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Advanced glass reinforced epoxy filled fly ash based geopolymer filler: preparation and characterization on piping materials

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Abstract. The preparation and characterization of glass reinforced epoxy filled with different weight percentage of geopolymers filler attained from fly ashand epoxy resins are reported limited of study. Recent glass reinforced epoxy pipe are reported exhibits relatively low mechanical properties, which limit their usage in structural applications and in oil and gas industrial. Thus, this restriction could be overcome through the formation of the addition of geopolymer fillers to improve their strength and toughness. The glass fiber was impregnated with different weight percentage and different molarity of fly ash-based geopolymer and epoxy hardener resin. Composite samples were made manually by filament winding technique and cured under room temperature. The sections perpendicular to the fibers and surfaces of the composites were analyzed by means of scanning electron microscope to estimate the adhesion between geopolymer matrices and fiber reinforcement. Relatively, wide range of geopolymer weight percentage from 10 % to 30 % at which can obtain high compressive properties, maximal values of compressive strength is 94.64 MPa and compressive modulus 2373.58 MPa for the sample with 30 % weight percentage of filler loading. These new composites materials show expressively enhanced mechanical properties if matched to straight glass reinforced epoxy pipe without any geopolymer filler. The positive mixture of synthetic method with the use of industrial by-products has acceptable fabricating novel low cost aluminosilicate binders, thanks to their suitable bondin contradiction of materials frequently used in structural application, could be used within the field of oil and gas industry.

1. Introduction

Thermoset materials are commonly used to replace heavier non-polymeric materials such as metals and ceramics for structural applications. The mechanical and physical properties of thermoset can be harshly reduced when exposed to corrosive environment and heavy duty environment such as in the oil and gas pipeline [1,2]. These problem could lead to disadvantage for using thermoset for the long-term in the structural applications, where mechanical and physical reliability are required to allow stability in these environmental conditions.

Some of the earlier researches stated GRE pipes have some weaknesses like poorerin strength compares to metal pipes and cannot withstand at high temperature due to the physical and mechanical properties of epoxy itself [3]. Under water maintenances of impaired piping using composites confront several challenges. Curing and materials property enlargement of composite systems that are based on liquid resins that wet-out reinforcement and then are applied while submerged was the main challenge. The coatings production has frequently established that epoxy-based thermosetting polymers have the precise mixture of viscosity, hydrophobicity, and chemical insensitivity to improve tolerable degrees of cure and material properties when practical submerged [2]. The piping system is issue to high mechanical loads, chemical experience, performance and stability of GRE pipes may be sensitive to damage suffered by poor handling and installation practices. Temperatures, pH level, and fluid composition can influence some serious values weakening pipeline consistency and ultimately producing terrible failure elongated before the predictable of the service life [4].

For a several years, a non-metallic pipe system like glass fiber reinforced plastics (GRP) pipes and nonmetallic material lined steel pipes have been extensively used not only in the oil and gas industry due to their several advantageous such as high corrosion resistance, light weight, low costs of cycle time and short in the process of installation time[3]. Glass fiber reinforced epoxy (GRE) pipes are usually deliberate to withstand some properties such high pressure strength, light in weight, comparatively thin-walled arrangement provide easiness of conduct and moving which can effect in shortened setting up budgets [5,6]. These advantageous also making these non-metallic pipes usually desired in the fields of structural engineering and also in aviation field [7]. The high usage of these non-metallic pipe systems requires dependable examination approaches to certify the protection and foresee their long-term performance. Nevertheless, some of earlier researches testified that GRE pipes also require some draw backs due to thermoset itself such as lower in strength compared to the metallic pipe that can't endure at elevated temperature appropriate to the properties of epoxy and epoxy itself have small corrosion protection that it can agonise strain corrosion cracking when exposed to the acidic environments [8-10]. This research paper is about to overcome these absolute disadvantages consist of the request in the especially in the field of oil and gas production, predominantly composite tubes for aqueous fluids and to create high mechanical asset and properties of existing industrial pipe. Fly ash based geopolymer is used as a filler in this research to overcome this drawback. Fly ash comprises of excellently separated ashes formed by crushed coal in power stations. Sphere-shaped of fly ash expands the strengthening of pipe, which similarly decreases porousness [11]. Consequently, this fly ash material has board potential to be used as a source material to alter with alkaline activator which is sodium silicate solution (Na_2SiO_3) and sodium hydroxide (NaOH) mixture [12].

