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THERMAL EFFECT ON FLEXURAL STRENGTH OF GEOPOLYMER MATRIX COMPOSITE WITH ALUMINA AND WOLLASTONITE AS FILLERS

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ABSTRACT

The addition of alumina and wollastonite in geopolymer resin is expected to increase the thermal behavior of the geopolymer matrix composite. In this work, fine granules of solid alumina and acicular wollastonite used as filler were mixed with a fly ash-based geopolymer resin paste to form a composite matrix. The filler additions were 2.5% to 10.0% of the total weight with sodium silicates and sodium hydroxide used as activators. The results showed that the addition of alumina and wollastonite as filler did not have much effect on the flexural and compressive strength of the geopolymer matrix composite at room temperature. Wollastonite fiber, which was added in the form of a short-sized fiber, only produced a very small bridging effect. Nevertheless, alumina filler composite showed a good result after being exposed to a temperature at 200°C, although the strength was reduced as the temperature increased. Moreover, wollastonite fibers only managed to maintain 50% of their flexural strength after 2 hours exposure at a temperature of 200°C due to the damage of the wollastonite fiber.

Keywords: Alumina; Composite; Flexural strength; Fly ash; Geopolymer; Wollastonite

1. INTRODUCTION

The use of geopolymer resin as a matrix composite is currently being studied to replace the application of Portland cement-based composite (Lin et al., 2008; Mingyu et al., 2009; Thang, 2010; Amuthakkannan et al., 2013; Phoo-ngernkham et al., 2014). Additonal fillers, such as granules, flakes, and fibers are added and expected to enhance the mechanical strength of the composite. Geopolymer resin as a matrix composite can be made as a fly ash precursor from coal combustion. However, the inconsistency of fly ash composition generates a different mechanical strength value, as studied among researchers. In general, fibers are commonly added to enhance the flexural strength, compressive strength, and resistance to high temperatures.

In the interest of improvement, investigators have shown that the addition of basalt fiber up to 70% can improve the composite flexural strength (Amuthakkannan et al., 2013). Fibers will form a bridging effect that can resist damage from flexural loading. Unfortunately, the addition of long-shaped fibers may complicate the mixing process, due to cross linking, which occurs during manual mixing. Other than fiber fillers, the addition of powder fillers on the geopolymer matrix composite can be applied to improve its mechanical strength. Other investigators have shown that the addition of 1.0% micro fiber Al_2O_3 can improve the flexural strength of the geopolymer

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matrix composite with carbon fiber (Thang et al., 2010).

The purpose of this present work is to study the filler addition of alumina (Al_2O_3) and wollastonite ($CaSiO_3$) in the geopolymer matrix composite and to determine their effect on the flexural strength, both before and after the thermal exposure. The filler concentrations were 2.5%, 5.0%, 7.5% and 10.0%, respectively, of the geopolymer matrix composite's total weight. Thermal exposure was performed at temperatures of 200°C, 600°C, and 1000°C, respectively, for 2 hours to test the flexural strength of the standard test specimen.

2. EXPERIMENTAL SETUP

In this study, a fly ash precursor originated from coal combustion in the Suralaya power plants in Banten. The major contents of fly ash include: SiO_2, Fe_2O_3 and CaO, and some minor oxides. This chemical composition of fly ash is shown in Table 1. The density of fly ash is 2.38 gr/cm^3, the water content is measured at 2.70% and chemical composition of fly the loss of ignition (LoI) is 3.02%. Based on ASTM C618, these raw materials can be classified as Class-F.

Table 1 Chemical composition of fly ash (in weight percent)

Al_20_3	SiO_2	S	K_2O	CaO	TiO_2	MnO_2	Fe_2O_3	ZrO_2
4.55	40.60	0.80	3.53	16.50	2.19	1.77	29.82	0.24

The sample was prepared by using activators such as sodium silicates (Merck. 1.05621.2500), NaOH (Merck No. 1.06498.1000) and distilled water with a ratio 6:1:3 of the weight, whereas the mixing ratio between precursor and activator is a ratio of 2:1 of the weight. Furthermore, filler, precursor and activator were mixed with a mechanical mixer for 5 minutes, then poured into the mold to produce flexural and compression test specimens. After that, the specimens were left in the molds for 24 hours and then they continued in the molds with a curing process for 24 hours at a temperature of 80°C. The pre-curing and curing processes were performed in high humidity conditions (over 80%).

