Original Article

Synergistic effects of processing and nanofiber reinforcement on the mechanical and ferroelectric performance of geopolymer matrix composites

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A B S T R A C T

This study involved the evaluation of mechanical and ferroelectric properties of a new class of nanofiller infused inorganic polymer (geopolymer, GP). To evaluate the mechanical performance, compressive strength and fracture resistance of neat and nanofillers infused GP were studied at various treatment temperatures. It was found that, addition of 5 vol% alumina nanofiber (ANF), increased compressive strength and modulus by over 30% and 60%, respectively, while it increased fracture toughness (KIC) by over 60% compared to the baseline specimens. Simultaneously, ferroelectric properties were investigated at various treatment temperatures (250 °C, 650 °C and 870 °C). Remarkably, higher ferroelectric hysteresis was observed with the GP treated at 870 °C and remnant polarization increased with the addition of alumina nanofiber. Scanning Electron Microscopy confirmed that neat materials are composed of particles embedded into the poly-condensed matrix, while particle nature existed until the treatment temperature reached above 870 °C. X-ray diffraction analysis suggests that, baseline geopolymer started becoming crystalline while the particle nature gradually disappeared with heating at or beyond 870 °C. The bonding between the polymer and alumina nanofiber tends to be stronger with increasing treatment temperature. The increase in KIC with the addition of 2 vol% and 5 vol% alumina nanofibers (ANF) is due to homogeneous dispersion of high interfacial strength nanofillers, which essentially create strong crack bridging and crack deflection effect. The increase in ferroelectric hysteresis is potentially due to the formation of hierarchical order and domain reorientation of the materials.

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1. Introduction

Geopolymers are new materials with excellent fire- and heat-resistant properties. The properties and uses of geopolymers are being explored in many scientific and industrial disciplines and engineering process technologies. Various studies have been performed to investigate the performance of geopolymer as the high temperature coatings [3] and the replacement...
of ordinary port-land cements [2]. However, minimum efforts have been made to establish these materials as the matrix of a continuous fiber reinforced composites. This effort has attempted to focus some mechanical and electrical properties as demanded by high temperature continuous fiber reinforced composites.

Conventional ceramic matrix composites require high temperature powder processing, which usually causes lack in wetting and interfacial reactions between constituent materials [3]. Inorganic materials derived geopolymer offer the potential to bridge between mechanical performances as a matrix material for high temperature capable fiber reinforced composites. Simultaneously it has potential to possess dielectric and ferroelectric behaviors upon certain processing and treatment conditions. This polymer can be readily processed at low temperature with similar technique as organic polymers but can be applicable above the upper use temperatures of conventional polymers [4]. Unfortunately, low toughness and high shrinkage often limit the mechanical performance of this material and restricts it from electronics applications. Previous publications have suggested that process optimization have the potential to improve compressive strength and modulus [5]. However, processing itself does not have enough potential to increase fracture toughness and bending strength. Nanofillers reinforcement has proven to increase the toughness of conventional polymer and monolithic ceramic materials [6–8]. Only few literature [9–11] suggested the improvement in toughness of geopolymer with nano-reinforcement.

Nanofillers in the conventional ceramic materials suffer from thermal degradation and mechanical distortion, which impedes the expected improvement in mechanical performance. Low temperature processing of inorganic polymer with nano-reinforcement can overcome this problem and are therefore expected to improve mechanical performance, especially the fracture toughness. Alumina nanofibers (ANF) have superior tensile strength and thermal stability than conventional fillers of organic polymer composites. Due to inorganic frame work, ANF also disperses well into geopolymer. Therefore, ANF can be potentially applied in order to toughen geopolymer.