The design formulation of geopolymer filler is indicate to the composite structure as detailed from the former investigator on composite classification which is practice the loading of flax fibers diverse from 0 to 60 wt%. [13].Fly ash-based geopolymer filler were mixed with epoxy resin to act as matrix resin which unique of the extreme existing benefits in thermo set-based clay composites meanwhile it proposed better in cost, simplicity of preparation, better grip to numerous substrates, and decent chemical confrontation for a extensive variety of applications [14].

2. Material and experimental details

2.1 Materials selection

In this research, glass reinforced epoxy (GRE) pipe which is epoxy resin type of diglycidyl ether of bisphenol A (DGEBA), were properly blend with fly ash-based geopolymer filler with different wt% and also different sodium hydroxide (NaOH) molarity concentration which is 8 M and 12 M and solid to liquid ratio is 1 respectively. In order to form a greater in strength of geopolymer filler, the maximum liquid to liquid ratio (sodium silicate to sodium hydroxide) should be in the area of 0.67 to 1.00 [15]. Epoxy resin which is DGEBA, was equipped by Euro Pharma Sdn Bhd and epoxy hardener, Isophorondiamine (IPDA) was commercially attain from an industry, Dr Rahmatullah Holdings. Raw materials of geopolymer filler were supplied by Saudi Arabia local based materials which are categorized as Class C Fly Ash that were used in the development of geopolymer filler. Geopolymer paste is obtained by alkaline activator to activate the silicon and aluminum atoms in the mineral material [16]. Liquid alkaline activator used in this research is the mixture of 8 M and 12 M of NaOH with sodium silicate (Na_2SiO_3).

Alkaline activator was prepared by mixing sodium hydroxide and sodium silicate before mixed with raw materials which is fly ash to boost the reactivity of solution with concentration of 8 M and 12 M of NaOH to regulate the best concentration. The ratio of raw materials (solid) to alkaline activator (liquid) and sodium silicate (liquid) to sodium hydroxide (liquid) is set to 1. Paste of the geopolymer then fully rectify in the oven for 24 hours at 80 ˚C before taken out to be crush. Fly ash-based geopolymer then being sieved using sieve size of 150 µm right after crushed it by using ring mill machined.

2.2 Developmental procedure of pipe making

Epoxy filled fly ash-based geopolymer filler resin was developed accordingly to the mix design in the Table 1 by using mechanical mixer. Epoxy filled fly ash-based geopolymer filler resinthen was cured by using cycloaliphatic amine curing agent, IPDA. Epoxy resin and fly ash based geopolymer filler were mixed for 2 hours to make it absolutely homogeneous, and then 5 more minutes mixed with curing agent/hardener. Then, epoxy filled fly ash based geopolymer resins were taken into the filament winding tank after mixed with the curing agent/hardener.

Table 1. Mix Design of Epoxy Geopolymer Resin.

Material	Epoxy resin + Epoxy Hardener (%)	Geopolymer Filler (%)
Fly Ash	100	0
	90	10
	80	20
	70	30
	60	40

Continuous glass fibers (E Type) were saturated ("wet-out") with theepoxy filled fly ash based geopolymer filler resin by channel of filament winding technique. To generate the desired winding angle patterns, winding speed of the machined must be controlled. The acceleration or quickness of the fiber during the impregnation process must be chosen based on the finest penetration on epoxy filled fly ash based geopolymer resin into the glass fibers. The mandrel rotational speed will controlled the feeding velocity of the fiber into the resin tank. It was preferred based on the suitable penetration of epoxy filled fly ash based geopolymer resin into the glass fibers.

Filament winding pipes samples were allowed to be cured at the mandrel in the room temperature for 24 hours after applicable number of layers has been applied according to perfectly wounded. The pipes sample is then ready for testing after the curing process is completed and the samples is taken out from the mandrel of filament winding machine. Certain analysis and evaluation were execute on the new piping materials which are compressive test and elasticity modulus in order to resolve the mechanical and physical properties of the new pipes.