A flexural test was conducted with a 3-point method on 70×10×10mm^3 specimens while a compression test was conducted on specimens of 10×10×10mm^3. A flexural strength test was performed using UTS Lloyd Instruments with a capacity of 1 kN, a span length of 50 mm and a cross-head speed of 0.5 mm/min. Ten pieces of the specimen were prepared and tested with the data only the average values shown. A X-ray diffraction (Philips, PW3020) method was used to determine phase changes during the mixing process. Microstructural observations using FE-SEM (FEI, Inspect F50) were performed to determine the filler morphology and the surface fracture. Thermal analysis with a Simultaneous Thermal Analysis (Perkin Elmer Analyzer, STA-6000), which combined TGA (Thermogravimetry Analysis) and DSC (Differential Scanning Calorimetry), was used to determine the weight changes and heat flow of phase transformation during high temperature exposure. Thermal analysis was carried out at a temperature of 35°C to 800°C with a scanning heat rate of 10°C min^{-1}.

3. RESULTS AND DISCUSSION

3.1. Materials Morphology and Microstructure

The fly ash precursor has been through the sieving stages with a mesh opening of 125 μm to separate it from the agglomerated fly ash particles. A SEM micrograph of fly ash shows the morphology of a near perfect solid sphere with differences in sizes, as seen in Figure 1. Furthermore, a micrograph of the filler shows different morphologies and shapes. Figure 2 showed irregular shapes of alumina particles with rounded edges and the average sizes were less than 2 µm, whereas, wollastonite showed an acicular fiber feature with lengths up to 200 µm, as seen in Figure 3.

