

# PROCESSING AND PROPERTIES OF POLYMER FILLED GEOPOLYMER CERAMICS FABRICATED VIA POWDER METALLURGY METHOD: A REVIEW

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Received: February 15, 2015

**Abstract:** Inorganic alumino-silicates polymers, known as geopolymers, result from the reaction of mineral clays or other source materials rich in silica and alumina with alkali silicate solution at 40-80 °C. Pure geopolymers, exhibits relatively low mechanical properties, which limit their usage in structural applications. Thus, this restriction could be overcome through the formation of ceramic geopolymers and the addition of fillers to improve their strength and toughness. This paper summarizes important research findings on the current knowledge of geopolymer ceramic, the addition of fine filler materials, and outlines potential effects using thermoplastic fillers on the physical and mechanical properties of clay-based geopolymer ceramic.

## 1. INTRODUCTION

Inorganic aluminosilicates produced at low temperatures, also known as geopolymers, have potential applications as matrix in ceramics, coatings, cements, and other composite materials [1-4]. They are normally made by mixing materials that contain aluminosilicate, such as kaolin, metakaolin and fly ash, into alkaline solution and curing the mixture at a certain temperature [5]. Theoretically, any alkali and alkali earth cations can be used as the alkali component in this exothermic process such as geopolymerization. In addition, any material composed of alumina and silica can be alkali-activated. During the last decade, extensive research has been

conducted to study the development of inorganic geopolymers and to investigate their physical properties and mechanical properties. However, most of the studies were focused on the effect of sodium (Na<sup>+</sup>) and potassium (K<sup>+</sup>) ions as their alkali components [6,7].

Sintering is a key method for controlling the properties of ceramics and powder metallurgy [8]. Ceramic materials, which are produced by a combination of compacting and sintering, have become increasingly important in modern industry due to their excellent mechanical and physical properties. However, cracks and distortions have been recognized as the most significant concerns, and they often

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**Table 1.** Typical methods used to fabricate ceramic material. Reprinted with permission from M.N. Rahaman, *Ceramics Processing*, (CRC/Taylor & Francis, Boca Raton, 2007), © 2007, Taylor & Francis Group.

Initial Phase	Method	Product
Gases	Chemical vapor deposition	Films, monoliths
Gas – liquid	Directed metal oxidation	Monoliths
Gas – solid	Reaction bonding	Monoliths
Liquid – solid	Reaction bonding	Monoliths
Liquids	Sol-gel process	Films, fibers
	Polymer pyrolysis	Fibers, films
Solids (powder)	Melt casting	Monoliths
	Sintering of powder	Monoliths, films

limit the applications of the ceramics. Generally geopolymers are X-ray amorphous if cured at standard temperature [1,9]. However, a unique feature of geopolymers is that heating at high temperature converts them into a crystalline ceramic phase [9-12].

Geopolymers have advantage to be used in various fields because of their properties are better than those of ceramics and cement-based materials. Due to their excellent physical and mechanical properties, geopolymer ceramic composites are expected to emerge as a potential robust material that can meet the demanding requirements in various material applications. Therefore, our study focuses on the fabrication of advanced ceramics with low-cost production, short fabrication time, and environmental friendliness with the goal of expanding the application of this geopolymer technology. This paper provides a review of the current state of development of geopolymer ceramics and their properties.

## 2. RAW MATERIALS

Geopolymers have a wide range of properties and characteristics that depends on the raw materials used and the processing conditions. The characteristics of geopolymer includes high compressive strength, low shrinkage, fast or low setting, acid resistance, fire resistance, and low thermal conductivity. With these advantages, geopolymers are considered to be suitable for a broad range of engineering materials applications [13,14-17]. In order to produce geopolymers, highly alkaline solutes, such as NaOH and KOH, are added to the source materials that are rich in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Geopolymers have been used extensively as alkaline activators [18], with the mass ratio of activator liquid to the source material in the range of 0.25-0.30 [18,19].