The chemical composition of raw materials fly ash is determined by using X-ray fluorescence (XRF) spectrometer with brand name of PAN analytic PW4030. Loss on ignition (LOI) was controlled by drying the samples at 105 °C and then calculating the mass loss after heating to 1000 °C. Results described as oxides consist of the details of a number of standards measured during the analysis. The mean percentage dissimilarity from the standards for each oxide has been calculated to determine the uncertainties.

Compression test are perform using Instron Universal Testing Machine according to ASTM D3410. Figure 1 shows the schematic diagram of pipe sample placement for compression testing. Each sample was placed centrally between the lower cross member and lower cross head in such a manner that the load shall be applied to opposite side of sample at rate 5 mm/minutes. The specimens are subjected to the compressive force for vertical position.

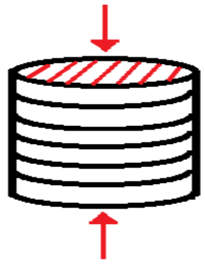

Figure 1. Schematic diagram of testing pipe sample on vertical position.

Morphology analysis is tested under scanning electron microscopy (SEM). The preparation for morphology analysis on the microstructure of SEM samples for GRE filled with fly ash-based geopolymer pipe, the samples were cut into smaller part (2 cm x 2 cm) before undergo the SEM machine. After GRE filled with geopolymer pipe were cut, the sample then is coated first by palladium using Auto Fine Coater model JEOL JFC 1600.

3. Result and discussion

3.1 Chemical Composition of Raw Material Fly Ash Analysis

X-ray fluorescence analysis (XRF) is the production of characteristic fluorescent X-rays from a material that has been agitated by bombarding with high-energy X-rays or gamma rays. This investigation is worked to present elemental analysis and chemical analysis of the materials. The chemical composition of fly ash from Saudi Arabia have been analyzed by X-Ray Fluorescence (XRF) was displayed in Table 2. Depending on the composition of original coal as shown in the Table 2, this fly ash material consists considerable high amount calcium oxide (CaO) which is (>20 wt%) and is categorized as Class C fly ash [17]. A few studies have been done by some of the researchers that reported on Class C fly ash [18-20]. Based on the chemical composition results shows by XRF machined, these previous raw materials that used in geopolymer filler comprise high content in Silica (Si), Alumina (Al), Calcium (Ca) and Iron (Fe). Materials contain mostly Silica (Si) and Aluminium (Al) in amorphous form is a possible source material for the production of geopolymer [21]. From the Table 2, it was clearly shows the fly ash was rich in Calcium Oxide (CaO), silicon dioxide (SiO_2), and Aluminium Oxide (Al_2O_3) which is more than 90% was found. The present of SiO_2 and Al_2O_3 is important to the geopolymer performance. All the characteristic and performance of geopolymer materials is good enough to be applying as geopolymer filler.

Table 2. Chemical composition of fly ash raw materials.

Chemical Composition	Fly ash (%)
SiO_2	9.07
Al_2O_3	3.1
CaO	80.59
Fe_2O_3	5.19
MgO	0.84
ZrO_2	0.032
TiO_2	0.39
K_2O	0.465
$V_2 O_5$	0.030

3.2 Compression analysis

Figure 2 display the common graph of existing glass reinforced epoxy (GRE) pipe that only contain epoxy resin and glass fiber and GRE pipes filled with different weight percentage (10 wt% - 40 wt%) of fly ash-based geopolymer filler from the tests of compression strength. This compression test was accomplish correspondingly to the ASTM D3410 by applying under Instron Universal Testing Machine [22]. The exists compression test lies on the impair of the hollow cylindrical specimen to generate a thinner cylindrical hollow of large diameter. It is an acceptable approach to deciding stress strain feedback.

From Figure 2, it is definitely determined that compressive strength of GRE pipe with fly ash-based geopolymer filler for both 8 M and 12 M of NaOH shows development with the increasing of geopolymer filler content until 30 wt% of geopolymer filler. Nonetheless, there are slightly drop in strength at 40 wt% geopolymer filler loading for both 8 M and 12 M of GRE filled with fly ash-based geopolymer filler pipes samples.