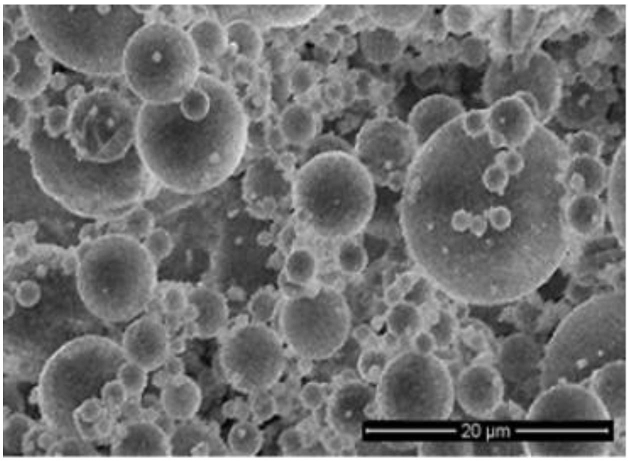


Figure 1 Morphology of fly ash used as precursor

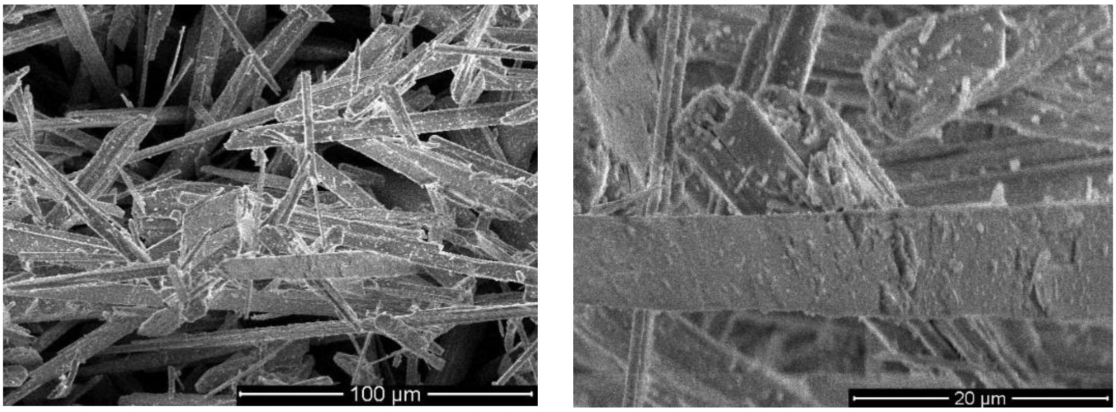


Figure 2 Morphology of alumina used as filler

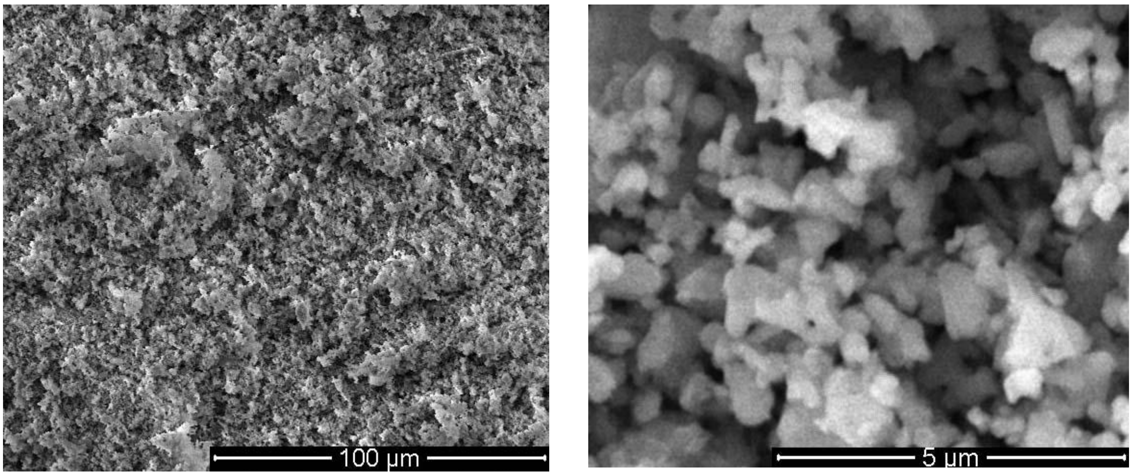


Figure 3 Morphology of wollastonite used as filler

3.2. Composite Phase

The X-ray diffraction patterns of the composite (Figure 4) shows that the addition of alumina and wollastonite to the composite matrix does not produce any new compounds or new phases. In this case, the diffraction pattern of the filler can still be separated from the geopolymer resin diffraction pattern. Peaks of γ-alumina are visible at angles 2θ of 35.15, 43.36, and 57.50, respectively. The main peaks for wollastonite are visible at angles 2θ of 26.88, 28.90 and 29.99, respectively.