The strength of geopolymers depends on the nature of the source materials. Geopolymers that

are synthesized using calcined source materials, e.g., fly ash, slag, and metakaolin, have higher compressive strength than those synthesized using non-calcined materials, such as kaolinite, and naturally-occurring minerals [6,20,21]. Many studies have focused on the use of metakaolin [9,12,22] because of its higher reactivity, which contributes to optimal performance, slightly than the less reactive of kaolin [23]. Furthermore, the use of metakaolin instead of other materials has been found to produce more homogeneous geopolymers [24]. Thus, there is a lack of study on green polymeric composites by using kaolin. In the development of geopolymer ceramic, kaolin is a potential material to be used since it can be calcined at high temperature.

## 3. PROCESSING

Several methods are available for fabricating ceramic materials, and the fabrication method is very important since it can affect the mechanical strength and relative density of the product. Depending on the initial material used, the main methods for fabricating ceramic materials can be classified as in gaseous phase, liquid phase or solid phase fabrication as in Table 1. Although some ceramics are fabricated using melt casting or vapor processing, most ceramics are fabricated via powder metallurgy (PM) method.

The increasing usage of PM method has the potential for making an almost infinite variety of materials and products, and this places greater significance on the appropriate utilization of experimental techniques. In general, the PM method consists of a few main steps, i.e., production of a controlled blend of powders, pressing the powders in suitable dies, and subsequently heating (sintering) the compacted powder in a controlled atmosphere and temperature to obtain the required density and strength [26,27]. By compressing and sintering, the powder

metallurgy technique can provide the desired final shape and dimension of parts. As a result, most ceramic materials are prepared by powder metallurgy techniques by the method of applying stresses on the powder's precursor [28]. In addition, this method is preferred because it produces a uniform distribution of the particles and reduces degradation due to the low processing temperature [29,30].

Xie *et al.* [24] studied the mechanical properties of leucite ceramic derived from a geopolymer where leucite ceramic was fabricated by grinding the geopolymer to a powder, followed by drying, isotactic pressing, and sintering. Peigang *et al.* [22] developed a leucite ceramic using a different fabrication method compared to Xie *et al.*, [24] study. In their study, a leucite ceramic disk was developed by sintering the geopolymer without first grinding it into a powder. The relative density was 93% after it was soaked at 1000 °C for 2 h. They prepared the geopolymer by mixing metakaolin with potassium silicate solution. After curing the geopolymer at 70 °C for 48 h, the geopolymer samples were sintered at different temperatures. In result, substantial amount of leucite was formed at a temperature of 800 °C.

In another study by Peigang and Dechang [31], the crystallization, sintering and thermal expansion behaviors of a synthetic-metakaolin, cesium-based geopolymer were investigated. A Cs-based geopolymer with the composition (mole ratios) of  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 4$ ,  $\text{Cs}_2\text{O}/\text{Al}_2\text{O}_3 = 0.9$ , and  $\text{H}_2\text{O}/\text{Cs}_2\text{O} = 11$  was obtained by mixing synthetic metakaolin with an alkaline silicate solution and curing the mixture at 50 °C for 48 h. The amorphous Cs-geopolymer completely crystallized into pollucite on heating at 1200 °C for 2 h. Jonathan *et al.* [32] also proved that it was possible to produce pollucite ceramic from the natural metakaolin-based geopolymer in the formation of pollucite ( $\text{Cs}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ ). A geopolymer that consist of a mixture of metakaolin and cesium silicate solution were prepared using an IKA overhead mixer. Then the resultant slurry was cured at 50 °C for 24 h. The pollucite crystallization occurred gradually during heating at temperatures in the range of 900 - 1250 °C.