This may due to the higher viscosity when added with higher content of geopolymer filler and it gives difficult workability between the epoxy and filler itself. Alike the compressive strength of GRE pipe filled with fly ash-based geopolymer filler decrease with the addition of bigger filler loading (40 wt%), the compressive strength for both GRE pipes with 8 M and 12 M is still higher than GRE pipe without any geopolymer filler.

Based on Figure 2 also, it can be seen that the higher compressive strength reveals a substantial synergy and interaction amongst epoxy resin itself which is the chain of polymer with the added geopolymer filler. Nonetheless, the decline in compressive strength which contain higher filler loading at 40 wt% may regulating the effectiveness and competence of dislocate load and plastic fracture between particles and the interface of the matrix.

It was approved by the theorem rule of mixture which the additions of micro particles attempt better stiffness than epoxy matrix [23].

There are two aspect that can be taken into justification that effect their strength behavior which is the matrix and the interface. The matrix characteristics are affected by the fly ash-based geopolymer filler and it was claimed that the inclusion of cementious material to a polymer enhanced the impact strength because the fly ash-based geopolymer filler formed a indirect crack path as well as the expansion of micro-cracks are blocked by the cementious platelets [24-27].

It is conclusive at this point when the distinct and durable of the interface compose between the matrix and the fibers in a polymer composite, the lower the compressive strength. This may be expected to the smaller accumulate of the filler itself and derangement essence of clay filler and also the adoption of lower NaOH molarity. Table 3 shows the full results of compressive properties strength, strain and modulus of elasticity for the 0 wt% – 40 wt% fly ash-based geopolymer filler loading.

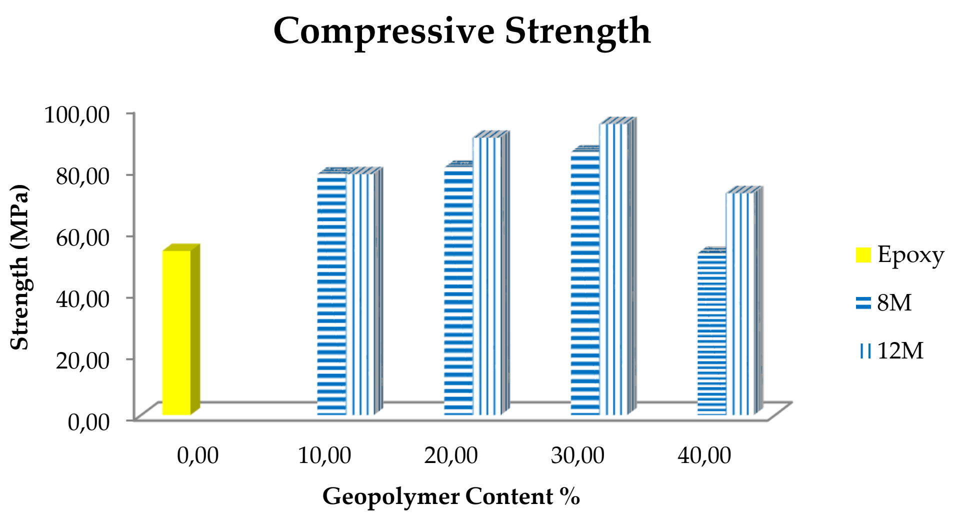

Figure 2. Compressive strength of GRE pipe with 0 wt% - 40 wt% geopolymer filler loading.

Table 3. Compression Properties of Epoxy Hardener and Epoxy Geopolymer.

	Compressive Strength (MPa)				**Compressive Strain (%)**				**Modulus Elasticity (MPa)**			
	10	**20**	**30**	**40**	**10**	**20**	**30**	**40**	**10**	**20**	**30**	**40**
Epoxy		53.36				0.04				1681.28		
8M	78.30	80.50	85.48	52.55	30.03	30.03	22.69	0.10	2166.61	2199.71	1984.72	1874.41
12M	78.33	90.19	94.64	72.13	0.04	0.06	0.06	0.05	2564.09	2699.54	2373.58	2183.51

3.3 Surface morphology of Glass Reinforced Epoxy filled with Geopolymer Filler

In order to study the adhesion between the glass fiber and epoxy geopolymer filler matrix, the Scanning Electron Microscope (SEM) images were investigated. From the Figure 3, at higher magnification it is clearly shown that the adhesion between epoxy geopolymer resin and glass fiber was very good.