High temperature capable ferroelectric materials have potential to the energy storage devices. As previously reported [12], several high temperature capable materials have shown their ferroelectric characteristics at various temperatures. The ferroelectric (polarization-electric field) hysteresis, is a defining property of ferroelectric materials [13]. It has been studied intensively due to the potential applications of ferroelectric thin films in nonvolatile memories [14]. The switching of polarization at high electric field is the main idea behind the applications of this type. The value of the switchable polarization (the difference between the positive and negative remnant polarization, \( PR - (-PR) \)) can be analyzed from the hysteresis. But, the switching characteristics are still not well agreed as the switching depends on the nature of the ferroelectric material itself, types of electrodes used, thickness of the ferroelectric, temperature, field profile, number of field cycles, and many other parameters [14–17]. However, the isolation of dielectric constant is necessary to isolate from the ferroelectric behavior if there is any dielectric properties existent. This can be measured by dielectric loss calculation. Many researchers have found that [18–20] an ideal dielectric material should have homogeneous and constant dielectric constant at the applicable frequency range. Most of the reported materials are crystalline in nature and therefore the extent of ferroelectricity was not necessarily investigated in the amorphous state. The current study highlighted the nature of polarization transformation with the transformation from amorphous to crystalline state. Investigating the polarization versus electric field (\( P-E \)) of a ferroelectric material yields a hysteresis loop, which allows us to estimate the remnant polarization (\( P_r \)) and coercive field (\( E_c \)). The polarization behavior and the coercive field of the consequent ferroelectric material vary with the applied voltage frequency.

High temperature treatment [12] and nano-reinforcement [21] are suggested to result in transformation to crystalline phases which possess the property of ferroelectricity at the high temperatures. Investigating mechanical as well as ferroelectric properties therefore explores the potential to use this material in high temperature energy storage devices. The current investigation is therefore focused on understanding the underlying processing and toughening mechanism of inorganic polymer through the knowledge developed from some advanced techniques such as phase transformation and ferroelectric hysteresis.

In the current investigation, a systematic study has been performed on this new class of geopolymer to investigate how the changes in compressive strength and fracture toughness with the heat treatment is related to the changes in ferroelectric property, such as hysteresis loop from the viewpoint of domain reorientation. The current investigation explores the scope of annealing of the material at a reasonably high temperature with and without nano-reinforcement on the ferroelectric phase transformation. The synergy between the heat treatment and nanofiller reinforcement were investigated throughout this study. The ferroelectric properties arising from domain reorientation are related to nanoparticles infusion. The electric displacement (polarization) versus electric field (\( P-E \)) hysteresis loops of neat and nano-reinforced geopolymer were studied at 500 Hz frequency. The mechanism of fracture resistance of nano-reinforced geopolymer has also been explored through this study.

2. **Experimental**

2.1. **Materials**

Base material of this investigation is MEYEB, which is a polysialate geopolymer in a suspension form containing various chemicals including potassium silicate, aluminum oxide, silicon dioxide, aluminum phosphate and water. These chemicals are mixed up in the proprietary proportions of Si/Al, K₂O/SiO₂ and H₂O/K₂O, which take place in the poly-condensation reaction during cure process. Nanofillers of this investigation are alumina nanofiber (ANF) and alumina nanoparticle (ANP), which are supplied by ANF technology (Estonia). Chemical configuration and hydrophilic nature of these nanomaterials allow them to disperse well into inorganic polymer, geopolymor in a large volume fraction.
2.2. Sample preparation

Pre-weighed nanomaterials were separately mixed in the geopolymer (GP) suspension using a slow shear mixing in a planetary ball mill. For compression testing samples, neat and nanofillers mixed GP suspensions were first poured into a customized tubular acetal resin molds with a nominal inside diameter of 6 mm and length of 20 mm. These molds were closed on both ends with vinyl caps and sealed with PTFE tape. To further ensure moisture retention, the molds were sealed in polyethylene (PE) bagging with atmospheric pressure inside. The molds were kept vertical in order for any bubbles to freely escape from the liquid state. To accomplish the initial cure, the samples were then heated at 1°C/min to 65°C, then at 0.5°C/min from 65°C to 80°C, and then held at 80°C for 24 h in the sealed environment. At the end of initial cure the samples were removed from the mold and dried in air at 80°C for 10 h. Additional drying at temperatures stepping up to 250°C is detailed in Table 1. Post heat treatment of the materials, which is a requirement for de-hydroxylation, is performed for 5 h at a constant annealing temperature of 650°C. After this post heat treatment, the sample was fully annealed in a furnace.