Barbosa and MacKenzie [20] reported that sodium polysialate polymers of suitable composition for optimum curing are remarkably thermal stable. This geopolymer loses the water of hydration in an endothermic reaction at 100 - 200 °C accompanied by a small degree of shrinkage. Hence, the polymer becomes dimensionally stable at high temperature. Sintering could potentially induce cracking, which can be minimized by the addition of a small

amount of glycerol, which acts as a plasticizer. In addition, He *et al.*, [4] used the ultrasonic vibration technique in order to produce geopolymer composites. Unidirectional carbon fibers were used as reinforcement in the geopolymer matrix. A geopolymer resin was obtained by mixing metakaolin powder with a potassium silicate solution with the molar ratios of  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3$ ,  $\text{K}_2\text{O}/\text{SiO}_2 = 0.33$ , and  $\text{H}_2\text{O}/\text{K}_2\text{O} = 11$ . Then, the composite samples were heated in the temperature range of 1000 to 1400 °C.

The mechanical properties and microstructure of metakaolin-based geopolymer mortar samples were investigated by Kuenzel *et al.* [33]. To enhance the mechanical properties, fine silica sand was added as filler particles. The activating solution was formed by mixing a sodium silicate solution, water and NaOH for 24 h. With the geopolymer to sand ratio of 50:50, the alkaline solution was mixed into the metakaolin and sand using a planetary mixer for 3 min. After casting in plastic moulds, the samples were cured and heated. Nair *et al.* [34] studied the compressive strength, microstructure, and the stability of the geopolymer matrix materials under hydrothermal exposure conditions in order to create polymer-based ceramic matrix composites (CMCs) that would be stable under hydrothermal oxidizing conditions.

## 4. PROPERTIES OF GEOPOLYMER CERAMICS

### 4.1. Chemical composition

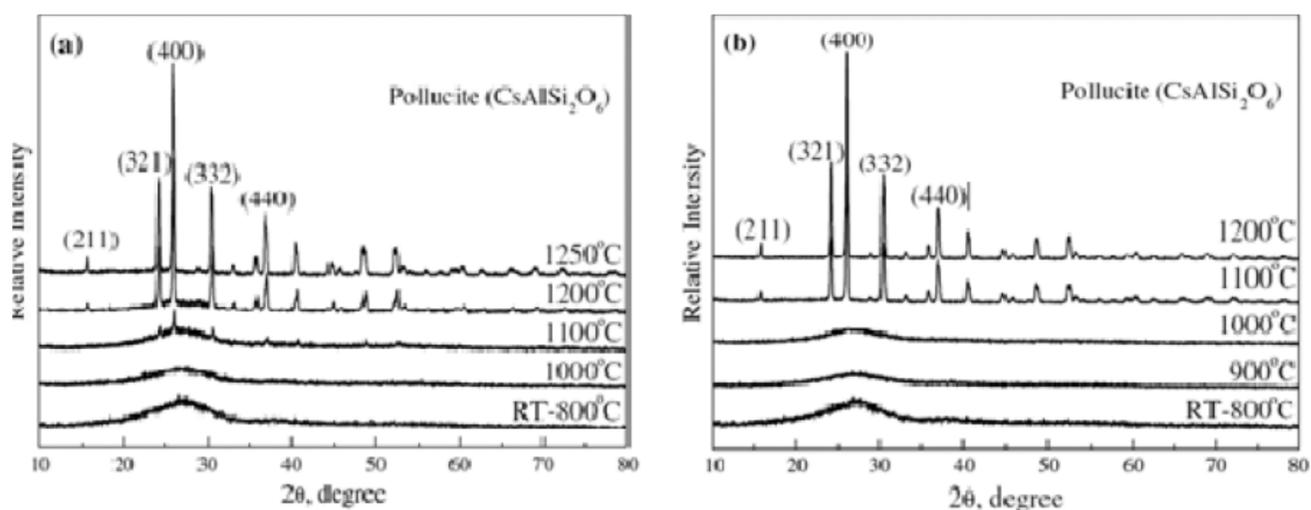
Table 2 provides the general chemical compositions of the raw materials of kaolin obtained by X-Ray fluorescence (XRF). The data indicate that  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  were the major components determined by researchers who used different sources.