However, as can be seen at (Figure 3d) with the higher filler content, it clearly indicates that epoxy geopolymer filler almost fully attach to the glass fiber when the resin wounded during the filament winding process which the internal structure of the composites was deteriorated, many cavities and agglomeration of the geopolymer filler itself were formed during mixing; that made the viscosity of composite increased and the strength went down significantly (Table 2). Figure 3a showed less quantity of matrix resin adheres to the glass fiber than the composite when added with fly ash-based geopolymer filler with higher percentages was added to the matrix resin. This could be due to the higher attraction between the fly ash-based geopolymer filler and the fibers surface.

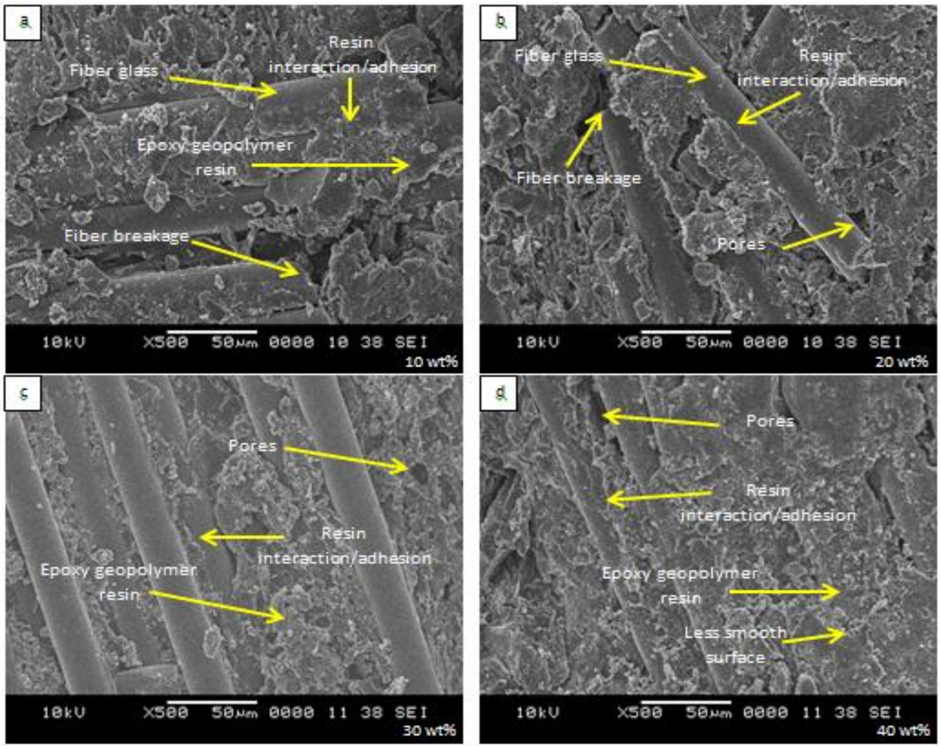

Figure 3. SEM images of GRE filled fly ash-based geopolymer filler pipe (a-d) with different wt% of filler loading (a) 10 wt%, (b) 20 wt%, (c) 30 wt%, (d) 40 wt%of 12 M with magnification 2000x.

In addition, in the glass reinforced epoxy composite without any geopolymer filler content a more brittle surface was observed in the SEM whereas the surface of the geopolymer filler appeared much rougher. This is accordance due to their increasing in the strength measured by the compression testing (Figure 2). Then, the mechanical properties of the GRE pipe with geopolymer filler content was observed in the compressive properties analysis.

4. Conclusion

In this research, glass reinforced epoxy (GRE) pipe filled with fly ash-based geopolymer was well-established based on DGEBA containing with the addition different weight percentage of the geopolymer material filled. The investigational outcome shows the implementation of the geopolymeric filler material with existing GRE pipes product over several tests. In general, the mechanical properties of GRE pipe filled with fly ash-based geopolymer filler shows the greater strength compare to the GRE pipe sample without any geopolymer filler. Appropriate to the decent characteristics of the waste materials based geopolymeric material has superior possible to become one of a matrix filler in the composite system and purposely not only globally but also decreasing the manufacture amount of the outcome.

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