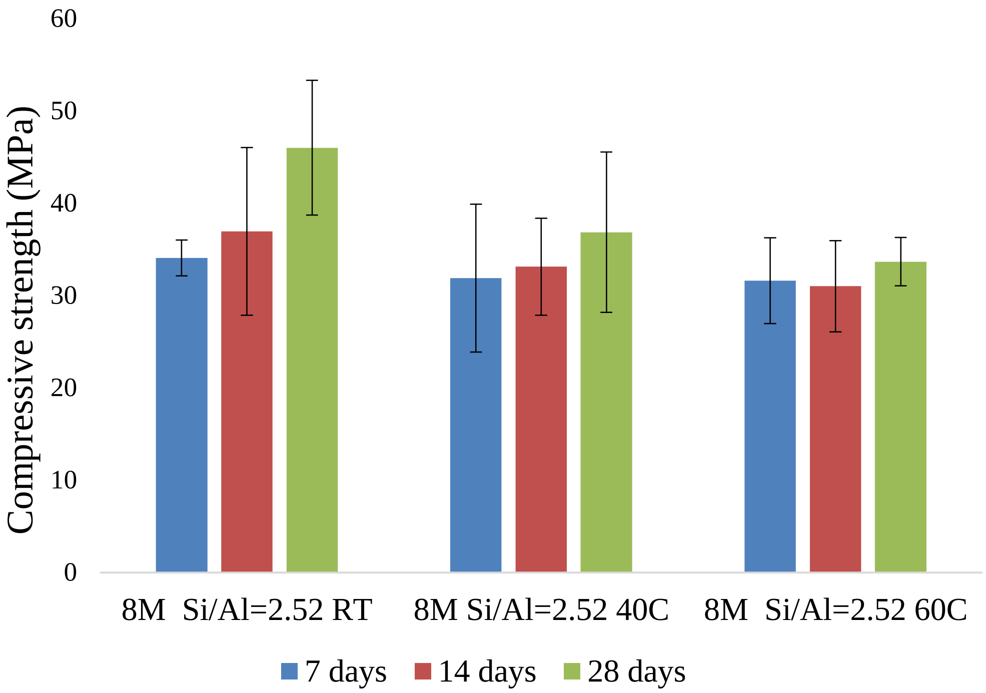


Figure 4.29 Influence of curing temperature on compressive strengths of PJ-GP cured at room temperature and elevated temperatures (40 and 60°C)

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

4.3.5.1. Conclusions

In this study focused on the synthesis geopolymers from local kaolin in Thailand as raw materials. From the experimental results and discussion of this study, the conclusion can be drawn as followings:

1. The Narathiwat and Prachin clays could be used as raw materials to synthesis metakaolin based geopolymers which had high compressive strength.

2. The IR spectra of all the NT-GP and PJ-GP samples showed the Si-Al of geopolymer bonds that were different from the raw materials (metakaolin).

3. The higher solid/liquid ratio affected to the compressive strength of geopolymer samples, since it gave the highest density. The lower solid/liquid ratio gave the higher porosity due to the ratio of liquid increasing which led to bubbles in geopolymer paste.

4. The concentration of NaOH had an influence on the compressive strength. When the increasing of NaOH concentration could improve the compressive strength, because the ability of dissolution of metakaolin particulates was higher than lower NaOH concentration so it will enhance the compressive strength.

5. The optimum curing temperature was a room temperature because it was not loss moisture rapidly which was the important factor of gelation in geopolymerization process.

6. The best curing time of geopolymer was 28 days, because the geopolymerization occurred slowly at the room temperature.

7. The maximum compressive strength of NT-GP (Si/Al=1.49) and PJ-GP (Si/Al=2.52) were 58 and 62 MPa, respectively.

4.4.5.2. Recommendations

1. Study the flowability of geopolymer in order to investigate the relation between flowability and compressive strength.

2. Other characterization, such as flowability test, bending test, thermal resistant etc. should be conducted.

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APPENDIX

VITA

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Acadamic Conference presentations

A.Anchaleerat, “Mechanical Properties of Metakaolin-based Geopolymer using Local Kaolin in Thailand”, International Conference on Traditional and Advanced Ceramics at Bitec, September, 2013, Bangkok Thailand

A.Anchaleerat, “Effects of Si/Al ratio on the mechanical properties of metakaolin-based geopolymer”, The Annual Conference on Engineering and Technology, October, 2014, Osaka Japan. (Proceeding)