### 4.2. Phase formation

Phases were characterized by using X-ray diffractometer (XRD) after the geopolymer samples were heated at different temperatures. Fig. 1 shows the XRD patterns for the geopolymer samples treated at various temperatures without soaking and with soaking for 2 h [31]. The geopolymer samples that were treated below 1000 °C were amorphous. However, after the samples were heated at 1100 °C for 2 h, they had significantly larger amounts of pollucite than that formed without soaking. In another study, Bell *et al.* [9,32] reported that the major reflection for leucite first appeared from the geopolymer ( $\text{K}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 11\text{H}_2\text{O}$ ) upon heating at 1050 °C.

**Table 2.** Chemical composition of raw materials for geopolymer ceramics.

Chemical	Component (wt.%)		
	Metakaolin [4]	Metakaolin [35]	Kaolin [20]
SiO <sub>2</sub>	54.64	51.46	44.40
Al <sub>2</sub> O <sub>3</sub>	42.53	41.71	39.80
Fe <sub>2</sub> O <sub>3</sub>	0.97	2.66	0.30
TiO <sub>2</sub>	0.80	0.95	0.11
CaO	0.12	0.10	<0.01
K <sub>2</sub> O	0.48	0.70	0.33
Na <sub>2</sub> O	-	0.39	0.04
P <sub>2</sub> O <sub>5</sub>	0.16	-	-

**Fig. 1.** XRD results of Cs-based geopolymer after being treated at different temperature: (a) without soaking and (b) with soaking for 2 h. Reprinted with permission from H. Peigang and J. Dechang // J. Mater. Sci. 48 (2013) 1812, © 2013 Springer.

A broad amorphous hump appeared at above 1200 °C and the samples were partially melted [4].

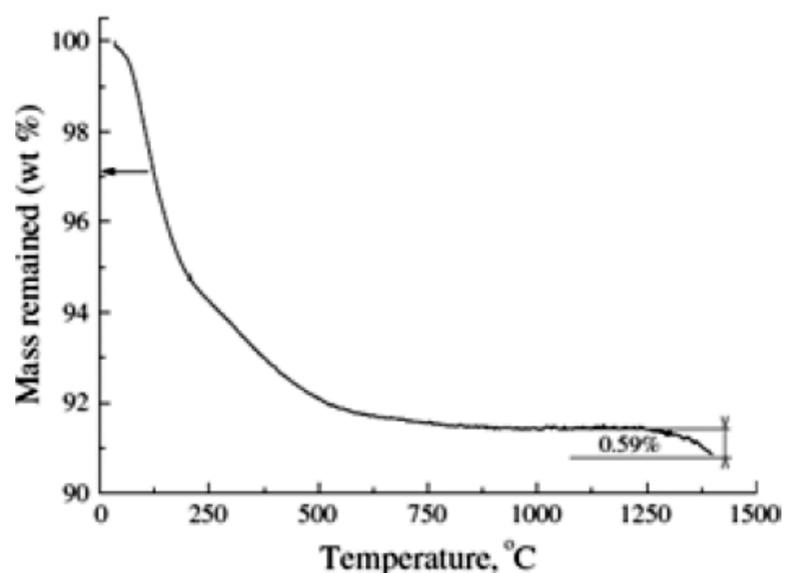
### 4.3. Thermal properties

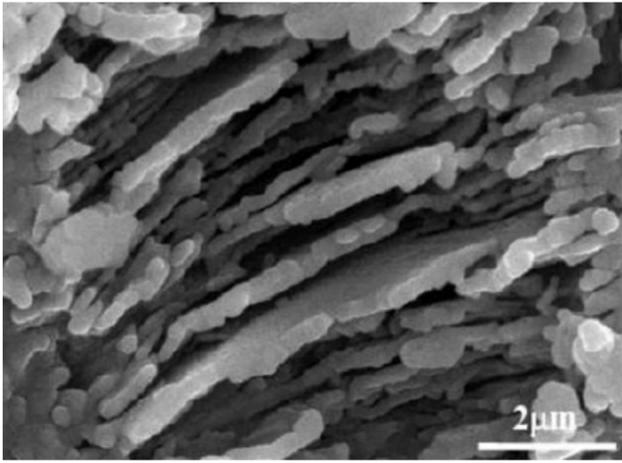
Thermal gravimetric analysis (TGA) was conducted to measure the weight change in the geopolymer samples accurately, either as a function of increasing temperature or isothermally as a function of time. Powder specimens were used to ensure the thermal equilibrium was achieved [36]. The thermal gravimetric results of Peigang *et al.* [31] are shown in Fig. 2. The dehydroxylation between the T and the OH groups (T= Al, Si) resulted in a weight loss of 8.44%, and the evaporation of free water was assumed to have contributed to the total weight loss of 9.03%. The weight remained unchanged until the temperature reached 1250 °C, after which additional weight loss occurred. The researchers concluded that the sintering temperature should not exceed 1250 °C to avoid the volatilization of cesium.