Samples for measuring fracture toughness and ferroelectric hysteresis were prepared using acetal resin mold with rectangular slots. These samples were prepared using the similar technique as for the cylindrical samples. For the purpose of measuring both mechanical and electrical properties various GP samples were prepared with no nanofillers, ANF and ANP with various volume fractions. Also, in order to evaluate the effect of temperatures on those properties, samples were separately treated at various temperature conditions, which are shown in Table 2. The samples were annealed after the subsequent heat treatment.

2.3. Characterization

2.3.1. Compression strength measurement

Compression strength was measured, as these are relatively insensitive to small cracks and flaws that would negatively affect the measured tensile strength, but are representative of the intrinsic binding strength of the material. Compression strength was measured using an Applied Test Systems, Inc. screw driven load frame. The tests were performed by placing the samples (with average length and diameter of 17 and 6 mm, respectively) in an aluminum compression cage and applying a crosshead loading rate of 0.5 mm/min. The strength was determined from the measured failure load. The test parameters were adjusted according to ASTM C 1424 standard [22]. At least five samples were tested for finding compressive strengths of neat and nanofilled type geopolymers processed through each set of processing and treatment schedule as specified in Table 2.

2.3.2. Fracture toughness testing

Mode-I fracture toughness was calculated from the fracture forces, test specimen dimension and the notch size of the specimen which underwent single edge V-notch bend beam (SENVB) test technique. This test was performed using Instron C1102 on a 3 point bend fixture with a span length S0 = 30 mm and test speed of 0.5 mm/min, under ASTM C1421-10 [23]. The dimension of the overall notched specimen is presented in Fig. 1.

According to this standard, the mode-I fracture toughness (KIC) was calculated, using the following equation:

\[
K_{IC} = g \left[ \frac{P_{\text{max}} S_0 10^{-6}}{b w^{1.5}} \right] \left[ \frac{3(a/w)^{0.5}}{2(1-a/w)^{1.5}} \right]
\]

where, \(P_{\text{max}}\) = maximum force, N; \(S_0\) = span length; \(a\) = crack length; \(b\) = width of the specimen; \(w\) = depth of the specimen and \(g\) is a geometry dependent polynomial. Typical span length, width and depth of the specimens for this test (see Fig. 1) are 30, 4.5 and 4 mm, respectively.

2.3.3. Ferroelectric hysteresis measurement

For the ferroelectric behavior of the geopolymer matrix under electric field, a Polarization-Electric Field P-E measurements were carried out using a modified Sawyer-Tower bridge.
configuration. A customized specimen holding apparatus was built [24,25]. The specimen is placed between two high-purity alumina spacers. A TREK high-voltage amplifier model 30/20 was used as the electric field supply. The specimen is immersed in a silicon oil bath to prevent electric arcing. Thin copper strips are placed between the electrode of the specimen and the alumina spacing. The TREK power amplifier, which provides precise control of output voltages in the range of 0 to ±30 kV, applies the electric field through the top thin copper. A 10 µF capacitor is connected to the bottom thin copper and the ground. A Keithley 6514 electrometer with the same polarity is connected to the capacitor to measure the voltage of the capacitor. The longitudinal displacement is measured by an MTI-2000 Photonic sensor from MTI Instruments, Inc. All data are recorded and collected through LabView. This electric loading system is settled on a VIBRAPLANE Model 9100/9200 Vibration Isolation Table from Kinetic System, Inc, which absorbs the vibration in the tests to ensure the accuracy of the data. The tests were performed under electric field loading, for about 10–30 cycles in the range of ±20 kV/cm at room temperature. After the initial cycle, the hysteresis loops of electric field vs. electric displacement become stabilized and repeatable. At frequency of 500 Hz measurement for the electric field sweep, a minimum of three specimens were tested and compared, to insure accuracy of the experiments.

2.3.4. Microstructure evaluation
In order to understand the microstructural variations at different stages of heat treatment, SEM analysis was performed on the fracture surfaces using JEOL JSM-6500 Field emission Scanning Electron Microscope (FE-SEM). Fracture surfaces of the specimens were coated in gold (10 nm thick) using a Hummer VII ion beam sputter coater to enable imaging. To obtain high-resolution images (less than 1 µm), a beam energy of 15 kV was applied on the samples (around 2 mm thick) inside the vacuum chamber which was maintained at 9.63 × 10⁻⁵ Torr.