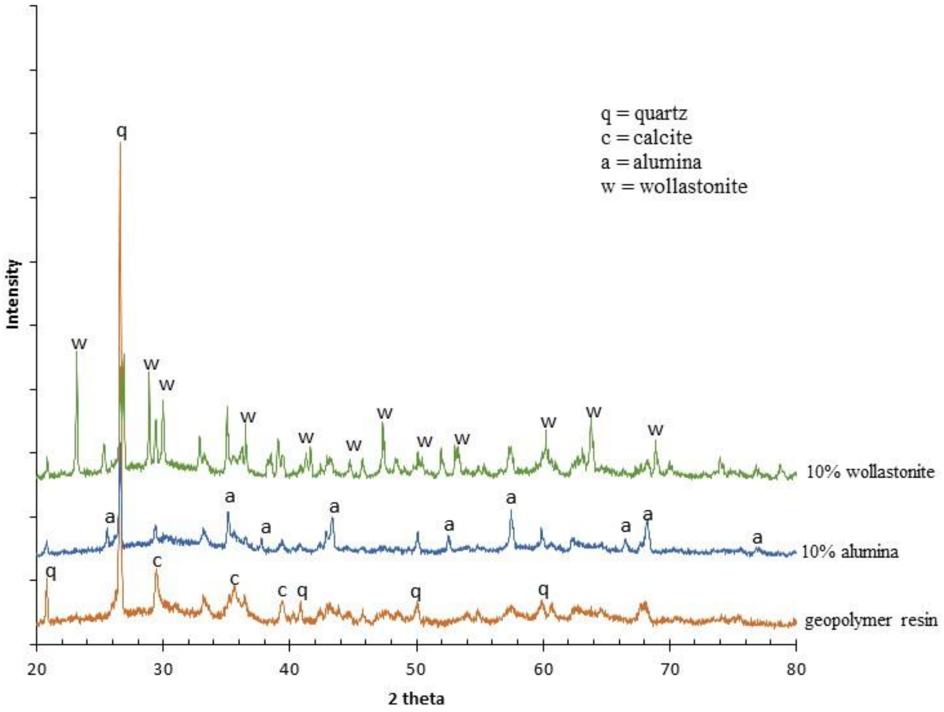


Figure 4 X-ray diffraction pattern of geopolymer resin matrix composite after filler additions

3.3. Flexural Strength

The flexural strength of geopolymer resin as a matrix composite without any filler addition at a room temperature condition is 13.53 MPa (shown as a dashed line in Figure 5). This mechanical strength became the baseline value for the manufacturing of geopolymer matrix composites using alumina and wollastonite filler. Figure 5 shows the effect of filler addition to the flexural strength of geopolymer matrix composites. The addition of 2.5% alumina on the matrix composite has slightly increased the flexural strength; however, the further addition of alumina is decreasing the composite strength. Different results are shown for the composite with addition of wollastonite, which indicate an increase in flexural strength to a concentration of 7.5% and a slightly lower result at a concentration of 10.0%.

Figure 6 shows the fracture microstructure after flexural test using FE-SEM. The micrograph reveals that small alumina particles are not bound and are partially accumulated in a geopolymer matrix (See arrow). Some of even smaller grains are trapped inside a round cavity of a micro porous structure or a dimple. At an addition of 7.5% and 10.0%, the agglomeration and segregation of alumina (See arrow) are clearly observed on the fracture surface. The formation of a micro porous structure and agglomeration of the alumina granules within the composite matrix apparently become the initial of crack propagation during the flexural testing.

Excessive filler addition results in this segregation, which decrease the flexural strength (Lin et al., 2008).

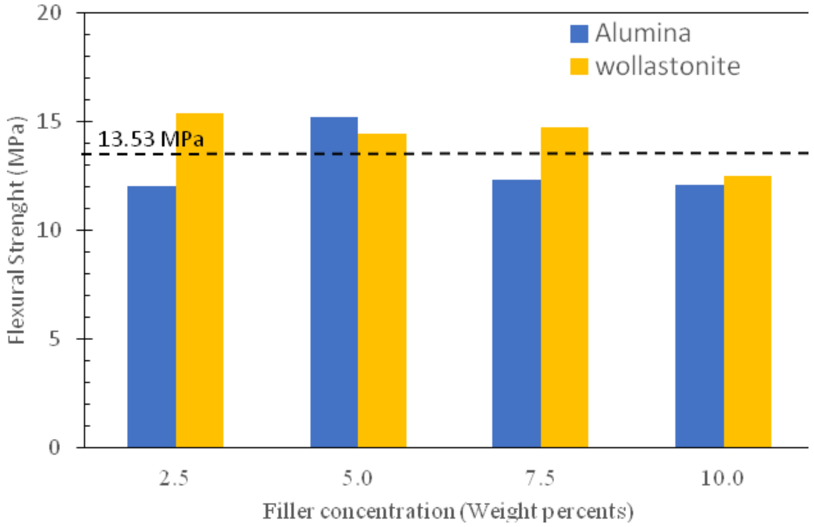


Figure 5 Effect of filler addition on flexural strength at room temperature. (Dashed line shows the baseline taken from the flexural strength of geopolymer matrix composite without any filler addition)