### 4.4. Microstructure observation

Fig. 3 shows the morphological features of the pure metakaolin [22]. The metakaolin particles are plate-

shaped, and the thickness of each plate is approximately 200 nm. Fig. 4 shows the typical microstructure with no heat treatment and after heat treatment at 1200 °C for 3 h by Peigang *et al.* [12]. According to their study of cesium-substituted potassium-based geopolymer ceramics, the SEM image for the unheated geopolymer ceramics still contained unreacted or partially-reacted metakaolin. Signifi-

**Fig. 2.** TG curves of the Cs-based geopolymer. Reprinted with permission from H. Peigang and J. Dechang // J. Mater. Sci. 48 (2013) 1812, © 2013 Springer.



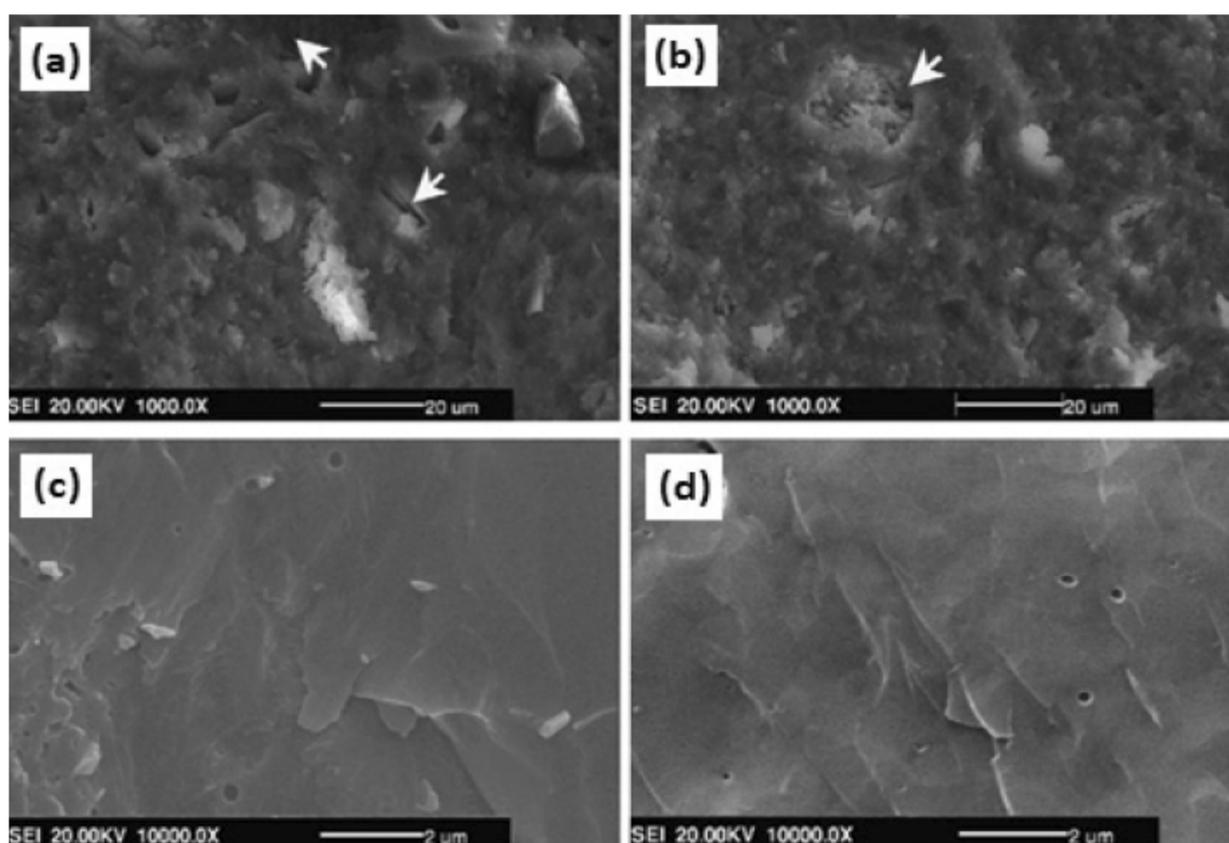
**Fig. 3.** Microstructure of pure metakaolin. Reprinted with permission from H. Peigang, J. Dechang, and W. Shengjin // J. Euro. Ceram. Soc. 33 (2013) 689, © 2013 Elsevier.