2.3.5. Phase transformation evaluation
X-ray diffractogram (XRD) study was performed to investigate the materials phases and their transformation with temperature. The X-ray diffractogram was measured separately on GP treated at 250 °C, 650 °C (O₂) and 870 °C (O₃) using Scintag X-2 X-ray powder diffractometer. All the samples were crushed separately to make fine powder. The 0.1542 nm wavelength CuKα radiation was used in this experiment to measure the intensity peaks of samples in a stationary sample stage in the range of 5–85 deg with a step size of 0.02 deg.

3. Results and discussion

3.1. Extended temperature response to compression strength
The purpose of studying compressive strength is to measure the strength and degree of bonding at various treatment temperatures under compression, since this material is weak in tension. Fig. 2 presents the compressive strengths of neat GP heat treated at processing and extended treatment temperatures. It is seen that compressive strength gradually increased up to 760 °C and then decreased at 870 °C. With the increase in temperature from 80 to 760 °C, the increase in compressive strength is almost 100%. The results indicate that extended temperature heat treatment made the geopolymer stronger which resulted in the further improvement in the compressive strength. However, beyond 870 °C this geopolymer is no longer strong, which is seen from the drop in compressive strength. The drop in compressive strength has been suggested by the formation of crystalline structure and reduction in particle reinforcement [9,26].

Fig. 1 – Notch geometry on a 30 mm span bend beam specimen: (a) overall view and (b) expanded view of the notch in (a).

Fig. 2 – Effect of temperature on compressive strength.
3.2. Understanding the phase and morphology of the polymer

The purpose of phase transformation study is to understand the crystallinity and its potential effect on the mechanical properties and ferroelectric hysteresis. Fig. 3 represents X-ray diffraction of GP treated at various temperatures. With the processing at 80 °C an amorphous phase is formed, which is shown in Fig. 3(a). The amorphous nature exists until the processing temperature exceeded 650 °C, which is found from Fig. 3(b). With the processing at 870 °C GP presented 3 peaks representative of crystalline phases at around 24, 29 and 36 deg respectively, among which, the one at 24 deg is prominent. These peaks indicate the formation of zeolite phases in GP at higher temperature [27] and amorphous to crystalline transformation near at 770–870 °C.

Geopolymers are generally X-ray amorphous or semi crystalline materials with less ordered structures [28] which gradually reach to the stability with the sacrifice in mechanical strength [29]. The amorphous nature of geopolymer persists while cured at temperatures less than 80 °C, however the crystalline phase is found upon heating and annealing, which depends on the temperature. At high temperature, geopolymer structure becomes more ordered and reveals some phases which correspond to zeolite [27]. Those studies have suggested that at the treatment temperature at around 1000 °C, those highly ordered crystalline structure can be formed. Amorphous-to-Crystalline phase transformation may be related to the drop in mechanical strength. However, this transformation has some potential benefits in increasing the ferroelectric properties which is explained with the investigation of ferroelectric hysteresis.

3.3. SEM investigations of neat and nano-reinforced inorganic polymer

The purpose of microstructure evaluation is to understand the temperature dependent microstructural variation in GP and correlate the transformation with mechanical and electrical properties. Fig. 4 is the presentation of the microstructure of specimens at various stages of processing (80 °C and 650 °C) and post treatment at 870 °C. According to the microstructure, the fracture surface of 80 °C cured specimen can be described as the particles of un-reacted materials distributed over the poly-condensed network of GP matrix [4]. It appears that the particles are bonded to each other on the surface. The average sizes of the un-reacted particles are in the range of 0.45 ± 0.2 μm. From Fig. 4(a) and (b) it is found that sample treated at both 80 °C and 250 °C contain-inter-particle porosities, however, higher pore densities are found in the sample treated at 80 °C. This suggests weak particle to particle bonding and incomplete polycondensation reaction at 80 °C. While neat GP is processed at 250 °C particles became more interconnected to each other with more poly-condensed structure. The poly-condensed structure in the 250 °C treated sample (see Fig. 4(b)) is approximately 20–30 vol%, which is higher compared to the sample cured at 80 °C (see Fig. 4(a)). The changes in morphology suggests that within 80–250 °C temperature range more ions are dissolved into liquid and creates more geopolymer network until the unreacted liquid is dried out [4]. It is also suggested that the polycondensation reaction does not complete at 80 °C rather it completes at elevated temperature.