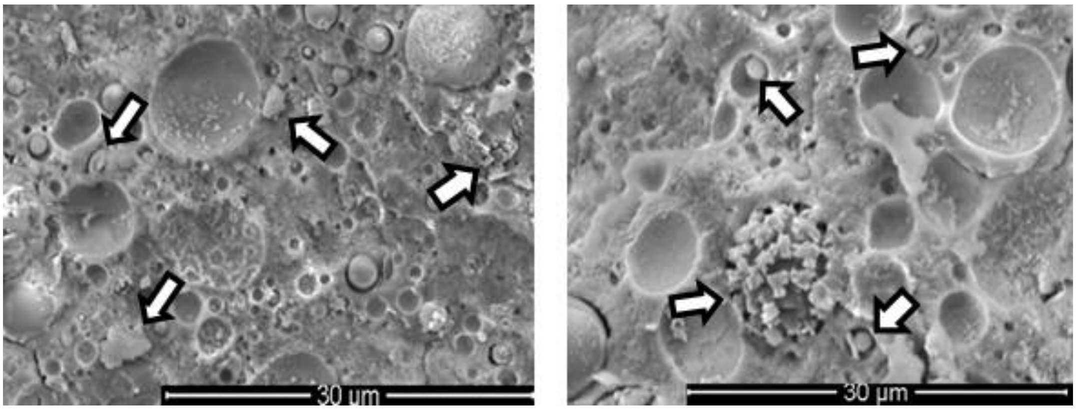


Figure 6 SEM micrograph on fracture surface after addition of 5.0% alumina (left) and 10.0% alumina (right). Arrows indicate the formation of alumina on matrix

The effect of the wollastonite filler addition to the geopolymer matrix composite is different in comparison to the alumina addition. Observations indicate that most of acicular wollastonite is attached to the geopolymer matrix. Figure 7 shows that the small size acicular structure appears to come out from the large porous structure. Wollastonite seems to be attached to the geopolymer matrix and is surrounded by a small dimple. The dimple is not a trace of uprooted wollastonite, but it is porous granules of detached fly ash from the matrix. Wollastonite appears to cluster together and some are separated to each other. The disappearance of larger wollastonite fibers on the fracture surface indicates that large acicular wollastonite fiber failed during flexural loading. The bonds, which exist between wollastonite within a geopolymer matrix, are causing the composite to be able to maintain its flexural strength up to 7.5% filler addition by weight.

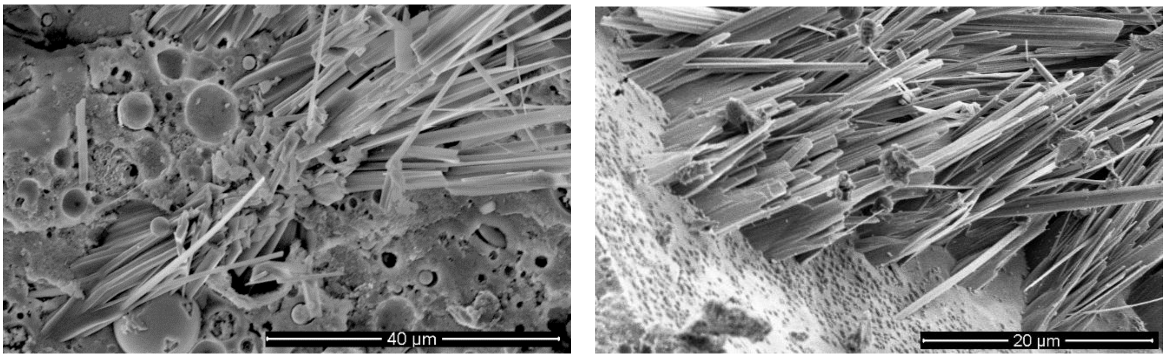
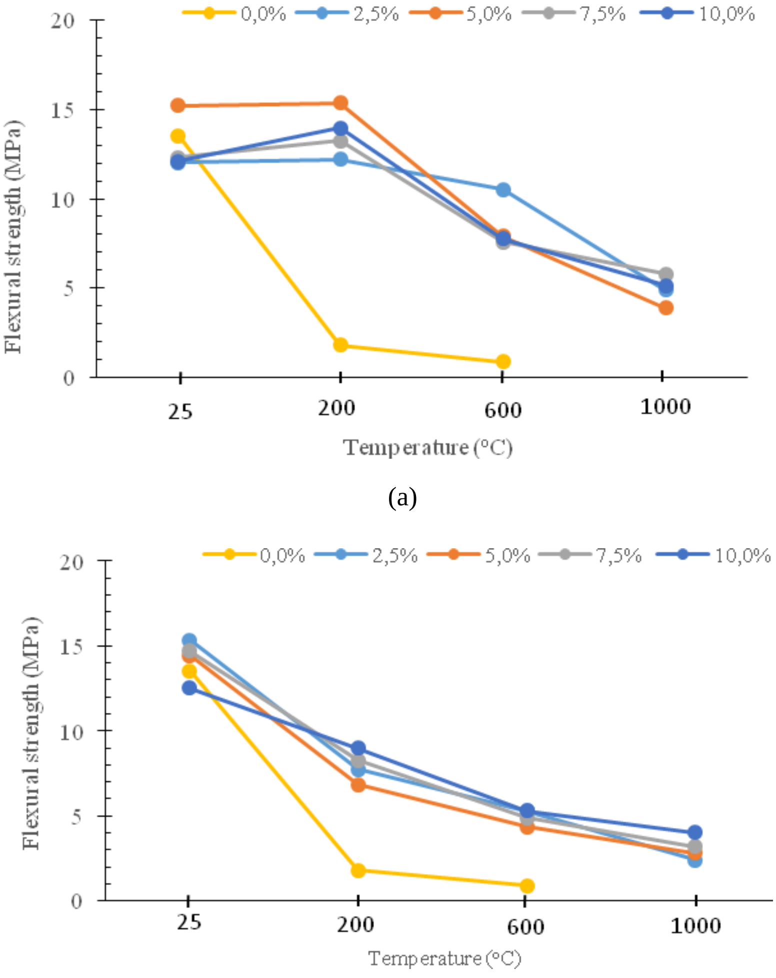