cant differences between the geopolymer with and without cesium substitution were observed. After being heated to 1200 °C, both geopolymers developed a smooth and glassy texture. The amorphousness of some of the elements in the metakaolin was almost transformed to the crystalline phase, and the surface became smoother. In the study in which by Peigang *et al.* [4] investigated unidirectional carbon fiber reinforced geopolymer composites, they discovered that many oval cracks formed after the geopolymer composites were heated. This occurred because of the extensive shrinkage caused by viscous sintering at a high temperature. These cracks would undoubtedly decrease the mechanical properties of the geopolymer ceramic composites.

#### 4.5. Mechanical strength

The increase in the mechanical strength was attributed to the sintering and crystallization of the geopolymer's precursor. In a study of the effect of heat treatment on the unidirectional carbon fiber reinforced geopolymer composites [4], the mechanical properties were improved significantly over a wide range of temperatures from 1000 to 1300 °C. Flexural strength, work of fracture and Young's modulus achieved to their peak values at 234.2 MPa, 4445.7 Jm<sup>-2</sup> and 63.8 GPa, respectively. The researchers reported that the improved mechanical properties contributed to the densification of the matrix, the formation of leucite, and the proper bonding strength of the carbon fiber interface. The addition of filler also can influence the strength of the geopolymer samples, and the strength is increased when finer fillers are used [37]. Xie *et al.* [24] studied the mechanical properties of leucite ceramic derived from the geopolymer, and a much higher flexural strength of 139.6 MPa was obtained. The geopolymer was ground into powder, pressed and heated at high temperature, in order to avoid cracking during heating.

Heat treatment has a significant impact on the mechanical strength of geopolymer ceramics. Water evaporates during heating. However, the rate of evaporation is considered low because of the existence of small porosity in micro size. Increasing the temperature of the geopolymer samples increased the internal pressure due to the expanding water



**Fig. 4.** Microstructure of (K<sub>1-x</sub>Cs<sub>x</sub>) geopolymer before and after heat treatment at 1200 °C for 3 h: (a), (c) x = 0, (b), (d) x = 0.3. (The white arrows point out the partially-reacted metakaolin). Reprinted with permission from H. Peigang, J. Dechang, W. Meirong and Z. Yu // Ceram. Int. 36 (2010) 2395, © 2010 Elsevier.

vapour. This pressure caused cracking and affected the flexural strength. Most of the water can be removed by controlling the drying temperature to reduce the cracks [38]. The width of the cracks in the geopolymer phase decreases as the particle size of the filler material decreases, and the cracks tended to heal during sintering.

## 5. CONCLUSIONS

Geopolymer ceramics show significant potential as a viable material for various usage since they are both environmental friendly and possess excellent mechanical properties. In this paper, the processing and properties of geopolymer ceramics and geopolymer ceramic composites were reviewed. Significant information are available and concluded in the review to fabricate geopolymer ceramic composites. Although extensive research has already been conducted, the development of clay geopolymer ceramics has yet to be explored. Several improvements remain to be researched and applied to enhance geopolymer ceramic materials.

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