With the successive treatment at 650 °C and 870 °C the particle nature of GP was reduced and more homogeneous structure was appeared, which is found in Fig. 4(c) and (d). This suggests thermal diffusion of particles into the poly-condensed network. Both particles and the poly-condensed structure contain similar chemical configuration, which favors this high temperature diffusion. Un-reacted particles are expected to work as reinforcement in the geopolymer and therefore to retain its mechanical strength [9]. Since there is no particle nature at 870 °C, geopolymer at this temperature behaves like a weak monolithic sintered material. Fig. 5 presents the poly-condensed and coalesced structures with temperature. It is found that at 870 °C approximately 90% of the total area is coalesced. This evidence therefore verifies the drop in compressive strength as seen in previous section.

3.4. Fracture toughness response with alumina nanofiber reinforcement

The purpose of fracture toughness (KIC) measurement is to understand the crack propagation resistance in the neat GP and GP with alumina nanofillers at various proportions and treatment temperatures. Fig. 6 presents fracture toughness response of neat GP and nanofiber reinforced GP at various treatment temperatures. With the changes in treatment...
temperature from 80 °C to 250 °C fracture toughness did not increase in neat GP, but with 2 vol% ANF and 2 vol% ANP fracture toughness increased by ~136% and ~25%. ANF is more effective in toughening than ANP due to high aspect ratio. High aspect ratio nanofillers act as the medium for crack bridging and crack deflection [30,31]. While treated at 650 °C, with 2 vol% ANF and 2 vol% ANP toughness increased only ~20% and 12%. While treated at 760 °C fracture toughness of neat GP increased to the maximum level, however, with 2 vol% ANF and ANP reinforcement fracture toughness reduced by ~33 and ~44%, respectively. 5 vol% ANF resulted in the proportional increase in fracture toughness at 250 °C in proportion
to 2% ANF. With the addition of 2 vol% and 5 vol% ANF fracture toughness of GP increased by 28.5 and 57%, respectively. At 650 °C the toughness contribution of ANF and ANP dropped down than at 250 °C. At 760 °C both ANF and ANP contribution to toughness was negative. The reduction in the effectiveness at high temperature is attributed to the structural instability of nanofillers due to thermal diffusion into the matrix with similar chemical configurations. More evidence on the diffusion is explained using the SEM images as shown in Fig. 7.

Fig. 7 presents fractured surfaces of 2 vol% ANF reinforced GP at two different temperatures (250 °C and 650 °C). From Fig. 7 it is found that ANFs created bridging in 2 vol% ANF reinforced GP treated at 250 °C. Similar bridging is not found in ANF reinforced samples treated at 650 °C (Fig. 7(b)). Only few traces of ANFs were found in the GP matrix. In the samples treated at 250 °C, the bridging of ANF is observed along the cracks of GP with less than 0.3 μm pull out length, which can be found from Fig. 7(c).

Due to similarities in structural and chemical configurations, at high temperature both ANF and ANP diffuses into GP and loses their structural integrity. The reason behind this diffusion is that the diameter of nanometer scale ANF is equivalent to only few molecules of alumina with higher surface area-to-volume ratio and higher porosity in comparison to bulk alumina [32]. This thermal diffusion negatively affects the mechanical performance. With the subsequent heat treatment, it is essential to understand the effect of amorphous and crystalline phases of neat GP followed by alumina nanofillers on the ferroelectric properties.