Figure 7 Acicular particles of wollastonite on the fracture surface of wollastonite geopolymer matrix composite at small magnification (left) and larger magnification (right)

3.4. Thermal Effect on Flexural Strength

Figure 8 showed the comparison of flexural strength on high temperature exposure before and after the filler addition. Testing to the sample of geopolymer resin heated at temperatures of 1000°C, which could not be performed owing to the large cracks occurring on most surfaces resulting from the heating process.



(a)

(b)

Figure 8 Effect of temperature exposure on the flexural strength of the composite with variations in the addition of: a) alumina; b) wollastonite

The alumina addition seems to produce a composite that can maintain its flexural strength after exposure to a temperature of 200°C. This strength is expected because of the presence of small alumina particles, which can reduce the shrinkage effect as a result of high temperature exposure. During high temperature exposure, the damage can be caused by crack propagation and/or the formation of new cracks as a result of water evaporation in the composite resin matrix. Consequently, the composite is losing its flexural strength. In the case of alumina, due to the Coefficient of Thermal Expansion (CTE), which is only 5.4×10^{-6} K^{-1} (Auerkari, 1996). The nature of alumina to resist high temperatures, is creating a better flexural strength compared to the wollastonite filler. However, as the temperature increases, the expansion of resin becomes higher than that of alumina. As a consequence, the alumina is detached from the composite matrix.

Heat exposure to the composite with the wollastonite addition is causing the composite to lose its flexural strength, at a rate of approximately up to 50% (15.52 MPa to 7.72 MPa) and at a temperature of 200°C. The flexural strength decreases more at a higher temperature. On the contrary to alumina, which has an isotropy thermal expansion, wollastonite has anisotropic characteristics on its thermal expansion, whereas the CTE value will be different in its parallel and lateral directions. The difference will be even greater after the temperature rise of 300°C (Weston & Rogers, 1976). In these conditions, the thermal expansion of the wollastonite fiber will be hindered by the matrix, causing fractures within the fiber. Wollastonite fiber breakage would cause the composite to be unable to maintain its flexural strength at high temperatures. Figure 9 shows a collection of failed wollastonite fibers that were broken after the heat exposure. As can be seen from the figure, the fracture appears in the longitudinal direction; therefore, the bridging effect due to the addition of the wollastonite fibers is diminished.