3.5. Ferroelectric response of neat GP with treatment temperature

Fig. 8 presents hysteresis loops of neat GP treated at 250 °C and 870 °C with electric field loading at a frequency of 500 Hz. From the results, it is found that the neat GP treated at 870 °C showed better hysteresis behavior based on remnant polarization and coercive field than that of the GP treated at 250 °C. The results suggest that temperature treatment induced ferroelectric properties of GP with the mechanism of phase transition. Similar increase in polarization has been reported in perovskite materials [33] with the increase in annealing temperature. Increase in remnant polarization with the increase in temperature is attributed to the development of crystalline phase [33,34]. Temperature increases the crystalline nature and more ordered structure. Also, the increase in particle size and more coalesced volume (see Figs. 4 and 5) of GP results in less defective structure which causes the decrease in coercive field and increase remnant polarization [35,36].
3.6. Ferroelectric response of GP with addition of nanofillers

The hysteresis loops (P–E loops) of neat GP and nanoparticles infused GP were evaluated in order to investigate the ferroelectric behavior of this new material system. Since the hysteresis characteristic of neat GP was found better at 870 °C (see Fig. 8), further ferroelectric study was performed on ANF and ANP treated GP at 870 °C. The results are presented in Fig. 9(a). Coercive field and remnant polarization were evaluated from the P–E loops and the results are charted in Fig. 9(b).

It is observed that with the addition of ANF, coercive field and remnant polarization increase. When electric field reaches to zero, remnant polarizations are around 5 μC/cm² for neat and 8 μC/cm² (60% increase) for 2 vol% ANF reinforced GP. Remnant polarizations are 7 and 6 μC/cm² for 5% ANF and ANP reinforced samples, respectively. The motion of domain walls cause the domain switching for ferroelectric material, and the motion of domain walls have difficulties for viscosity or resistance against domain reorientation through the material. With the addition of fillers, ferroelectric material becomes more viscous, which produce more resistance. This resistance in ferroelectric materials prevents the domain motion [37,38]. For this behavior, the fillers infused GP shows better remnant polarization. The effective electric field is the field required to overcome this resistance through material to switch the domains [39].

The proportional increase in the polarization was expected with the increase in the volume fraction of nanofillers; however, the expected increase was not seen may be due to the formation of bundles of nanofillers with high volume fraction. The higher remnant polarization increases the energy storage capacity of this material system. This type of material can be used in energy storage application at high temperature facilities.

According to these test results, the P–E hysteresis loop occurs and this new GP material may show ferroelectric behavior. To confirm the ferroelectric properties, it is essential to evaluate the dielectric constants [18–20] and Switchable polarization [14] over a range of frequencies and temperature. Further demonstration of the strain-electric field loop and current-electric field loop provides supportive information on ferroelectric hysteresis, which is an ongoing effort of this project.

4. Summary

Compression strengths of neat GP were measured with various treatment temperatures. Phase transformation of neat GP was observed with various treatment temperatures as well. Fracture toughness, $K_{IC}$ and ferroelectric response of neat and
alumina nanofillers reinforced GP were investigated with the variations in the treatment temperatures as well. The results suggested that compressive strength and fracture toughness, $K_{IC}$ of both neat and nanofilled GP increased with temperature until a significant microstructural changes and phase transformation occurred. $K_{IC}$ also increased proportionally with the addition of nanofibers, which resulted from the increase in crack bridging and pull-out mechanism, however, phase transformation of GP and thermal degradation of nanofillers affected the expected performance of nanofillers at high temperature. With the sufficient annealing temperature, more ordered crystalline and coalesced structures were formed into GP matrix, which resulted in the increase in remnant polarization with some sacrifice in the mechanical performance. In addition, Nanofillers assisted in increase in the viscosity of the GP matrix which resulted in the increase in ferroelectric performance.

The strength and fracture resistance of neat GP increased with the increase in bond strength on the particle surface and the balance between the area fractions of particles and poly-condensed structures. High aspect ratio alumina nanofillers further increased fracture resistance of GP by crack bridging and pull out mechanism. Remnant polarization increased with heat treatment and high aspect ratio nanofillers. Amorphous-to-crystalline transformation and coalesced particle structure are two important variables to control ferroelectric hysteresis and mechanical strength. Thus, this study highlighted the scope of this material as a matrix for the continuous fiber reinforced composite with high temperature energy and data storage capability with reasonable mechanical performance.

**Conflicts of interest**

The authors declare no conflicts of interest.

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