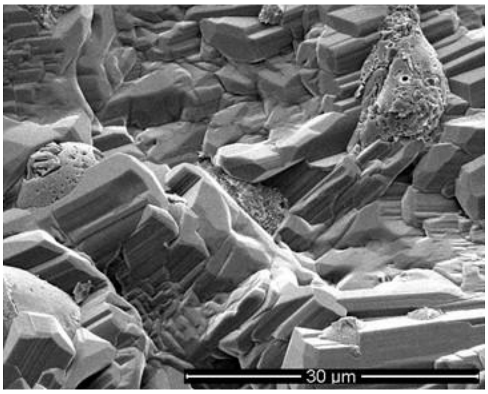
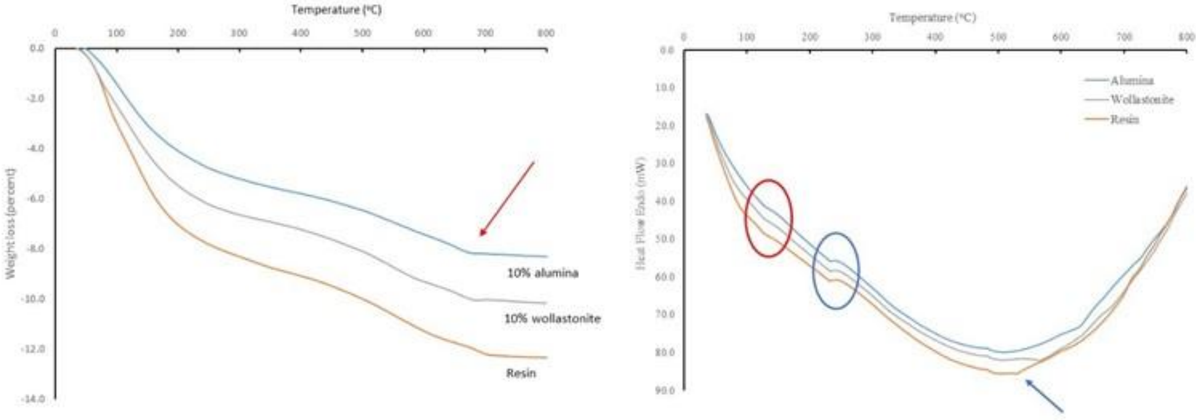


Figure 9 The damage to wollastonite after heat exposure at 600°C

3.5. Thermal properties

Simultaneous Thermal Analysis (STA) in Figure10 shows that the addition of alumina and wollastonite will restrain the rate of weight reduction, due to the increasing temperature. In Figure 10(a), the Thermogravimetry Analysis (TGA) thermogram shows the weight loss of the material is reduced and it reaches a stable value (See red arrow) at approximately 690°C. This temperature indicates that the polymer resin had already decomposed. The step curve in the beginning is related to the water evaporation. From the Differential Scanning Calorimetry (DSC), the heat flow shown in Figure 10(b), is the first thermal arrest (See blue circle) and that probably corresponds to the water evaporation. The second thermal arrest (See red circle) is associated with the geopolymer resin hydrate water decomposition, which is shown at a temperature level of 210°C. Furthermore, the endothermic heat flow reaction reaches the approximate peak temperature at 500°C (See blue arrow). In comparison with the samples, it seems that the addition of alumina generates the lowest endothermic heat flow curve compared with the wollastonite addition. The STA results indicate that the composite with the alumina addition has a better and higher temperature resistance than the composite with the wollastonite addition.



(a) (b)

Figure 10 Influence of increasing temperature to geopolymer composite: a) weight loss; b) endothermic heat flow signal

4. CONCLUSION

The filler additions on the geopolymer resin with alumina and wollastonite powder to form the geopolymer matrix composite have slight influence on the flexural strength and compressive strength of the geopolymer. The alumina addition tends to decrease the flexural strength due to the formation of a micro porous structure and the segregation of alumina, while the wollastonite addition slightly increases the flexural strength, due to the bridging effect of the wollastonite fibers. After a 2-hour exposure to high temperatures, composites with alumina filler are able to maintain their flexural strength by accommodating the shrinkage phenomenon during the heating process. However, the anisotropic thermal expansion that occurs in the wollastonite fiber resulted in damage to the fiber during the heating process. As a result, the wollastonite addition is only able to resist approximately 50% of its flexural strength after the heat exposure.

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